ELSEVIER

Journal of Photochemistry and Photobiology A: Chemistry 96 (1996) 199–202

Journal of
PHOTOCHEMISTRY
AND
PHOTOBIOLOGY
A: CHEMISTRY

The new fluorescent probe in the process of methyl methacrylate polymerization

Zhèng-Lin Yan *, Shi-Kang Wu

Institute of Photographic Chemistry, Chinese Academy of Sciences, Beijing 100101, People's Republic of China

Received 10 October 1995; accepted 14 December 1995

Abstract

On the basis of the preparation of two 2-pyrazoline compounds, 1,5-diphenyl-3-nitrophenyl-2-pyrazoline and 1,5-diphenyl-3-styryl-2-pyrazoline, the steady-state photophysical properties have been studied. Results indicated that there is a close relationship between a good fluorescence probe and the intramolecular charge transfer extent, and the strong intramolecular charge transfer is essential for a good fluorescence probe.

Keywords: Intramolecular charge transfer; Fluorescence probe; 1,3,5-Triaryl-2-pyrazoline

1. Introduction

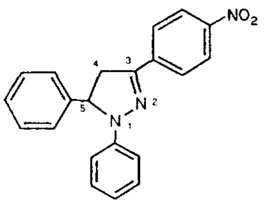
In recent years, the donor–acceptor (D–A) compounds, whose fluorescent spectra are sensitive to the change in the solvent properties, have usually been used as the fluorescent probe to study microenvironments [1–7], e.g. the polarity and viscosity change in micelle, microemulsion, vesicle and liposome.

The 1,3,5-triaryl-2-pyrazolines, as typical D–A compounds, are fluorescent dyes which are widely used for whitening textile fibres, plastics and papers [8,9]. Most studies have concentrated on the absorption and fluorescence spectrum of these compounds [10]. In our previous report [11], we pointed out that 2-pyrazolines have strong fluorescent emitting properties, and their spectrum behaviors are more sensitive in media. When the 2-pyrazoline molecule is excited, intramolecular charge transfer can occur from N(1) to C(3). On the basis of all this, 1,3,5-triaryl-2-pyrazoline may be a good fluorescent probe for microenvironments.

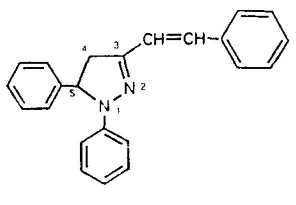
In this work, two 2-pyrazoline compounds have been synthesized, and their steady-state photophysical properties were studied in solution and in the process of methyl methacrylate (MMA) polymerization.

2. Experimental details

The molecular structures of the 1,3,5-triaryl-2-pyrazoline compounds (1,5-diphenyl-3-nitrophenyl-2-pyrazoline (TPP1) and 1,5-diphenyl-3-styryl-2-pyrazoline (TPP2)) prepared are as follows:



TPP I



TPP 2

These two compounds were synthesized in our laboratory according to the method given in the literature [12] and were purified by repeated recrystallization prior to use. Their structures were confirmed by main spectroscopy and ^{1}H nuclear magnetic resonance spectroscopy.

Poly(methyl methacrylate) (PMMA) was made by radical polymerization in thoroughly outgassed MMA, using 2,2′-azobis (isobutyronitrile) as initiator (0.1 wt.%) at 60 °C in a sealed quartz cell. The concentration of the 2-pyrazoline compound in MMA solution is 1×10^{-5} M.

All solvents used were supplied by Beijing Chemical Works and purified by the usual methods before use.

The absorption spectra were recorded on a Hitachi-330 UV–visible spectrophotometer, and corrected emission spectra were obtained on a Hitachi MPF-4 fluorescence spectrophotometer. Fluorescence quantum yields of pyrazoline compounds in various solvents were obtained by comparison of the integrated areas under their corrected emission spectra with that of a 0.1 N sulfuric acid solution of quinine sulfate.

---

* Corresponding author.

1010-6030/96/$15.00 © 1996 Elsevier Science S.A. All rights reserved
SSDI 1010-6030(95)04295-4

3. Results and discussion

The absorption spectra of TPP1 and TPP2 shown in Figs. 1 and 2 respectively have been recorded in solvents of different polarities. The data indicated that, when an electron-withdrawing nitro group is located on the phenyl ring at position 3, the absorption peaks of TPP1 are at longer wavelengths than those of TPP2 in which the nitro group is absent. Nevertheless, the absorption spectra of these compounds change very little with increasing solvent polarity.

The fluorescence spectra of TPP1 and TPP2 in various solvents are presented in Figs. 3 and 4 respectively. In comparison with the absorption spectra, the fluorescence peak wavelengths of these two compounds exhibit a large red shift with increase in the polarity of the solvents. When the solvent is changed from cyclohexane to THF, the red shift in the emission spectrum is about 25 nm, and for TPP1 it increases to about 100 nm. It is obvious that the introduction of the nitrobenzene group at position 3 exerts a stronger effect on the molecular polarization in the excited state. When TPP1 is excited, compared with TPP2, a stronger intramolecular charge transfer occurs from N(1) to C(3).

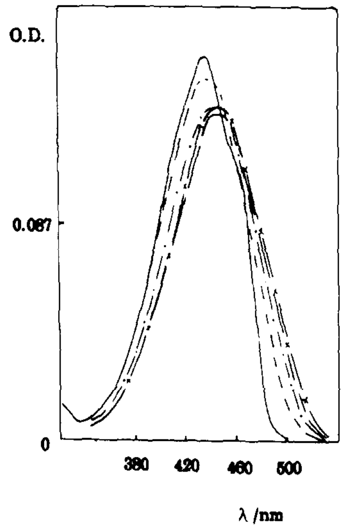


Fig. 1. The absorption spectra of TPP1 in various solvents: ———, cyclohexane; - - -, ether; ——— ———, toluene; – · –, 1,4-dioxane; – X –, tetrahydrofuran.

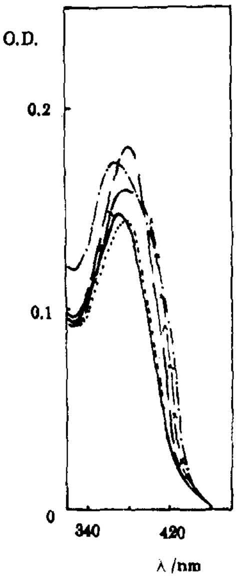


Fig. 2. The absorption spectra of TPP2 in various solvents: ———, cyclohexane; - - -, ether; ——— ———, 1,4-dioxane; – · –, THF; – X –, ethyl acetate.

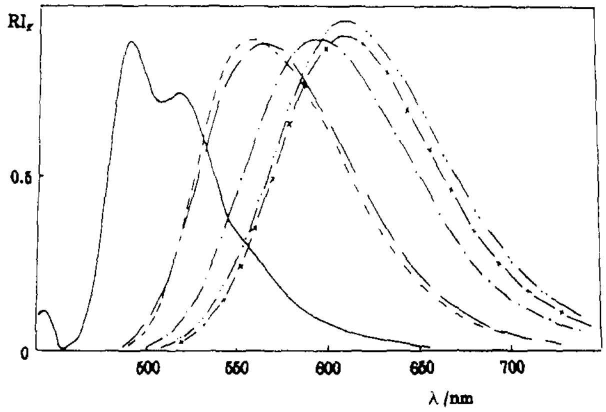


Fig. 3. The fluorescence spectra of TPP1 in various solvents: ———, cyclohexane; ——— ———, ether; - - -, toluene; – · –, 1,4-dioxane; – X –, THF; – · · –, ethyl acetate.

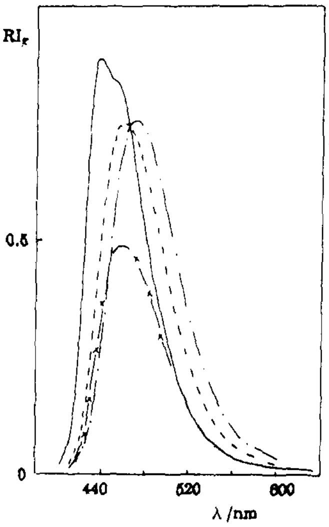


Fig. 4. The fluorescence spectra of TPP2 in various solvents: ———, cyclohexane; - - -, ether; – X –, toluene; – · –, ethyl acetate.

The fluorescence quantum yields of the title compounds in various solvents are listed in Table 1, where it can be seen that the fluorescence quantum yields of all compounds

Table 1
The fluorescence quantum yields of the title compounds in various solvents

Solvent	Quantum yield of TPP1	Quantum yield of TPP2
Cyclohexane	0.43	0.65
Ether	0.23	0.63
1,4-dioxane	0.09	0.62
THF	0.05	0.62
Ethyl acetate	0.03	0.59

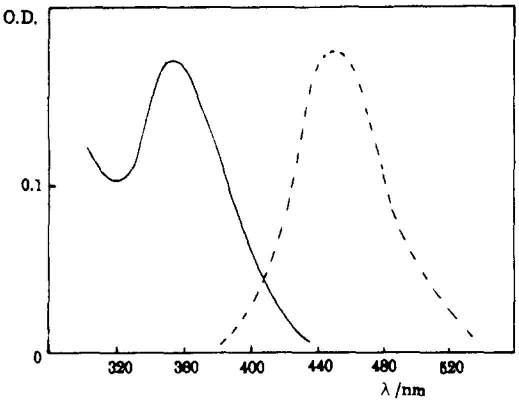


Fig. 5. The absorption spectra of TPP1 and TPP2 in MMA: ———, TPP2; - -, TPP1.

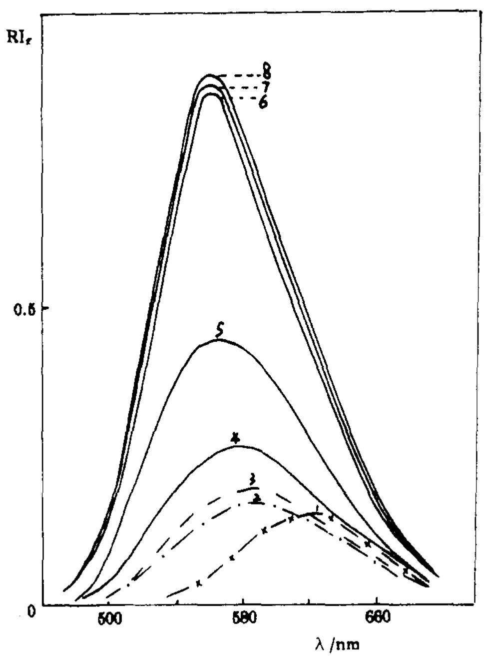


Fig. 6. The fluorescence spectra of TPP1 at different polymerization times: curve 1, 0; curve 2, 435 min; curve 3, 440 min; curve 4, 445 min; curve 5, 450 min; curve 6, 455 min; curve 7, 460 min; curve 8, 500 min.

decrease with increasing solvent polarity. The data also indicate that TPP1 has a dramatic decrease compared with TPP2, and this is because of the strong solvent relaxation process led by the stronger intramolecular charge transfer.

The absorption spectra of TPP1 and TPP2 in MMA are presented in Fig. 5. The experimental variation in the fluorescence emission spectra of TPP1 with the MMA polymerization time is shown in Fig. 6. In the process of polymerization, with the lapse of the time, the emission intensity of TPP1 gradually increases and the emission peaks blue-shift. At the beginning of the polymerization (before 435 min), the emission intensities and peak wavelengths scarcely change but, just 20 min after that time, the fluorescence intensities of TPP1 sharply increase and its peak wavelength blue-shifts to 560 nm (the polymerization time is 460 min) from 620 nm at the starting time. When the polymerization reaction has occurred for some time (after 475 min), the emission intensities and peak wavelengths change slightly.

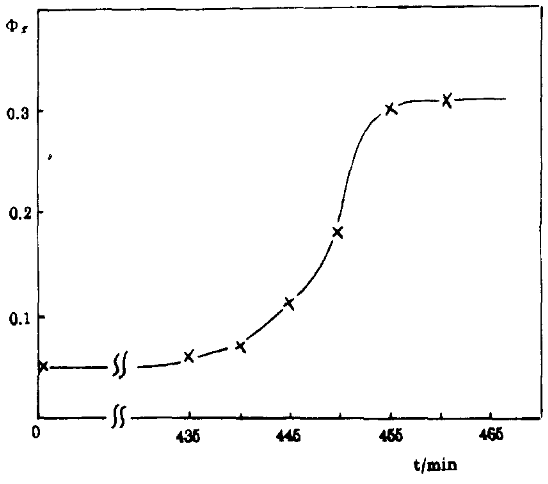


Fig. 7. The fluorescence quantum yields of TPP1 at different polymerization times.

The variation with the polymerization time of the fluorescence quantum yields of TPP1 are given in Table 2. Because MMA has a similar polarity to ethyl acetate, the fluorescence quantum yield Φf of TPP1 in MMA is nearly the same as that in ethyl acetate, only 0.05. As observed in the fluorescence spectra, although Φf scarcely changes before 435 min, there is a clear change in Φf after that time, from 0.05 to 0.30. The fluorescence quantum yield increases by an order of what it was previously, and this implies that a larger change may have taken place in the reaction system. This mutation process is depicted in Fig. 7.

As reported in our previous papers, when the 2-pyrazoline molecule is excited, intramolecular charge transfer can occur according to $N(1) \rightarrow N(2) \rightarrow C(3)$. Thus a large difference between the dipole moments of the ground state and excited state exists. To meet the new charge distribution of solute molecules, the solvent molecules reorient around the solute molecule. This is called the solvent relaxation process. Here, we should take into account the limited relaxation time τ_R in which the solvent molecules reorient and the limited lifetime τ_e of the excited molecule to explain the experimental phenomenon obtained.

The MMA polymerization system is an ideal bulk polymerization system, in which there is a close relation between

Table 2
The variation in the fluorescence quantum yields of TPP1 with polymerization time

t (min)	0	435	440	445	450	455	460	500
Φf	0.05	0.06	0.07	0.11	0.18	0.30	0.31	0.31

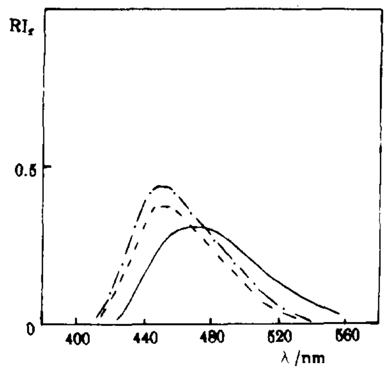


Fig. 8. The fluorescence spectra of TPP2 at different polymerization times: curve 1, 0; curve 2, 440 min; curve 3, 500 min.

the increasing media viscosity and the solvent relaxation process. Before polymerization or when the polymerization proceeds for a certain time (before 435 min), the viscosity of MMA changes slightly owing to a slight increase in PMMA molecular weight. The solvent molecules are easy to reorient ($\tau_R \ll \tau_e$) to fit the increase in dipole moment of the TPP1 excited state. The fluorescence is emitted from the excited state S_1' through the solvent relaxation process. So, at this time, the fluorescence quantum yields of TPP1 scarcely change.

When the polymerization reaction has occurred to a certain extent (435 min), the chain cessation speed sharply decreases and the amounts of free radicals dramatically increase. So the polymerization reaction speed sharply increases. In a short time, the molecular weight of PMMA undergoes a larger increase and the viscosity of the MMA system sharply increases.

In this auto-acceleration process of the polymer system, the sharp increase in the system viscosity leads to the situation in which Φf is equal to or larger than the system. Thus it is rather difficult for solvent relaxation to occur, and fluorescence is emitted from the Franck-Condon excited state S_1 to the ground state, rather than the relaxed state. The fluorescence quantum yields are larger than those for which solvent relaxation has taken place. Compared with the energy gap after the solvent relaxation, the energy gap of TPP1 between the excited state and ground became larger, and the fluorescence emission peak wavelength gradually blue-shifts.

Therefore we can draw a conclusion from the above discussion that the compound TPP1 is a better fluorescence probe for the MMA polymerization system (especially during the last half of the polymerization process), because of a sharp change in the fluorescence quantum yield in a short time.

For comparison with TPP1, we did the experiments in which the fluorescence quantum yield of TPP2 varies with the MMA polymerization time, as shown in Fig. 8. In the whole polymerization time, we observed that the fluorescence intensity of TPP2 has a slight increase, and the fluorescence quantum yield changes from 0.55 before polymerization to only 0.60 after a time of 500 min. In addition, the emission peak wavelength changes from 470 to 450 nm, i.e. by only 20 nm. The changes in the fluorescence quantum yield and emission peak wavelength are much smaller than for TPP1, implying that TPP2 is not a good fluorescence probe for the MMA polymerization process.

Observing the molecular structures of TPP1 and TPP2, we found that, for TPP1, a strong electron-withdrawing group, namely the *p*-nitrophenyl group, is attached to C(3) but, for TPP2, there is an electron-donating group, namely the styryl group, attached to C(3). So the excited TPP1 molecule exhibits very strong intramolecular charge transfer and the molecular dipole moments are very different (the difference $\Delta\mu$ between the dipole moment is 8.7 Debye), and the dipole–dipole force between the solvent molecule and solute molecule strengthens. However, for TPP2, the intramolecular charge transfer is not strong, and the dipole moment changes slightly (only 2.3 Debye). Because of the small dipole–dipole force between the solute and solvent molecules, the solvent relaxation process exerts little effect on the fluorescence properties of TPP2. Thus, in the process of MMA polymerization, with increase in the system viscosity, the fluorescence quantum yields scarcely change and the emission peak wavelength slightly blue-shifts.

Therefore we conclude that, for 1,3,5-triaryl-2-pyrazoline derivatives, the compound which contains a strong electron-withdrawing group on position 3 is a good fluorescence probe used in the process of MMA bulk polymerization but, if an electron-donating group is located on C(3), the compound is not a good fluorescence probe. In other words, there is a close relationship between good fluorescence probes and the extent of intramolecular charge transfer. Very strong intramolecular charge transfer is essential for a good fluorescence probe.

Acknowledgments

This work was supported by the National Science Foundation of China.

References

[1] J.K. Thomas, *Am. Chem. Soc. Symp. Ser., 199* (1982) 327.
[2] P.A. Brgger, P.P. Infelta, A.M. Braun and M. Gratzel, *J. Am. Chem. Soc., 103* (1981) 320.
[3] T. Nagamura, T. Kurihara and T. Matsuo, *J. Phys. Chem., 86* (1982) 1886.
[4] R.H. Schmchl and D.G. Whitten, *J. Phys. Chem., 85* (1981) 3473.
[5] S.S. Atik and J.K. Thomas, *J. Am. Chem. Soc., 104* (1982) 5868.
[6] J.H. Fendler, *J. Phys. Chem., 84* (1980) 1485.
[7] I. Wilner, J.W. Otvos and M. Calvin, *J. Am. Chem. Soc., 103* (1981) 2507.
[8] A. Wagner, C.W. Schellhammer and S. Petersen, *Angew. Chem., Int. Edn. Engl., 5* (1966) 699.
[9] H. Dorlars, C.W. Schellhammer and J. Schroeder, *Angew. Chem., Int. Edn. Engl., 14* (1975) 665.
[10] D.E. Rivett, J. Rosevear and J.F.K. Wilshire, *Aust. J. Chem., 32* (1979) 1601.
[11] Z. Yan and S. Wu, *J. Lumin., 54* (1993) 303.
[12] S.R. Sandler and K.C. Tsou, *J. Chem. Phys., 39* (1963) 1062.