

A KIND OF FLUORESCENCE PROBE TO STUDY THE KINETICS OF POLYMERIZATION PROCESS*

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ABSTRACT

Fluorescence properties of 1-phenyl-3-(4'-nitrophenyl) pyrazoline (PNP) were studied in bulk polymerization process of methylmethacrylate (MMA). The fluorescence intensity of PNP was enhanced and the emission maximum was blue shifted with the polymerization progress. In the period of auto-acceleration of the polymerization the enhancement of fluorescence intensity and blue shift of peak wavelength in spectra could be observed evidently. This means that the solvatochromic properties of PNP are influenced not only by the solvent polarity but also by the viscosity of the medium (especially by the phase transition). In solid state PNP emits from the charge transfer excited state without solvent relaxation. The transient emission spectra and the results from Bakhshiev model of solvent relaxation coincide with that from the polymerization experiment.

INTRODUCTION

In recent years solvatochromic effects of conjugated intramolecular charge transfer compounds in solution have attracted considerable attention.^[1-5] The absorption and fluorescence spectra of these compounds in solution show variations with the polarity of the solvent. This effect has been applied for the determination of some empirical parameters of solvent polarity, such as Dimroth Et (30) values, etc.^[6-9]. The fluorescence probe study using the solvatochromic effects was also applied to characterize the polarity of the microenvironment, such as the polarities of micelle and LB films.^[10-16]

In general, shifts of the emission band of the conjugated compounds in solvents with different polarity are due to the relaxation of surrounding

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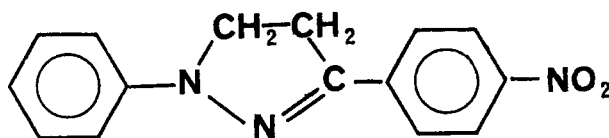
solvent molecules, related to their reorganization, caused by the change of their dipole moment before and after photo-excitation^[17]. With the increase of solvent polarity the fluorescence emission band shows red shift.

Because of the reorganization of solvent molecules, the relaxation of solvent molecules should be affected not only by the interaction between solute and solvent molecules or the polarity of solvent but also by the viscosity of the medium of environment. Law and Loutfy et al. studied the change of emission band of aminobenzylidenemalononitrile compounds and coumarin derivatives in the polymerization process of methyl methacrylate.^[11,18] They indicated that the variations of fluorescence properties were due to the change of free volume of the environment.

1, 3-Diphenyl pyrazoline and its derivatives are known to be typical conjugated intramolecular charge transfer compounds.^[19] The photophysical properties of these compounds in solvents with different polarity have previously been investigated.^[20-21] In this work, the fluorescence properties of 1-phenyl-3-(4'-nitrophenyl) pyrazoline (PNP) in polymerization process of MMA have been studied. The results indicate that this compound can be used as fluorescence probe for the polymerization process. In addition, it has been further proved that the variations of the emission properties in polymerization process are due to the solvent dynamic relaxation.

EXPERIMENTAL

The structure of 1-phenyl-3-(4'-nitrophenyl)-2-pyrazoline (PNP) studied in this work is:



It was synthesized according to reference^[22] and characterized by IR, ¹H NMR and mass-spectroscopy. The results indicate that the structure of product coincides with the formula showed.

All solvents were purified by washing, drying and distillation several times prior to use. The absorption and fluorescence spectra were recorded using a HITACHI 330 UV-Vis spectrophotometer and PE LS-5 Fluorescence spectrophotometer, respectively. The transient fluorescence spectra were

measured in a HORIBA NAES1100 time resolved fluorescence spectrometer.

Experiment of polymerization

PNP was dissolved in methyl methacrylate ($5.0 \times 10^{-6} \text{ mol} \cdot \text{dm}^{-3}$) and polymerization at $60 \pm 1^\circ\text{C}$, initiated by 0.5% AIBN. The solution was bubbled by nitrogen for 20 minutes for removing the oxygen contained. Fluorescence spectra of the solution were recorded after various time intervals of the polymerization. In the measurement of the fluorescence quantum yield, an aqueous solution of 0.5 mol/L H_2SO_4 of quinine bisulfate was used as a fluorescence standard ($\Phi_f = 0.55$).^[23]

Time resolved fluorescence spectrum measurement

A $5.0 \times 10^{-5} \text{ mol} \cdot \text{dm}^{-3}$ solution of PNP was prepared for measuring the fluorescence decay of different emission wavelengths and the fluorescence emission spectra at different delay time can be obtained.

RESULTS AND DISCUSSION

The fluorescence spectra of PNP change dramatically with the solvent, in which a red shift increases with increasing solvent polarity, are shown in Fig 1. For instance, the emission peak wavelength(s) of PNP in cyclohexane are 489 and 518 nm, but in ethyl acetate it is 630 nm. In addition, the fluorescence quantum yields of PNP decrease from 0.58 (in cyclohexane) to 0.026 (in ethyl acetate). The strong solvatochromism of this compound could be explained by the solvent relaxation. In excited state of PNP, its dipole moment increases by intramolecular charge transfer. This causes a reorganization of solvent molecules which surround the PNP molecules. The larger the polarity of the solvent, the greater the solvent-solute interactions, and the more the excited PNP molecules stabilized, leading to a red-shift of the emission peak. At the same time, because the energy gap between excited and ground states decreases, the non-radiative decay process of excited state increases, reducing the fluorescence quantum yield.

Since solvatochromism and solvent relaxation involve the reorganization of solvent molecules, the mobility of solvent molecules around the solute molecule should affect the relaxation process strongly. If the excited PNP molecule is located in a solid, the relaxation of surrounding molecules should be quite difficult. To study the viscosity effect on the relaxation, the polarity of the medium should be kept as constant as possible, because the medium polarity possesses large effect on the solvent relaxation as mentioned above.

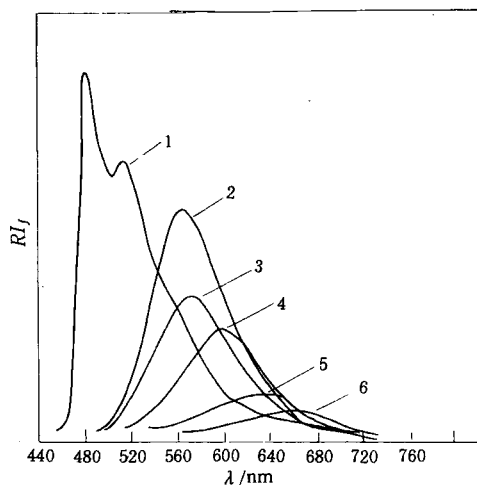


Fig. 1 The fluorescence spectra of PNP in different solvents
 $[PNP] = 5.0 \times 10^{-6} \text{ mol} \cdot \text{dm}^{-3}$,
 $\lambda_{\text{ex}} = 435 \text{ nm}$.
 Solvents: 1) Cyclohexane; 2) Toluene;
 3) Diethyl ether; 4) 1,4-Dioxane;
 5) THF; 6) Ethyl acetate.

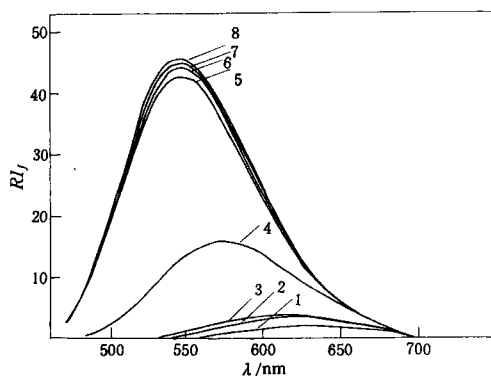


Fig. 2 The fluorescence spectra of PNP in the bulk polymerization process of MMA
 $[PNP] = 5.0 \times 10^{-6} \text{ mol} \cdot \text{dm}^{-3}$,
 $\lambda_{\text{ex}} = 435 \text{ nm}$.
 Polymerization time (min.):
 1) 0; 2) 150; 3) 160; 4) 165;
 5) 170; 6) 175; 7) 180; 8) 300.

During a bulk polymerization, the viscosity of system increases gradually but the change of polarity of system is negligible, so that, the medium effect on the relaxation can be considered to be due to viscosity only. Before polymerization, the solvent relaxation of PNP in monomer is rapid due to the low viscosity. The emission takes place from the equilibrium state after solvent relaxation. After complete polymerization, the PNP molecule is located in a rigid solid, relaxation is difficult and emission occurs from another equilibrium state formed after self-relaxation of the excited molecule via Franck-Condon process. Therefore, during polymerization, it is possible to observe the change of fluorescence behavior of PNP with the changing of viscosity.

In this work, the methyl methacrylate (MMA) was selected as the monomer of bulk polymerization system. Because the polarity of MMA is similar to that of ethyl acetate, the fluorescence quantum yield of PNP in MMA before polymerization is quite low.

The change of the fluorescence behavior of PNP with different time of polymerization was recorded as in Fig. 2. It can be seen that there is a quite

long time period (about 160 mins) at the beginning in which the enhancement of fluorescence intensity of PNP is not significant. After this period, the fluorescence intensity of PNP increases evidently in a very short time range (10 mins). In Table 1, the fluorescence quantum yields of PNP in different polymerization time in MMA system are listed and a plot of the results is shown in Fig. 3.

Table 1 The fluorescence quantum yield of PNP in different time intervals of polymerization of MMA

Time (mins)	0	15	45	75	100	120	140	150
Φ_f	0.020	0.024	0.025	0.026	0.027	0.028	0.029	0.030

Time (mins)	160	165	170	175	180	190	200	210	300
Φ_f	0.035	0.13	0.32	0.31	0.31	0.31	0.31	0.29	0.30

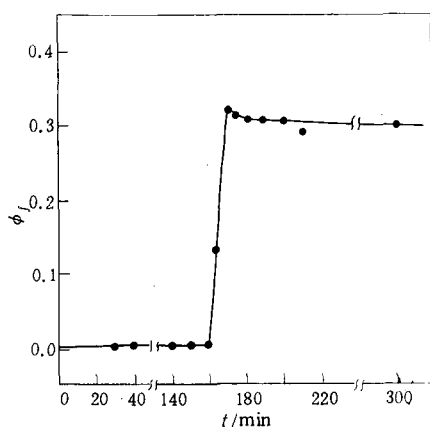


Fig. 3 The plot of fluorescence quantum yield of PNP in the bulk polymerization process of MMA to the polymerization time

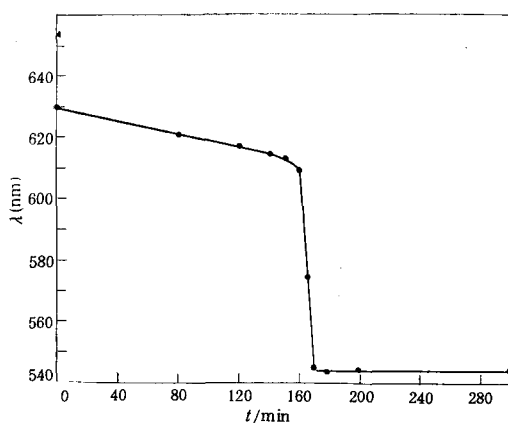


Fig. 4 The plot of maximum emission peak wavelength of PNP in the bulk polymerization process of MMA to the polymerization time

It could be observed in the experiment that the viscosity of the studied system was increased clearly after 100 mins polymerization and the fluidity of the system was almost lost after 160 mins., but at these moments the fluorescence quantum yields of PNP still kept low values. However, just after this period the fluorescence quantum yield of PNP increased promptly about ten times. It demonstrates that there is a great change existed in this period.

The change of the PNP emission peak wavelengths in the

polymerization system with the polymerization time is shown in Fig. 4. It can be found that the peak wavelength of PNP fluorescence spectra shifts to blue side gradually from 630nm. It is evident however that after arriving at a critical time of polymerization (about 160–165 mins. in this work), the peak wavelength of fluorescence has a sudden blue shift and then keeps invariable at 545nm.

It is observed clearly that there is a critical point existed in the process of polymerization which was monitored whether by the fluorescence intensity or by the peak wavelength of fluorescence spectrum. It is well known that, in the process of radical polymerization of olefinic monomers, an auto-acceleration process can occur due to the decrease of the rate of chain termination after a certain conversion ratio arrived. It makes the number of radicals in system increase rapidly and leads the rate of polymerization to increase dramatically. Owing to the presence of the auto-acceleration process, the viscosity of system should increase rapidly in a very short period. As a result of the viscosity changing, the relaxation time of solvent molecules (polymethyl methacrylate molecules) increases greatly. The relaxation process should be stopped. Subsequent to this, the peak wavelength of fluorescence shifts to blue side and the fluorescence intensity increase strongly owing to the decrease of free volume of system and the increase of energy gap between the ground and excited states, which affects on the reduction of non-radiative decay process of excited state of the pyrazoline.

Law and Loutfy et al. studied the change of fluorescence spectra of aminobenzylidenemalononitrile compounds and coumarin derivatives in the polymerization process of methyl methacrylate (MMA)^[11,18]. They indicated the variation of fluorescence properties were due to the change of free volume of the environment and the compounds could be used as fluorescence probe in polymerization process. The results we get in pyrazoline compound are similar to their results and PNP can also be used as a fluorescence probe in polymerization process, especially in high inversion period of polymerization reaction.

As consideration of interaction of excited molecule with solvent molecules, the relaxation time of solvent (τ_r) around the excited molecules of the solute and the life time of excited molecules (τ_f) should be thought out together. When $\tau_r \ll \tau_f$, it implies that the rate of solvent reorganization is much faster than that of radiative decay of the excited molecules. Therefore,

the fluorescence emitted is resulted from a new equilibrium state via the rapid solvent relaxation. If the solvent viscosity increases to a certain degree, the relaxation time of the solvent should be prolonged. In this case, it is possible to use the rapid time resolved fluorescence spectroscopic technique to study the process of the solvent relaxation^[24]. Due to the low fluorescence intensity and short fluorescence life time of PNP in the solvents with large polarity, it is difficult to measure the fluorescence decay process in our equipment. On that account, 1,4-dioxane was selected as solvent to study the solvent relaxation process of excited PNP molecule by transient spectrum.

The time-resolved fluorescence emission spectra of PNP at different delay time in 1,4-dioxane were obtained with single photon counting technique, as shown in Fig. 5. It can be seen that the peak wavelength in spectrum is 580 nm at 1.5 ns, 590 nm at 3.0 ns, 595 nm at 4.5 ns and 600 nm at 7.0 ns respectively.

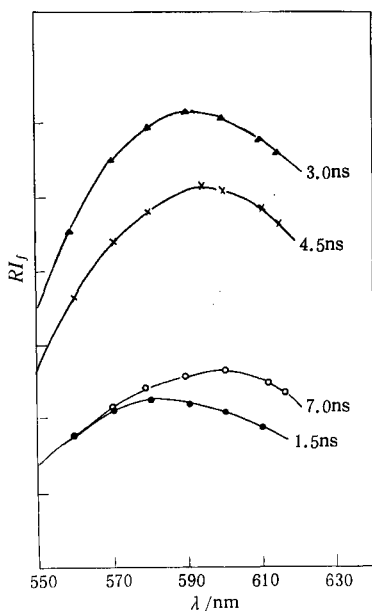


Fig. 5 The time-resolved fluorescence spectra of PNP in 1,4-dioxane
 $[PNP] = 5.0 \times 10^{-5} \text{ mol} \cdot \text{dm}^{-3}$,
 $\lambda_{\text{ex}} = 435 \text{ nm}$

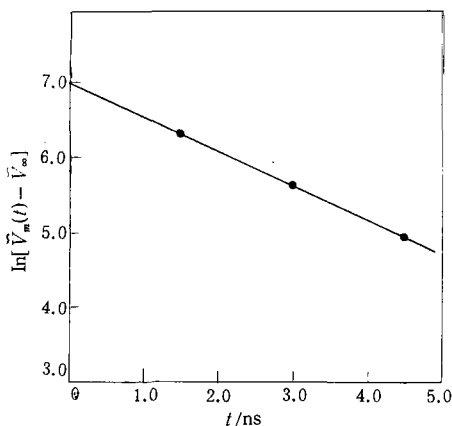


Fig. 6 The result of the treatment of time-resolved fluorescence spectra by the Bakhshiev model of solvent relaxation

Using Bakhshiev equation of solvent relaxation^[25-26] some quantitative results of excited PNP molecule in 1,4-dioxane can be obtained.

According to the Bakhshiev theory, the time-resolved emission $I(\tilde{\nu}, t)$ can be described as a product of decay of the total fluorescence intensity $i(t)$ and a normalized time dependent spectral relaxation $\rho[\tilde{\nu}_m(t), \tilde{\nu}]$:

$$I(\tilde{\nu}, t) = i(t) \cdot \rho[\tilde{\nu}_m(t), \tilde{\nu}] \quad (1)$$

where $\tilde{\nu}_m(t)$ is the center of gravity of the emission spectrum or the wavenumber of emission maximum and is assumed to shift to lower energy in an exponential fashion with a solvent relaxation time τ_r :

$$\tilde{\nu}_m(t) = \tilde{\nu}_\infty + (\tilde{\nu}_0 - \tilde{\nu}_\infty) \exp(-t/\tau_r) \quad (2)$$

where $\tilde{\nu}_0$ and $\tilde{\nu}_\infty$ represent the wavenumber of emission maximum for $t=0$ and $t=\infty$ respectively. Formula (2) can be changed to logarithmic form:

$$\ln[\tilde{\nu}_m(t) - \tilde{\nu}_\infty] = \ln(\tilde{\nu}_0 - \tilde{\nu}_\infty) - t/\tau_r \quad (3)$$

As $\tilde{\nu}_m(t)$ can be measured, the $\tilde{\nu}_\infty$ may be considered as the wavenumber of an unchangeable emission maximum after suitable long time decay, $\tilde{\nu}_0$ is the wavenumber of emission maximum of nonsolvent relaxation, it ought to be a linear correlation between the $\ln[\tilde{\nu}_m(t) - \tilde{\nu}_\infty]$ and reciprocal of the solvent relaxation time, $1/\tau_r$.

Table 2 shows the wavenumber of emission maximum of PNP in 1,4-dioxane at different delay time, $\tilde{\nu}_m(t)$. Fig. 6 is a plot of $\ln[\tilde{\nu}_m(t) - \tilde{\nu}_\infty]$ against the delay time, t . In this experiment, because the emission maximum keeps unchanged after 7.0 ns, the wavenumber $\tilde{\nu}_\infty$ is equal to $\tilde{\nu}(7.0\text{ ns})$.

In Fig. 6 it can be seen that there is a good linear correlation between $\ln[\tilde{\nu}_m(t) - \tilde{\nu}_\infty]$ and the delay time t . From the slope of the linear correlation the solvent relaxation time (τ_r) was obtained (2.2 ns).

Table 2 The results of time-resolved fluorescence spectra

$t(\text{ns})$	1.5	3.0	4.5	7.0
$\lambda \text{ max}(\text{nm})$	580	590	595	600
$\tilde{\nu}_m(t) (\text{cm}^{-1})$	17240	16950	16810	16667
$\tilde{\nu}_m(t) - \tilde{\nu}_\infty$	573	283	143	---
$\ln[\tilde{\nu}_m(t) - \tilde{\nu}_\infty]$	6.35	5.65	4.96	---

From the intercept of the plot, the $\tilde{\nu}_0$ was obtained (17764 cm^{-1}), the wavelength responded is 560 nm. It means that if there is no solvent relaxation existed, the emission maximum of PNP in solution is about 560 nm. This result approaches well to that obtained in the polymerization

experiment, i. e. in solid PMMA the PNP molecule emits fluorescence with maximum wavelength at 545 nm. It proved further that the variation of fluorescence emission spectra of PNP in polymerization process is due to the solvent relaxation.

Keywords:

Fluorescence probe; Polymerization; Solvatochromism; 1-Phenyl-3-(4'-nitrophenyl)pyrazoline

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REFERENCES

- [1] Buncel, E. and Rajagopal, S., *Acc. Chem. Res.*, **1990**, 23, 226.
- [2] Lakowicz, J. R. "Principles of Fluorescence Spectroscopy", Plenum, New York, **1986**, p187.
- [3] Mazumdar, S.; Manoharan, R. and Dogra, S. et al., *J. Photochem. Photobiol. A, Chem.*, **1989**, 46, 301.
- [4] Palay, M. S.; Harris, J. M. and Looser, H. et al., *J. Org. Chem.*, **1989**, 54, 3774.
- [5] S.-Schwok, A.; B.-Desce, M. and Lehn, J.-M., *J. Phys. Chem.*, **1990**, 94, 3894.
- [6] Reichardt, C. and Dimroth, K., *Fortschr. Chem. Forsch.*, **1968**, 1, 11.
- [7] (a). Dimroth, K.; Reichardt, C. and Siepmann, T., *Liebigs Ann. Chem.*, **1963**, 661, 1.
(b). Reichardt, C. and *Liebigs, Ann., Chem.*, **1971**, 752, 64.
- [8] Dimroth, K. and Reichardt, C. and *Liebigs Ann. Chem.*, **1969**, 727, 93.
- [9] Dimroth, K. and Reichardt, C., *Z. Anal. Chem.*, **1966**, 215, 344.
- [10] Law, K. Y., *Photochem. Photobiol.*, **1981**, 33, 799.
- [11] (a). Loutfy, R. O., *Macromolecules*, **1981**, 14, 270.
(b). Law, K. Y. and Loutfy, R. O., *Macromolecules*, **1981**, 14, 587.
(c). Loutfy, K. Y. and Teegarden, D. M., *Macromolecules*, **1983**, 16, 452.
(d). Law, K. Y. and Loutfy, R. O., *Polymer*, **1983**, 24, 439.
- [12] (a). Schanze, K. S.; Shin, D. M. and Whitten, D. G., *J. Am. Chem. Soc.*, **1985**, 107, 507.
(b). Shin, D. M. and Whitten, D. G., *J. Phys. Chem.*, **1988**, 92, 2945.
- [13] S.-Amiri, A.; Thompson, M. and Krull, U. J., *J. Photochem. Photobiol. A, Chem.*, **1989**, 47, 299.
- [14] Kung, C. E. and Reed, J. K., *Biochemistry*, **1986**, 25, 6114.
- [15] Lukac, S., *J. Am. Chem. Soc.*, **1984**, 106, 4386.
- [16] Zachariasse, K. A.; Vaz, W. L. C.; Sotomayer, O., et al., *Biochem. Biophys. Acta*, **1982**, 688, 323.
- [17] Lippert, E., *Z. Elektrochem., Ber. Bunsenges. Phys. Chem.*, **1958**, 61, 962.
- [18] A.-Mottaleb, M. S. A.; E.-Kady, Y.; Loutfy, R. O., et al., *J. Photochem. Photobiol. A, Chem.*, **1990**, 53, 384.
- [19] Morley, J. O.; Docherty, V. J. and Pugh, D. J., *Molecular Electronics*, **1989**, 5, 117.
- [20] Yang, G. Q. and Wu, S. K., *Acta Physico-Chimica Sinica*, **1992**, 8(5), 602.
- [21] Yang, G. Q. and Wu, S. K., *J. Photochem. Photobiol. A, Chem.*, **1992**, 66, 69.
- [22] Wiley, R. H. and Jarboe, C. H., "The Chemistry of Heterocyclic Compounds", Vol. 22, Part 2, Interscience Publishers, New York, **1967**, p183.
- [23] Meech, S. R. and Phillips, D., *J. Photochem.*, **1983**, 23, 193.
- [24] Sardar, M. and Sengupta, P. K., *J. Photochem. Photobiol. A, Chem.*, **1990**, 53, 191.
- [25] Bakhshiev, N. C.; Mazurenko, Yu T. and Pitserskaya, I. V., *Opt. Spectrosc.*, **1966**, 21, 307.
- [26] Pant, D.; Tripathi, H. B. and Pant, D. D., *J. Photochem. Photobiol. A, Chem.*, **1991**, 56, 207.