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Photophysics of Poly(methylphenylphosphazene)

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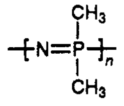
ABSTRACT: The photophysical properties of poly(methylphenylphosphazene), PMPP, with methyl and phenyl groups attached to the phosphazene phosphorous have been investigated using absorption and emission spectroscopy, as well as laser flash photolysis. The fluorescence spectrum of PMPP shows a red-shifted emission (decay time of 1.9 ns) with a maximum at 430 nm when excited at 270 nm in solvents of varying polarity. The absence of a strong solvent effect on the position and the structure of the fluorescence spectrum suggests that the emission is not due to either an n,π^* or a charge-transfer state, but originates from an excited state with a significant geometry shift. The triplet state of PMPP was identified by laser flash photolysis, and the phosphorescence spectrum of PMPP indicated a triplet energy of 79 kcal mol^{-1} in a glass at low temperature.

Introduction

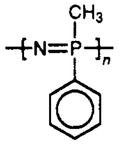
Since the synthesis of linear and soluble poly(organophosphazenes) by Allcock,[1,2] a great deal of work has been devoted to the preparation and characterization of phosphazene polymers containing different substituent groups suitable for use in many technological applications.[3-6] Gleria *et al.*[7-16] carried out a series of investigations on the photochemical and photophysical behavior of poly(organophosphazenes) with heteroatoms attached directly to the phosphazene repeat unit in the backbone. Studies on the photochemistry and photophysics of similar poly(organophosphazenes) were also performed by Allcock[17] and Webber.[18] In 1980, we described[19] a straightforward one-step condensation polymerization of a *N*-silylphosphoranimine (phosphinimine) resulting in the ultimate synthesis of a variety of poly(phosphazene)s bearing alkyl and aryl groups connected to the parent polymer chain via attachment to phosphorous. This relatively new class of poly(phosphazenes) presents an interesting opportunity to investigate the photochemical and photophysical consequences of direct attachment of aromatic groups to the phosphorous atom on the phosphazene unit. We might well expect the excited state of such a system to have quite different, and perhaps unusual, properties.

Recently, in a preliminary paper on the photochemical and photophysical behavior of this class of polymers, we reported[20] that poly(methylphenylphosphazene), PMPP, gives a very large Stokes' shifted emission when excited around 270 nm. In this paper we will present a more detailed account of our investigation on the photophysical properties of PMPP and provide a detailed analysis of the unusual excited-state fluorescence and the possible effect of geometry relaxation on the position of the emission spectrum. For comparison, results for a methylphenylphosphazene cyclic oligomer (MPCO) model compound will also be presented. Results for poly(dimethylphosphazene), PDMP, will be furnished for comparison as a nonaromatic analog of PMPP.



$-\!\!\left[N{=}\underset{CH_3}{\overset{CH_3}{P}}\right]_n\!\!-$

PDMP



PMPP

Experimental Section

Both PMPP and PDMP were prepared and purified by the method described earlier.[19] All solvents were obtained from Burdick and Jackson and used as received. Absorption spectra were recorded on a Perkin-Elmer Lambda 6 UV-vis spectrophotometer. Corrected fluorescence spectra were obtained on a Spex Fluorolog-2 spectrofluorometer with 3.5-nm bandpass excitation and emission slits using a rhodamine B solution as a quantum counter to generate the correction files. Phosphorescence spectra were recorded on a Spex Phosphorimeter model 1934D. Fluorescence decay lifetimes were measured by a single-photon counting apparatus from Photochemical Research Associates International Inc. which is interfaced with a Digital PDP-11 computer. Transient absorption spectra were obtained with a laser flash photolysis apparatus based on an excimer laser excitation source (Lumonics HyperEx 440, 15-ns FWHM, nominal output at 248 nm was 80 mJ/pulse) and an Applied Photophysics xenon lamp/monochromator/PMT monitoring system as reported elsewhere.[21] The ultimate time resolution of the system employed was about 15-20 ns (obtained by progressive quenching of a benzophenone standard).

Results and Discussion

Figure 1 shows the UV spectra of PMPP, PDMP, and MPCO, in methylene chloride. The absorption spectrum of PMPP indicates the perturbation of the —P=N— backbone by the presence of the phenyl group resulting in a distinct absorption above 245 nm. MPCO (a mixture of trimer, tetramer, and a small amount of larger oligomeric species) also exhibits an absorption spectrum similar to PMPP in methylene chloride. In contrast to the results for PMPP and MPCO, PDMP has little absorption above 245 nm due to the lack of an aromatic chromophore.

The emission spectra of PMPP and MPCO in methylene chloride are shown in Figure 2. The most striking feature of the spectra is a red-shifted emission with a maximum intensity at about 430 nm. Excitation at any wavelength within the main absorption band (λ_{ex} <280 nm) of PMPP produced the same emission spectrum. In order to determine whether the red-shifted emission for PMPP

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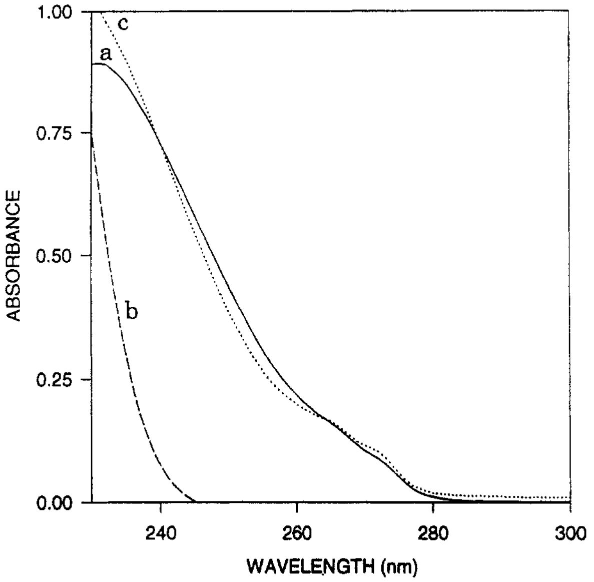

Figure 1. UV spectra of (a) PMPP (0.03 mg/mL), (b) PDMP (2 mg/mL), and (c) MPCO (0.03 mg/mL) in CH_2Cl_2.

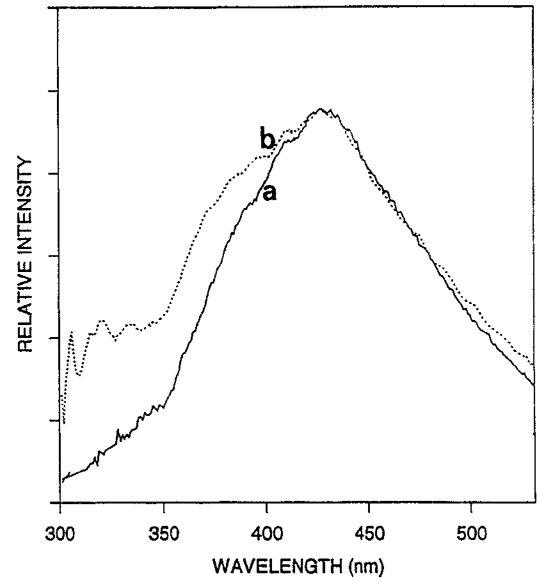

Figure 2. Fluorescence spectra of (a) PMPP (0.03 mg/mL) in CH_2Cl_2 (λ_{ex} 270 nm), and (b) MPCO (0.03 mg/mL) in CH_2Cl_2 (λ_{ex} 290 nm).

and MPCO at 430 nm results from an inherent property of the phosphazene —P=N— backbone, we investigated PDMP which contains no aromatic side groups. A PDMP solution in methylene chloride is essentially nonemissive, which is not surprising considering its nonaromatic structure. It thus appears that the red-shifted emission at 430 nm for PMPP is not a result of the phosphazene backbone. The results for PDMP are quite informative in this respect. In general, we note that the phosphorus–nitrogen bond distances in poly(phosphazenes) are shorter than expected for pure covalent σ bonds.[22] Nonetheless, spectral effects normally associated with highly conjugated organic π-electron systems, such as the bathochromic ultraviolet shifts which accompany increased delocalization, are not found for PDMP and, by analogy, we conclude are not important for the PMPP systems. Thus, even though the phosphorus–nitrogen bond in poly(phosphazenes) differs somewhat from a covalent σ bond, it does not resemble the familiar σ–π bond of organic aromatic compounds[22] and exhibits no emission which might be attributed to an extended conjugation.

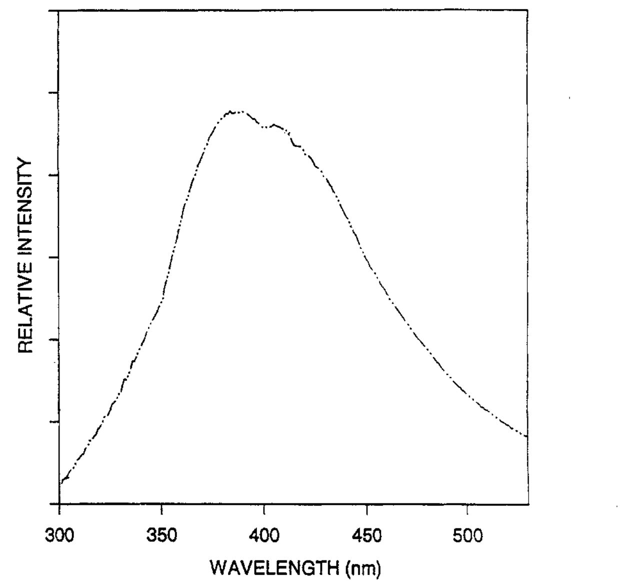

Figure 3. Fluorescence spectrum of PMPP film (λ_{ex} 270 nm).

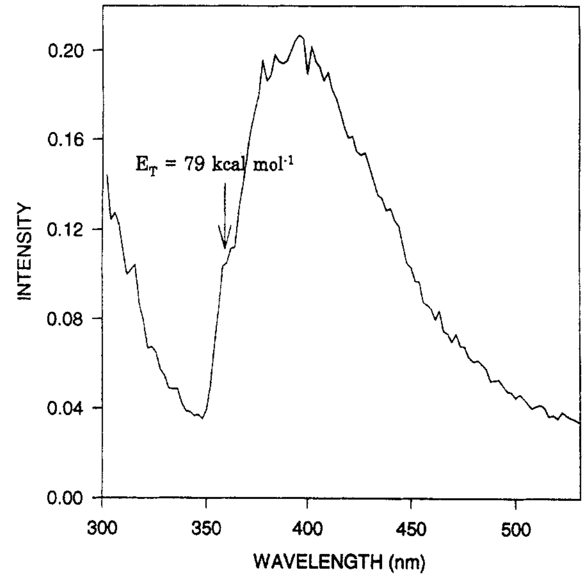

Figure 4. Phosphorescence spectrum of PMPP (1 mg/mL) in ether–THF at 77 K (λ_{ex} 270 nm) with a 200-μs delay.

The emission spectrum of a cast film of PMPP (Figure 3) is unusual in that the peak maximum is blue-shifted (λ_{max} at 385 nm) compared to that in solution (λ_{max} at 430 nm). Excited-state geometry restrictions in the film, which might be the reason for this shift, will be subsequently discussed in detail. The phosphorescence spectrum of PMPP in ether–tetrahydrofuran at 77 K gives a triplet energy (E_T) of 79 kcal mol^{-1} (Figure 4), based on a shoulder at 360 nm that is assumed to be due to the 0,0 band of the phosphorescence emission. The phosphorescence lifetime is about 160 ms. The total emission spectrum of PMPP recorded at 77 K (not shown) resembled the phosphorescence spectrum: The emission from the singlet excited state is presumably buried under the phosphorescence emission. Emission observed at room temperature for the PMPP film and methylene chloride solution (Figure 2a and Figure 3) are catagorized as fluorescence since the lifetime in the nanosecond range (1.9 ns), determined by single-photon counter, is much too short to be phosphorescence. Since no vibrational structure is apparent in the fluorescence spectra of either the film or the solution, precise determination of the singlet energy (E_s) is not possible. However, taking the wavelength at which the fluorescence intensity is 20–30% of its value at λ_{max} as a

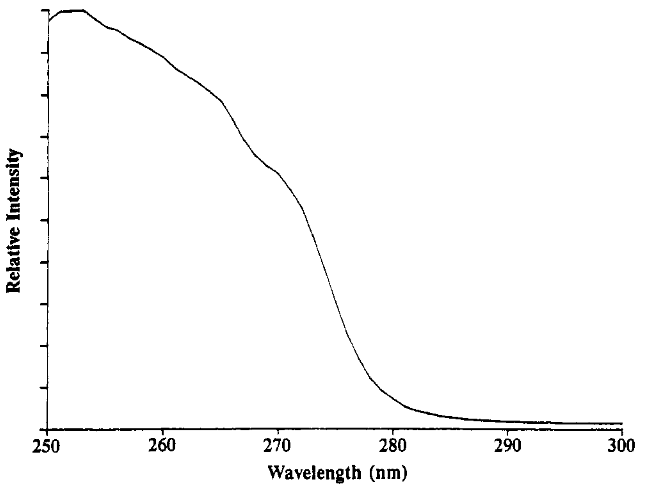

Figure 5. Excitation spectrum of PMPP (0.03 mg/mL) in CH_2Cl_2 (λ_{em} = 430 nm).

rough approximation for the position of the 0,0 band, we obtain an estimated value for E_s of *ca.* 79–80 kcal mol^{-1} in methylene chloride and *ca.* 82–84 kcal mol^{-1} for the film. A similar "unrelaxed" and "relaxed" triplet state may also be possible and hence the triplet energies of these states could be different. The E_T of the fluid solution, therefore, might well be less than 79 kcal mol^{-1}. We are currently attempting to determine the E_T of PMPP in solution by laser flash photolysis using triplet quenchers with varying triplet energies.

We next probe the spectral origin of the red-shifted emission of PMPP. The excitation spectra of PMPP in Figure 5 is essentially identical to the absorption spectrum in Figure 1, strongly indicating that the origin of the emission with maximum at 430 nm is indeed initial absorption by the phosphazene unit, and that in the excited state the emission comes from the lowest energy level, regardless of the excitation wavelength. These results suggest that the emission at 430 nm is not due to any impurity, but is rather an inherent property of the PMPP molecule. Multiple re-precipitations of PMPP resulted in no noticeable changes in the fluorescence emission spectrum, further suggesting that the emission is not the result of an impurity. At first glance, the broad, red-shifted, structureless emission in Figure 2 is reminiscent of the intrapolymer excimer fluorescence associated with the aromatic moieties substituted on the polymer chain.[23-27] For example, the fluorescence spectrum of polystyrene shows emission bands at about 280 and 335 nm, attributed to monomer and excimer emission, respectively.[27] However, for PMPP the broad band is located at a very low energy precluding excimer fluorescence. In general,[25] the peak of the excimer fluorescence from interacting phenyl type species is separated from the 0,0 band of the monomer fluorescence by ~6000 cm^{-1}. In PMPP, interestingly, there is no detectable emission on the sensitivity settings available to us which corresponds to a phenyl monomer fluorescence (that should be at about 280–300 nm, if present). Further, the broad band in question differs significantly from the known[26] excimer fluorescence of alkyl-substituted phenyl groups whose peaks are located at ~320 nm. Even though the configuration of the excimer, if it existed in the present polymer, might well be different from that found in the carbon-based polymers, such a low-energy excimer is unlikely. Also, in support of a single chromophore nonexcimeric excited species for PMPP, we note that the fluorescence decay of the emission at 420 nm is single exponential (within our capabilities of measuring) with a lifetime of 1.9 ns. The effect of concentration on the emission spectrum was also examined for polymer solutions in methylene chloride ranging from 0.03 to 1.0 mg/mL. The intensity of the broad band is essentially independent of the polymer concentration, indicating that interpolymer excimer fluorescence does not occur either. Thus, although we cannot totally exclude the possibility, the emission with maximum at 430 nm does not appear to result from an excimer state.

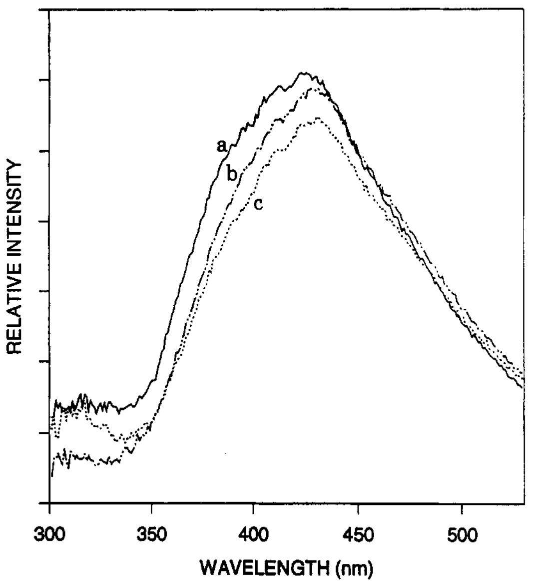

Figure 6. Fluorescence spectra of PMPP (0.03 mg/mL) in various solvents (λ_{ex} 270 nm): (a) dioxane, (b) CH_2Cl_2, and (c) 1:1 CH_3CN–CH_2Cl_2 mixture.

A plausible explanation for the emission at 430 nm might be a charge-transfer state between the —P=N— skeleton and the phenyl group. However, the position of the emission maximum does not shift when the solvent polarity is increased from dioxane, to methylene chloride, to 1:1 acetonitrile–methylene chloride (Figure 6). The lack of response of the emission to solvent polarity indicates that the red-shifted emission with peak maximum at 430 nm is not due to an intrapolymer charge-transfer state. Furthermore, in view of the experimental finding that the intensity of the red-shifted emission is independent of the concentration of the polymer, we can also conclude that interpolymer charge-transfer states are not formed. Finally, we note that the emission of the cast film of PMPP is not due to phosphorescence, since the phosphorescence spectrum recorded in ether–tetrahydrofuran at 77 K (Figure 4) has some structure, the 0,0 band appearing at 79 kcal mol^{-1}, and appears quite different from that recorded in a film at room temperature (Figure 3).

We propose that the red-shifted emission of PMPP with maximum at 430 nm in solution is due to a marked geometry shift in the excited state (compared to the ground state). Bearing this assumption in mind, we stress that the fluorescence spectra of PMPP in methylene chloride and in the film (Figures 2 and 3) are distinctly different: In the film at room temperature the fluorescence maximum is blue-shifted to 385 nm compared to 430 nm in solution. Apparently the restricted polymer mobility at room temperature in the film (T_g = 42 °C) results in emission from an excited state with a geometry more like that of the ground state, i.e. from the vertical excited state, whereas, in solution, vibrational relaxation to a nonvertical excited state within the time scale of the emission process can occur with a concomitant red-shifted emission. In support of this supposition, the fluorescence spectrum of PMPP film above its T_g (i.e., at 80 °C) shows a broad emission with a maximum between 385 and 430 nm (Figure

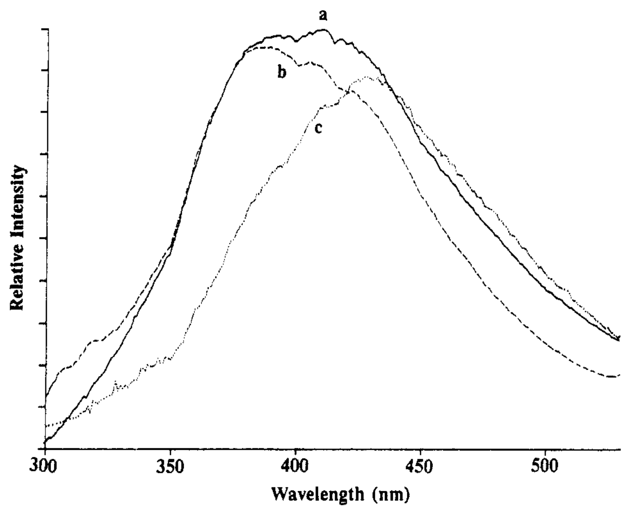

Figure 7. Fluorescence spectra of PMPP film at different temperatures and of solution (λ_{ex} 270 nm): (a) film at 80 °C, (b) film at 25 °C, and (c) in CH_2Cl_2.

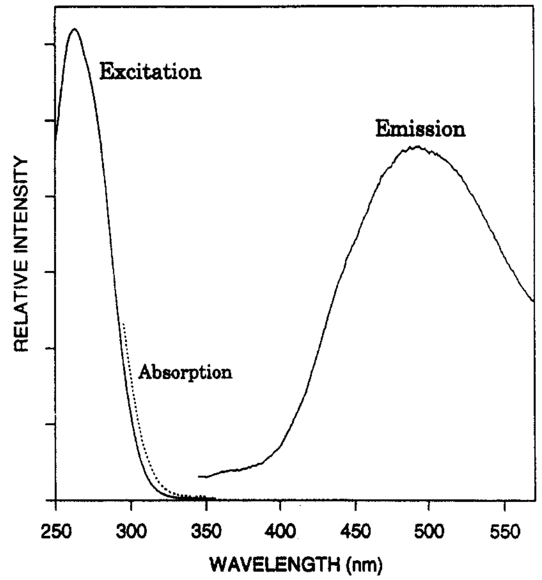

Figure 8. Excitation and emission spectra of Ph_3P (1×10^{-3} M) in CH_2Cl_2 (λ_{ex} 290 nm, λ_{em} 490 nm). The UV spectrum is indicated for comparison with excitation spectrum.

7) instead of 385 nm. Careful examination of the film spectrum at 80 °C (Figure 7a) indicates that the fluorescence of the PMPP film above T_g resembles a combination of the film and the solution fluorescence of PMPP (for a direct comparison, the fluorescence spectra of PMPP film at 25 °C and solution are shown in Figure 7, parts b and c, respectively). We speculate that above the T_g of PMPP there is a mixture of excited species that emit from a range of relaxed and vertical geometries.

In a paper pertinent to the results in this work for PMPP, Fife *et al.*[28] have reported a similar "anomalous" emission spectra of aryl phosphines [Ph_3P, $MePh_2P$, and $Ph_2P(CH_2)_nPPh_2$ ($n = 1$–6)], indicating the existence of a lower energy excited state associated with the maximum absorption of Ph_3P at 250–260 nm. The arylphosphines showed a very small singlet (S_1)–triplet (T_1) splitting, indicating that the lowest excited state is an $1 \rightarrow a_\pi$ state (n,π* character) and that the nonbonding electrons of the phosphorus have essentially no interaction with the phenyl π system in the ground state.[28] We also have observed this "anomalous" emission when Ph_3P is excited at 290 nm. Figure 8 shows the absorption, fluorescence emission, and excitation spectra of Ph_3P (10^{-3} M) in methylene chloride. Ph_3P exhibits a broad and red-shifted emission with a maximum at about 490 nm. It has been reported[28] that triphenylphosphine oxide ($Ph_3P{=}O$), on the contrary, gives normal fluorescence (with a small Stokes' shift) around 290–300 nm. It is of interest to compare the emission spectral behavior of the methylphenylphosphazene chromophore with that of Ph_3P and $Ph_3P{=}O$. In the case of both PMPP and $Ph_3P{=}O$ there are no lone pair of electrons on the phosphorus atom. Nonetheless, for PMPP we observe an "anomalous" emission with a maximum at about 430 nm, similar to the red-shifted emission of Ph_3P but quite different from the fluorescence of $Ph_3P{=}O$. The shapes of the fluorescence spectra of PMPP and Ph_3P (see Figures 2 and 8) indicate a substantial difference in geometry between the ground state and the excited singlet state for each of these two systems. We find a significant solvent shift of the fluorescence maximum of Ph_3P (red shifted from λ_{max} 460 to 500 nm as the solvent becomes more polar in changing from cyclohexane to acetonitrile) that supports the assignment of a singlet state with 1–a_π (n,π*) character.[28] Interestingly, no such solvent dependence is observed for PMPP (see Figure 6). This suggests that the PMPP singlet state does not have significant n,π* character. A plausible explanation for the broad, red-shifted fluorescence for PMPP is as follows. We first note that the excitation of PMPP above 270 nm leads mainly to generation of a π,π* state essentially localized on the phenyl group. This must be the case since the absorption spectrum of PMPP above 270 nm (Figure 1) resembles those of polystyrene and toluene, two compounds with "simple" monosubstituted phenyl groups. Subsequent to formation of the π,π* state localized on the phenyl ring when exciting above 270 nm, which we presume is an *upper* singlet state (S_2), rapid relaxation occurs to the lowest singlet state, S_1, for which we envisage two possible electronic configurations. Either the electron initially localized on the π* orbital of the phenyl group occupies one of the antibonding orbitals of the backbone or an electron from a backbone bonding orbital occupies the half-vacant π orbital of the phenyl group. In light of the electronegativities of the atoms involved and considering that the phenyl groups are delocalized and the backbone is not (vide supra), we favor the former possibility. Either configuration for S_1 would result in loss of bonding character in the N–P–N backbone which could contribute to the apparently large geometry difference between S_0 and relaxed S_1, leading to a dramatic red shift of fluorescence relative to absorption. *Poor* overlap between the phenyl and backbone orbitals in S_1 and T_1 would explain the *small* S_1–T_1 gap in PMPP (typical π,π* states of simple organic compounds have *large* S_1–T_1 energy gaps because of *good* π/π* orbital overlap). The direct S_0–S_1 transition of PMPP is presumably the broad, unstructured absorption that originates at about the same position as the onset of the phenyl group π,π* absorption and is superimposed upon the latter, completely dominating the absorption spectrum below about 260 nm (Figure 1).

Fluorescence quenching studies provide an opportunity for examination of the polymer chain in terms of its accessibility to small quenching molecules. In our studies we have employed carbon tetrachloride (CCl_4)[30–33] as a simple quencher using the standard Stern–Volmer[34] equation

$$I_0/I_Q = 1 + k_q\tau_0[Q]$$

to evaluate the quenching rate constant, k_q, where I_0 and I_Q are the relative fluorescence intensity in the absence

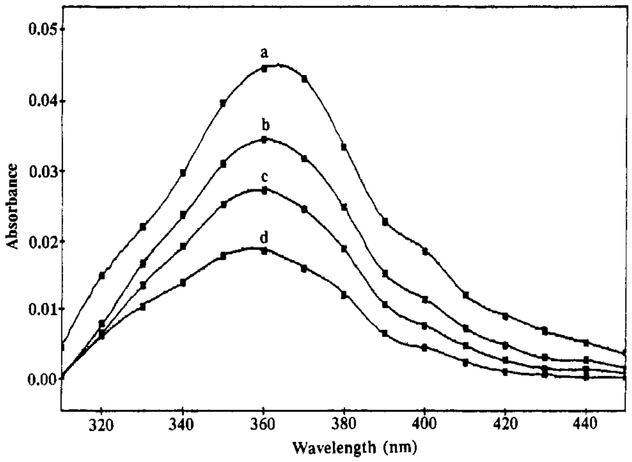

Figure 9. Triple–triplet absorption spectra of PMPP (0.03 mg/mL) in nitrogen-saturated CH_2Cl_2 at different time intervals after the flash (λ_{ex} 248 nm): (a) 2 μs after the flash, (b) 4 μs, (c) 6 μs, and (d) 10 μs.

and presence of a quencher, with concentration [Q] respectively, and τ_0 is the intrinsic lifetime of the excited state in the absence of quencher. The bimolecular quenching rate constant, k_q, was 1.8×10^{10} L mol^{-1} s^{-1}, typical of a dynamic quenching of a single excited state at a diffusion-controlled rate. Nonlinearity of Stern–Volmer plots can result from the presence of two or more species emitting at the same wavelength being quenched simultaneously, or else complex formation in the ground state: Such behavior was not observed in our system up to concentrations of 0.03 M CCl_4.

In order to investigate singlet–triplet intersystem crossing, the transient absorption spectrum (Figure 9) of a nitrogen-saturated PMPP solution (methylene chloride) was recorded (laser flash photolysis, 248 nm excitation). The transient absorption spectrum is characterized by a peak around 360 nm with a single exponential decay time of 9.1 μs. In the presence of oxygen (air-saturated solvent) the transient decay time is shorter (τ_T = 2.8 μs), yielding a rate constant for oxygen quenching of about 1.8×10^9 L mol^{-1} s^{-1}, suggesting that the transient arises from either a radical species or a triplet state, both of which can be effectively quenched by oxygen. Addition of low concentrations of a typical triplet quencher, 1,3-cyclohexadiene (1×10^{-4} M or less), results in a uniform reduction in the lifetime of the transient species from PMPP in a nitrogen-saturated methylene chloride solution. A Stern–Volmer plot of the ratio of the transient lifetime before and after adding quencher *versus* the cyclohexadiene concentration is linear with a slope of 5.1×10^4 L mol^{-1} affording a quenching rate constant of 5.6×10^9 L mol^{-1} s^{-1}. This is consistent with triplet quenching since cyclohexadiene has a triplet energy of 54 kcal mol^{-1} compared to ~79 kcal mol^{-1} for PMPP. In principle, the triplet state can also be generated directly by triplet sensitization experiments.[21] Attempts to sensitize triplet state formation using acetophenone (E_T = 74 kcal mol^{-1}) as a sensitizer (351 nm excitation) failed even in the presence of an excess of PMPP (1 mg/mL). This, of course, is not surprising since the triplet energy of PMPP is estimated to be about 79 kcal mol^{-1} in the film: However, as noted previously, it could be somewhat lower in solution.

In summarizing the photophysical results, the energy levels and the radiative and radiationless deactivation processes of PMPP are presented in Figure 10 for reference. This scheme accounts for the red-shifted emission of PMPP with peak maximum near 430 nm. As stated previously, the red-shifted emission is proposed to result from an excited-state species with a substantial geometry change that is formed within the radiative lifetime of the polymer in fluid solution: The restricted mobility in the film prevents such a geometry shift, and hence leads to emission with a maximum at 385 nm. The fact that the absorption and excitation spectra of PMPP in solution coincide indicates that rapid radiationless deactivation processes occur from the unrelaxed to the relaxed ($S'_1 \rightarrow S_1$) excited state. Due to this rapid radiationless process, only emission from the relaxed excited singlet state is observed in solution.

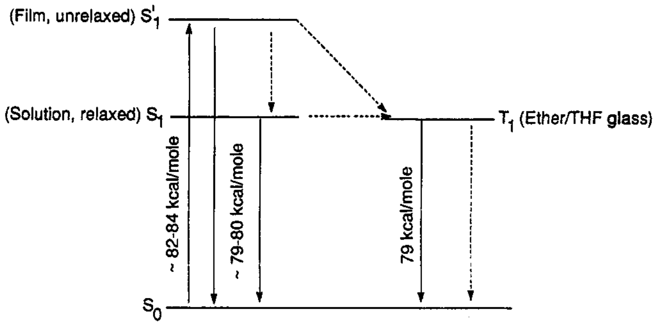

Figure 10. Schematic representation of the energy levels, radiative, and nonradiative processes of PMPP. The solid arrows indicate the radiative processes and the broken arrows indicate the nonradiative processes.

Conclusions

In summary, we have reported the photophysical behavior of a poly(alkylarylphosphazene). The fluorescence of the PMPP polymer is red-shifted with a maximum around 430 nm in fluid solution and 385 nm in film. The particularly large red shift in the emission spectrum of PMPP is attributed to a significant geometry change in the relaxed singlet state manifold. Although one cannot ever completely rule out emission from a stabilized red-shifted excimer or, since we are dealing with a polymer system, the presence of an impurity with high fluorescence quantum efficiency, we nonetheless feel that the geometry shift provides the best interpretation of the data. The singlet emission of PMPP with maximum at 430 nm in solution is readily quenched by CCl_4. The triplet state of PMPP has been observed by laser flash photolysis and tentatively identified by triplet quenching experiments. The phosphorescence spectrum at 77 K indicates a high triplet energy (~79 kcal mol^{-1}) for PMPP.

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