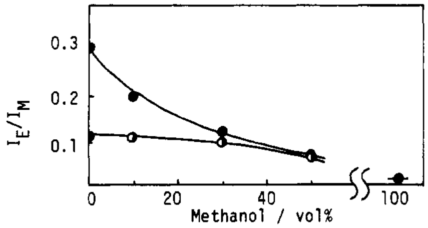


Figure 7. Effect of methanol on excimer emission of PIA-6 (●) and DIA (◑). I_E = 500 nm, $I_M \simeq$ 417 nm, [PIA-6] = 2.9 × 10^{-4} mol/dm^3, and [DIA] = 1.4 × 10^{-4} mol/dm^3.

pend on the size and conformation of polymer chain.

From the study on the environmental effects on the excimer emission, we have found that the excimer intensity reflects sharply the aggregation nature of the pendant groups. The overall features of PIA-6 molecules in solution can be visualized as shown in Table IV by combining the results of the spectroscopy, photodimerizability, and viscosity studies. In a conclusion, the PIA-6 conformation is very much affected by environment, which is quite different from the case for polyesters bearing anthryl groups in organic solvents in which the chemical structure of the polymer is the dominant factor determining excimer formation and photodimerizability.

References and Notes

(1) Tazuke, S.; Suzuki, Y. *J. Polym. Sci., Polym. Lett. Ed.* **1978**, *16*, 223.

(2) Suzuki, Y.; Tazuke, S. *Macromolecules* **1980**, *13*, 25.

(3) Tazuke, S.; Banba, F. *J. Polym. Sci., Polym. Chem. Ed.* **1976**, *14*, 2463.

(4) Tazuke, S.; Hayashi, N. *Polym. J.* **1978**, *10*, 443.

(5) Sato, K.; Hayashi, N.; Tazuke, S. *J. Polym. Sci., Polym. Lett. Ed.* **1977**, *15*, 671.

(6) (a) Iwaya, Y.; Tazuke, S. *Polym. Prepr., Jpn.* **1979**, *28*, 1334. (b) *Ibid.* **1980**, *29*, 1333. (c) Tazuke, S.; Yuan, H. L.; Iwaya, Y.; Sato, K. *Macromolecules* **1981**, *14*, 267.

(7) Tazuke, S.; Tomono, H.; Kawasaki, Y.; Kitamura, N.; Inoue, T. *Nippon Kagaku Kaishi* **1980**, 418.

(8) Tazuke, S.; Banba, F. *Macromolecules* **1976**, *9*, 451.

(9) Although excimer formation by ethylenic polymers is often molecular weight independent, excimer as well as exciplex formation by the present series of polyesters increases with the degree of polymerization, indicating nonneighboring group participation.

(10) (a) Matsuyama, Y.; Tazuke, S. *Polym. J.* **1976**, *8*, 481. (b) Tazuke, S.; Yuan, H. L.; Iwaya, Y. The U.S./Japan Polymer Symposium, Nov 1980, Palm Springs, to be published as *Contemp. Top. Polym. Sci.*, Plenum Press, and references therein.

(11) (a) Chandross, E. A.; Ferguson, J.; McRae, F. G. *J. Chem. Phys.* **1966**, *10*, 3546. (b) Chandross, E. A.; Ferguson, J. *Ibid.* **1966**, *10*, 3554.

(12) To compare with previous results of photodimerization and absorption spectroscopy, we used relatively high concentrations for fluorescence spectroscopy. Even with the front-side irradiation method, the linear relationship between concentration and fluorescence intensity is no longer found.

(13) Fendler, L. H.; Fendler, E. J. "Catalysis in Micellar and Macromolecular Systems"; Academic Press: New York, 1975; pp 306–11.

(14) Lanlande, R.; Calas, R. *Bull. Soc. Chim. Fr.* **1960**, 144.

(15) (a) Birks, J. B. "Photophysics of Aromatic Molecules"; Wiley-Interscience: New York, 1970; p 319. (b) Laurent, H. B.; Castellan, A.; Desvergne, J. P. *Pure Appl. Chem.* **1980**, *52*, 2633.

Absorption and Fluorescence Spectra of Vinyl and Methacrylate Polymers Containing Pendant 1,3,5-Triphenyl-2-pyrazoline Chromophores

Fujio Iinuma, Hiroshi Mikawa, and Yasuhiko Shirota*

Department of Applied Chemistry, Faculty of Engineering, Osaka University, Yamadaoka 2-1, Suita, Osaka 565, Japan. *Received February 4, 1981*

ABSTRACT: In order to gain insight into polymer effects on spectroscopic properties of polymers containing polar pendant chromophores, the absorption and emission spectra of vinyl and methacrylate polymers containing pendant 1,3,5-triphenyl-2-pyrazoline (TPP) chromophores were studied in various solvents and compared with those of low-molecular-weight model compounds. The polymers were found to exhibit no excimer fluorescence, emitting only normal fluorescence. The polymer effects on the spectroscopic properties relative to those of low-molecular-weight model compounds were characterized by the following three features: larger Stokes shifts for the fluorescence, decreased quantum yields of the fluorescence, and less sensitivity of the fluorescence band position to the solvent polarity. These characteristic effects of the polymers result from perturbation by neighboring groups and are understood in terms of nearby pendant TPP chromophores in the ground state solvating TPP chromophores in the electronically excited singlet state.

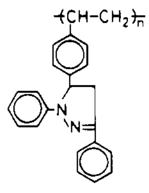
Studies of the absorption and emission spectra of polymers are expected to provide information on the conformation and microenvironment of polymers as well as interactions between chromophores bound to polymers; these will be observed as polymer effects on spectroscopic properties. In addition, an understanding of spectroscopic and photophysical properties of polymers will be of importance for the understanding of the function and in the design of photosensitive functional polymers such as photoconducting polymers.

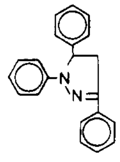
There have been a few studies comparing the absorption spectra of vinyl aromatic polymers with those of low-molecular-weight analogues, indicating hypochromism in polymers,[1-3] and extensive studies of the emission spectra of vinyl aromatic polymers from the viewpoint of excimer formation[4-15] have been made. Ground-state dimer formation between the pendant chromophores has also been indicated from the absorption and emission spectra of certain vinyl polymers.[16-18] However, there are still some basic questions remaining to be studied concerning polymer effects on spectroscopic properties. For example, except for reports concerning the phosphorescence spectra of a few polymers,[19,20] the question of how the normal emission is affected by the polymeric framework has not been fully studied. Little attention has been paid to the problem of how solvent effects on the absorption and emission spectra of polymers differ from those of low-molecular-weight analogues. Spectroscopic studies on vinyl

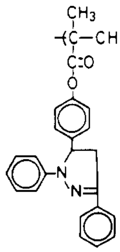
0024-9297/81/2214-1747$01.25/0

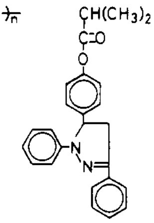
aromatic and heterocyclic polymers with no excimer formation have been rare.

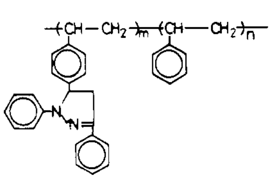
In view of this, the present investigation was undertaken to gain some insight into polymer effects on spectroscopic properties of polymers. The great majority of previous studies of spectroscopic properties of synthetic polymers which deal mainly with excimer formation have concentrated on vinyl aromatic polymers, e.g., polystyrene,[4,5] poly(vinylnaphthalene),[5-8] polyacenaphthalene,[8,9] poly(vinylpyrene),[10,11] poly(vinylphenanthrene),[12] poly(*N*-vinylcarbazole),[13,14] and their related polymers,[11,15] the pendant chromophores of which show very little solvatochromism in their absorption and emission spectra. The present study has been directed to polymers containing solvatochromic pendant chromophores, particularly in their emission spectra. The 1,3,5-triphenyl-2-pyrazoline (TPP) chromophore has been selected for the present study since TPP is known to have a relatively large dipole moment in the ground state (μ_g = 2.58)[21,22] and a much greater one in its electronically excited singlet state (μ_e = 8.16,[21] 7.7;[22] $\mu_e - \mu_g$ = 5.53[23]) by virtue of the intramolecular charge-transfer structure, and spectroscopic and photophysical properties of TPP and its derivatives have recently been studied extensively.[24-27] In this paper we describe spectroscopic properties of poly[1,3-diphenyl-5-(*p*-vinylphenyl)-2-pyrazoline] (PVTPP), poly[1,3-diphenyl-5-[*p*-(methacryloyloxy)phenyl]-2-pyrazoline] (PMTPP), and their copolymers with styrene, copoly(VTPP–St) and copoly(MTPP–St), and compare them with those of their low-molecular-weight model compounds, TPP and 1,3-diphenyl-5-[*p*-(isobutyryloxy)phenyl]-2-pyrazoline (i-BTPP), focusing attention on polymer effects on spectroscopic properties. The synthesis of these homo- and copolymers, which are new photoconducting polymers, has been described in previous papers.[28] A part of the present work has been reported as a short communication.[29] Migration of the singlet excitation energy in these polymers has also been reported.[30]

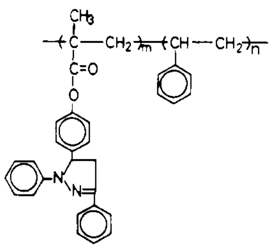

PVTPP


TPP


PMTPP


i-BTPP


Copoly(VTPP-St)


Copoly(MTPP-St)

Experimental Section

Materials. PVTPP and PMTPP were prepared by radical polymerization of the corresponding monomers, 1,3-diphenyl-5-(*p*-vinylphenyl)-2-pyrazoline (VTPP) and 1,3-diphenyl-5-[*p*-(methacryloyloxy)phenyl]-2-pyrazoline (MTPP), as described in the previous paper,[28b] purified by repeated reprecipitation from THF–methanol, and dried in vacuo. The number-average molecular weights ($\bar{M}_n$) of the polymers employed in this study were 17800 for PVTPP and 25000 for PMTPP. The copolymers, copoly(VTPP–St) and copoly(MTPP–St), were prepared by radical copolymerization of VTPP and MTPP with styrene,[28b] reprecipitated from THF–methanol, and dried in vacuo. Copoly(VTPP–St) with VTPP:St ratios of ca. 0.8:0.2 and 0.25:0.75 and copoly(MTPP–St) with MTPP:St ratios of ca. 0.65:0.35 and 0.3:0.7 were used for the spectral measurement. TPP (mp 140.5–141.5 °C) was prepared according to a known procedure,[31] purified by repeated recrystallization from ethanol, and dried in vacuo. i-BTPP was prepared by reaction of 1,3-diphenyl-5-(*p*-hydroxyphenyl)-2-pyrazoline whch had been prepared by a known method[31] with commerically available isobutyryl chloride in the presence of triethylamine in THF, purified by silica gel column chromatography, followed by repeated recrystallization from cyclohexane, and dried; mp 124.5–125.5 °C. All solvents were purified and dried by ordinary methods.

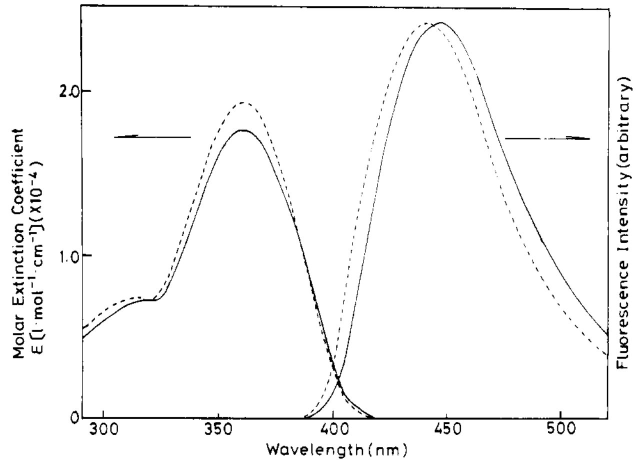


Figure 1. Absorption and fluorescence spectra (corrected) of PVTPP (—) and TPP (- - -) in benzene at room temperature. [PVTPP] = 2 × 10^{-5} M (in monomer unit); [TPP] = 2 × 10^{-5} M. Excitation wavelength: 360 nm.

Spectral Measurements. The electronic absorption spectra were recorded with a Hitachi 124 spectrometer. The fluorescence and excitation spectra were recorded with a Hitachi MPF-3 spectrofluorometer fitted with an HTVR-446F photomultiplier. The spectral measurement at room temperature was made with the use of a fused-quartz cell of 1-cm path length. For measurement of the fluorescence spectra in 2-methyltetrahydrofuran (MTHF) at 77 K, the solution was sealed in a 3-mm-diameter Pyrex glass capillary tube after being degassed by freeze–pump–thaw cycles. The spectra were measured in dilute solutions, the concentration of the solution for both the polymers and the model compounds being from 2 × 10^{-5} to 4 × 10^{-5} M to give an absorbance of ca. 0.4–0.8 at λ 360 nm unless otherwise indicated. The fluorescence quantum yield was measured in THF at 20 °C relative to quinine sulfate in 1.0 N sulfuric acid (ϕ = 0.546, excited at 366 nm at 25 °C.

Results and Discussion

Figures 1 and 2 show the electronic absorption and fluorescence spectra of the hompppolymer PVTPP and its low-molecular-weight model compound TPP measured in dilute, fluid benzene and rigid MTHF solutions at room temperature and 77 K, respectively. Table I lists the absorption and fluorescence band maxima for PVTPP and its copolymers with styrene, copoly(VTPP–St), in various solvents together with those for TPP. The trends for the methacrylate homo– and copolymers are virtually the same for the vinyl polymers. Figures 3 and 4 show the spectra of PMTPP and copoly(MTPP–St), and their low-molecular-weight model compound, i-BTPP, measured in dilute benzene solutions at room temperature and in rigid MTHF solutions at 77 K, respectively. The values of the fluorescence quantum yield for both vinyl and methacrylate polymers and for the model compounds are listed in Table II.

Table I
Absorption and Fluorescence Band Maxima for TPP, PVTPP, and Copoly(VTPP-St) in Various Solvents

	absorption band maxima,[a] nm				fluorescence band maxima, nm			
			copoly(VTPP-St)[c]				copoly(VTPP-St)[c]	
solvent	TPP	PVTPP[b]	1	2	TPP	PVTPP[b]	1	2
			Room Temperature					
benzene	362	362	362	362	441	447	444	446
dioxane	360	360			444	448		
THF	359	359	359	359	446	450	446	448
$ClCH_2CH_2Cl$	360	360			450	452		
acetone	358	358	359	358	453	453	453	453
DMF	361	361			455	455		
			77 K[d]					
MTHF	375	365	371	366	415	425	419	425
	392	391	392	391	433	447	442	447

[a] log ϵ in benzene: 4.29 for TPP, 4.27 for PVTPP. [b] $\overline{M}_n = 1.78 \times 10^4$, $\overline{M}_w = 3.08 \times 10^4$. [c] Copolymer composition: VTPP:St = 0.25:0.75 for 1; VTPP:St = 0.8:0.2 for 2. PVTPP and copoly(VTPP-St) are easily soluble in the solvents examined except for acetone. [d] Vibrational structures appear at 77 K.

Table II
Fluorescence Quantum Yields for PVTPP, PMTPP, TPP, and i-BTPP in Solutions at 20 °C

solvent	TPP	PVTPP	i-BTPP	PMTPP
benzene	0.90	0.76	0.90	0.73
THF	0.77	0.73	0.72	0.67

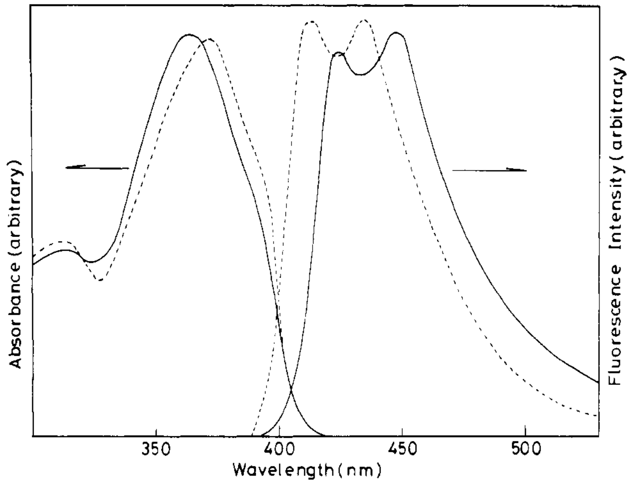


Figure 2. Absorption and fluorescence spectra (corrected) of PVTPP (—) and TPP (---) in MTHF at 77 K. [PVTPP] = 2 × 10^{-5} M (in monomer unit); [TPP] = 2 × 10^{-5} M. Excitation wavelength: 360 nm.

TPP and its derivatives are known to show an intense absorption band in the wavelength region from ca. 330 to 420 nm, which is assigned to the intramolecular charge-transfer absorption band with the electron density shift in the direction from the 1- to the 3-position of the conjugated π system Ar—N—N=C—Ar in the pyrazoline ring. On excitation of this band, an intense fluorescence appears in the wavelength region around 400–500 nm with no phosphorescence emission. As the figures show, the two polymers under investigation were found to exhibit no excimer fluorescence, emitting only normal fluorescence that can be assigned as due to the TPP chromophore in the polymer environment. The absorption and fluorescence spectra of the two polymers were found to be very similar. It was confirmed that the fluorescence excitation spectra correspond well to the absorption spectra. No phosphorescence was observed for the polymers by excitation of the intramolecular charge-transfer absorption band.

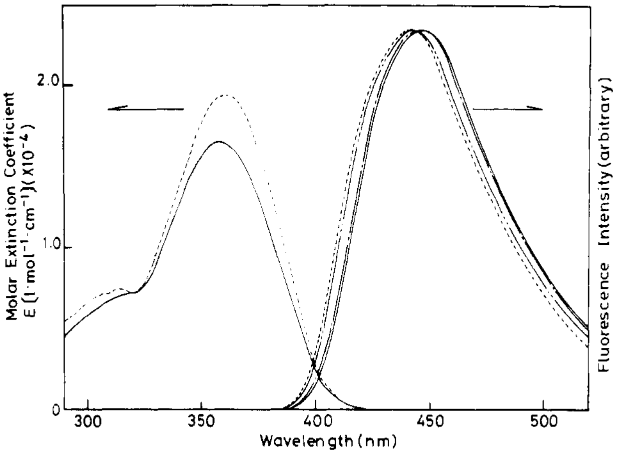


Figure 3. Absorption and fluorescence spectra (corrected) of PMTPP (—), i-BTPP (---), and copoly(MTPP-St) with copolymer compositions of ca. 0.65:0.35 (– – –) and 0.3:0.7 (– - –) in benzene at room temperature. [PMTPP] = 3 × 10^{-5} M (in monomer unit); [i-BTPP] = 3 × 10^{-5} M; [copoly(MTPP-St)] = 3 × 10^{-5} M (in MTPP monomer unit). Excitation wavelength: 360 nm.

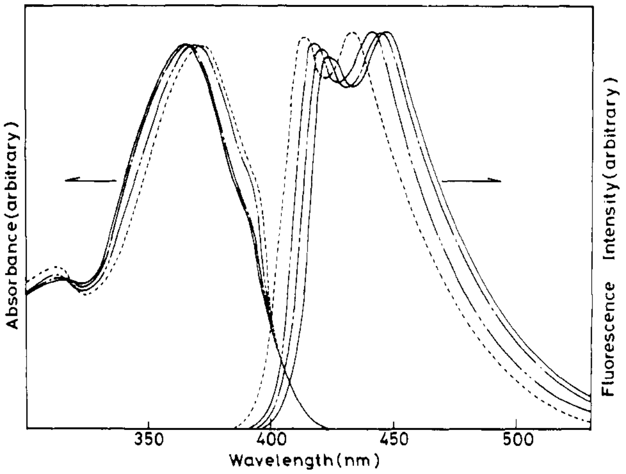


Figure 4. Absorption and fluorescence spectra (corrected) of PMTPP (—), i-BTPP (---), and copoly(MTPP-St) with copolymer compositions of ca. 0.65:0.35 (– – –) and 0.3:0.7 (– - –) in MTHF at 77 K. [PMTPP] = 3 × 10^{-5} M (in monomer unit); [i-BTPP] = 3 × 10^{-5} M; [copoly(MTPP-St)] = 3 × 10^{-5} M (in MTPP monomer unit). Excitation wavelength: 360 nm.

Comparison between the spectra of the polymers and their monomeric model compounds shows that the absorption spectra in fluid solutions are almost the same for the polymers and their model compounds, although both polymers show a slight hypochromism (Table I) and the

PMTPP polymer shows a slight blue shift relative to i-BTPP (Figure 3), but that the fluorescence bands of the polymers are distinctly red shifted, 305 cm^{-1} for PVTPP and 253 cm^{-1} for PMTPP, relative to those of the model compounds in benzene solutions (Figures 1 and 3). The extent of the red shift of the fluorescence band of the polymers relative to that of the model compounds was found to be more significant in a rigid solution at 77 K than in a fluid solution as shown in Figures 2 and 4: the spectra taken at 77 K show a vibrational structure, and the 0–0 and 0–1 bands of the fluorescence spectra of the polymers are red shifted by 567 and 774 cm^{-1} for PVTPP and by 567 and 724 cm^{-1} for PMTPP, respectively, relative to those of the model compounds. At the same time, the absorption band maxima of both polymers in a rigid solution at 77 K are blue shifted 730 cm^{-1} relative to those of the model compounds. Inspection of Table I indicates that the fluorescence band position for the polymer PVTPP as well as the model compound TPP undergoes a red shift on going from nonpolar to polar solvents but that the polymer is less sensitive to changes in solvent polarity than the model compound. The polymer PMTPP gives exactly the same solvent dependence as PVTPP. The extent of the red shift on going from benzene to DMF is 698 and 646 cm^{-1} for TPP and i-BTPP, respectively, but 393 cm^{-1} for the polymers. This stems from the fact that the fluorescence band position of the polymers is significantly red shifted in nonpolar solvents, whereas in polar solvents it does not differ between the polymers and the model compounds. On the other hand, the absorption bands of both the polymers and their model compounds in fluid solutions, which are almost the same, tend to shift slightly to higher energies in solvents of increasing polarity but do not greatly differ in various solvents. The quantum yields for the flourescence of TPP and its derivatives drop with an increase in solvent polarity. The data listed in Table II show that the fluorescence quantum yields for the polymers in benzene are reduced compared to those of the model compounds in the same solvent but that the extent of the drop with an increase in solvent polarity is smaller for the polymers than for the model compounds.

As described above, the present study has revealed that the PVTPP and PMTPP polymers show no excimer fluorescence and that the polymer effects on the spectroscopic properties of these polymers relative to those of the monomeric compounds are characterized by the following three features: (1) larger Stokes shifts for the fluorescence band, (2) less sensitivity of the fluorescence band position to changes in solvent polarity, and (3) decreased fluorescence quantum yields. The absence of the intramolecular excimer formation in the present polymers may be due to negligible binding energy between excited- and ground-state chromophores. The molecular structure of the pendant TPP chromophore may also be responsible for the absence of excimer formation, since the structure is thought to be unfavorable for the formation of the generally accepted specific conformation of excimers, i.e., a sandwitch-type fact-to-face arrangement of excited- and ground-state chromophores. The results of an X-ray structural analysis of 1,3-diphenyl-5-(*p*-chlorophenyl)-2-pyrazoline show that the plane of the phenyl ring at the 5-position is almost perpendicular to the plane of the pyrazoline ring.[32] It should also be noted that TPP and its derivatives do not form an intermolecular excimer in their concentrated solutions.

The spectroscopic features characteristic of the polymers described above result from perturbation by neighboring pendant chromophores and have led us to consider intramolecular solvation by the pendant chromophores;[28a,29] namely, in nonpolar to weakly polar solvents, TPP chromophores in the ground state contribute toward solvation of the polar chromophores in the electronically excited state, in addition to solvation by the solvent. This will be more significant in rigid matrices where solvent reorientation is more restricted in fluid solutions. It is probable that the singlet excitation energy migrates to the chromophore sites where intramolecular solvation by nearby pendant TPP chromophores is operative. In polar fluid solvents such as acetone or DMF, however, solvation by polar solvents may become predominant over the intramolecular solvation by the pendant TPP chromophores; hence, the fluorescence band position of the polymers in polar solvents does not differ from that of the model compounds. The data in Table I suggest that the solvation of the electronically excited TPP chromophores by nearby pendant ground-state TPP chromophores nearly equals the solvation by a solvent of polarity intermediate between that of THF and 1,2-dichloroethane. The decreased fluorescence quantum yield for the polymers relative to the monomeric model compounds (Table II) is consistent with this concept. It has been shown that the polymer microenvironment polarity in synthetic vinylic polymers is lower than the polarity of the bulk solution due to the shielding effect by a less polar polymer chain.[33,34] In spite of this fact, the singlet excited fluorescing TPP chromophores in the present polymers exist in more polar microenvironments than in bulk solutions of nonpolar or weakly polar solvents because of the solvation by the pendant TPP chromophores. A blue shift of the absorption band of polymers in MTHF at 77 K suggests that interactions between the pendant chromophores in the ground state may also be operative (Figures 2 and 4).

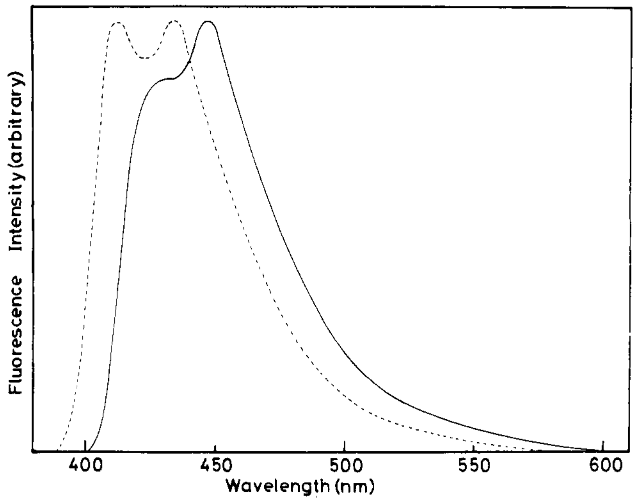


Figure 5. Fluorescence spectra (corrected) of TPP in MTHF at 77 K. [TPP] = 2 × 10^{-1} M (—); [TPP] = 2 × 10^{-5} M (- - -). Excitation wavelength: 360 nm.

The concept of solvation by pendant chromophores is further supported from the spectal properties of the copolymer and the monomeric model compound in concentrated solutions. The results in Table I and Figures 3 and 4 show that as the copolymer composition becomes rich in styrene, the spectra resemble those of the low-molecular-weight model compounds. Figure 5 shows the fluorescence spectrum of TPP in a concentrated solution at 77 K. The fluorescence spectra of TPP in concentrated solutions shift to lower energies with an increase in TPP concentration compared to the spectra in dilute solutions. This phenomenon is also explained in terms of solvation of the electronically excited TPP molecules by ground-state TPP molecules. In polymers, solvation by the pendant chromophores can occur in dilute solutions because of a high local concentration of chromophores along the polymer chain. A related phenomenon has been observed which shows that the fluorescence spectrum of 1,3-diphenyl-2-pyrazoline undergoes a red shift in the presence of indole in *n*-heptane. This has been explained in terms of a specific solvation by the indole molecules.[35] Related to the present study, a few works which take into account the solvation of chromophores by ester groups bound to polymers have recently appeared. To explain the emission characteristics of the polymer-bound exciplex in polymers having a polyester main chain, solvation of the exciplex by the ester groups in the main chain has been suggested.[36] Solvation of pendant merocyanine chromophores by pendant ester groups bound to polymes has been suggested for the phenomenon of the photoinduced viscosity change in poly(methyl methacrylate) containing spirobenzopyran pendant groups.[37-39]

The present study has aimed at illuminating basic questions in polymer spectroscopy such as described in the introduction by using polymers containing polar pendant chromophores, particularly in the electronically excited state. Spectroscopic features characteristic of the polymers have been made clear and systematically understood in terms of solvation by the pendant chromophores. The generality of the present phenomena in spectroscopy for other polymers containing polar pendant chromophores is currently under investigation.

References and Notes

(1) Vala, M. T., Jr.; Rice, S. A. *J. Chem. Phys.* **1963**, *39*, 2348.
(2) Okamoto, K.; Itaya, A.; Kusabayashi, S. *Chem. Lett.* **1974**, 1167.
(3) Gallo, B. M.; Russo, S. *J. Macromol. Sci., Chem.* **1974**, *A8*, 521.
(4) Yanari, S. S.; Bovey, F. A.; Lumy, R. *Nature (London)* **1963**, *200*, 242.
(5) Vala, M. T., Jr.; Haebig, J.; Rice, S. A. *J. Chem. Phys.* **1965**, *43*, 886.
(6) Harrah, L. A. *J. Chem. Phys.* **1972**, *56*, 385.
(7) Nishijima, Y.; Yamamoto, M.; Katayama, S.; Hirata, K.; Sasaki, Y.; Tsujisaka, M. *Rep. Prog. Polym. Phys. Jpn.* **1972**, *15*, 445.
(8) Fox, R. B.; Price, T. R.; Cozzens, R. F.; McDonald, J. R. *J. Chem. Phys.* **1972**, *57*, 534.
(9) David, C.; Piens, M.; Geuskens, G. *Eur. Polym. J.* **1972**, *8*, 1019.
(10) McDonald, J. R.; Echols, W. E.; Rice, T. R.; Fox, R. B. *J. Chem. Phys.* **1972**, *57*, 1746.
(11) Yokoyama, M.; Tamamura, T.; Nakano, T.; Mikawa, H. *Chem. Lett.* **1972**, 499.
(12) Itaya, A.; Okamoto, K.; Kusabayashi, S. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 52.
(13) Johnson, G. E. *J. Chem. Phys.* **1975**, *62*, 4697.
(14) Yokoyama, M.; Tamamura, T.; Atsumi, M.; Yoshimura, M.; Shirota, Y.; Mikawa, H. *Macromolecules* **1975**, *8*, 101.
(15) Sommersall, A. C.; Guillet, J. B. *Macromolecules* **1973**, *6*, 218.
(16) Johnson, P. C.; Offen, H. W. *J. Chem. Phys.* **1971**, *55*, 2945.
(17) Irie, M.; Kamijo, T.; Aikawa, M.; Takemura, T.; Hayashi, K.; Baba, H. *J. Phys. Chem.* **1977**, *81*, 1571.
(18) Aikawa, M.; Takemura, T.; Baba, H.; Irie, M.; Hayashi, K. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 3643.
(19) David, C.; Naegelen, V.; Piret, W.; Geuskens, G. *Eur. Polym. J.* **1975**, *11*, 569.
(20) Klöpffer, W.; Fischer, D. *J. Polym. Sci., Polym. Symp.* **1973**, *No. 40*, 43.
(21) Kutsyna, L. M.; Voevoda, L. V.; Kornilovskaya, L. D. *Opt. Spectrosc.* **1965**, *18*, 294.
(22) Kutsyna, L. M.; Voevoda, L. V.; Tishchenko, V. G.; Shepel, A. V. *Opt. Spectrosc.* **1969**, *26*, 91.
(23) Tsukerman, S. V.; Buryakovskaya, E. G.; Lavrushin, V. F. *Opt. Spectrosc.* **1969**, *26*, 299.
(24) Strahle, H.; Sertz, W.; Guster, H. *Ber. Bunsenges. Phys. Chem.* **1976**, *80*, 288 and references cited therein.
(25) Yamamoto, H.; Sano, Y.; Shirota, Y.; Seki, H.; Mikawa, H. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 1533.
(26) Sano, Y.; Yokoyama, M.; Shirota, Y.; Mikawa, H. *Mol. Cryst. Liq. Cryst.* **1979**, *53*, 291.
(27) Sano, Y.; Shirota, Y.; Mikawa, H. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 2192.
(28) (a) Iinuma, F.; Mikawa, H.; Shirota, Y. *Polym. Bull.* **1979**, *1*, 315. (b) *Polym. J.* **1981**, *13*, 641.
(29) Iinuma, F.; Mikawa, H.; Shirota, Y. *Polym. Photochem.* **1981**, *1*, 315.
(30) Iinuma, F.; Mikawa, H.; Shirota, Y. *Mol. Cryst. Liq. Cryst.*, in press.
(31) Wiley, R. H.; Jarboe, C. H.; Hayes, F. N.; Hansbury, E.; Nielsen, J. T.; Callahan, P. X.; Sellars, M. C. *J. Org. Chem.* **1958**, *23*, 732.
(32) Kimura, T.; Kai, Y.; Yasuoka, N.; Kasai, N. *Acta Crystallogr., Sect. B* **1977**, *33*, 1786.
(33) Strop, R.; Mikes, F.; Kalal, J. *J. Polym. Sci., Polym. Symp.* **1974**, *No. 47*, 345.
(34) Strop, R.; Mikes, F.; Kalal, J. *J. Phys. Chem.* **1976**, *80*, 694.
(35) Zdysiewicz, J. R. *Aust. J. Chem.* **1972**, *25*, 2631.
(36) Tazuke, S.; Sato, K.; Bamba, F. *Macromolecules* **1977**, *10*, 1244.
(37) Irie, M.; Menju, A.; Hayashi, K.; Smets, G. *J. Polym. Sci., Polym. Lett. Ed.* **1979**, *17*, 29.
(38) Irie, M.; Hayashi, K. *J. Macromol. Sci., Chem.* **1979**, *A13*, 511.
(39) Irie, M.; Menju, A.; Hayashi, K. *Macromolecules* **1979**, *12*, 1176.