

Excimer fluorescence in polyphosphazenes: 1. Cyclic trimer and polymer solutions

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Excimer fluorescence in aryloxyphosphazene cyclic trimers and polymers has been measured as a function of substituent, solvent and temperature. While only one type of excimer forming site (EFS) is possible in the cyclic trimers, the phosphazene polymers exhibit three possible types of EFS which are responsible for a blue shift and broadening of their excimer bands relative to the trimers. Excimer band assignment for intramolecular EFS formed between two aryloxy groups bonded to the same phosphorus atom (type I) is possible from a comparison of trimer and polymer spectra. The type II EFS, which results from intramolecular interactions between aryloxy groups appended to adjacent phosphorus atoms, is considered less favourable than the type III EFS, which is the intermolecular EFS. Increasing the size of substituents from poly[bis(phenoxy)phosphazene] (PBPP) to poly[bis(*p*-cresoxy)phosphazene] (PBCP) increases the steric effect of the side groups while changing the main chain conformation of the polymers. We observe a strong dependence of excimer formation on solvent and temperature in terms of the excimer-to-monomer intensity ratio, I_D/I_M , excimer bandwidth and excimer band maximum position. The binding energies for excimer formation in dichloromethane were found to be 14.0 and 15.5 kJ mol⁻¹ for PBPP and PBCP, respectively, and are considerably greater than those for type I EFS previously reported. The activation energy for PBPP in dioxane was found to be 2.6 kJ mol⁻¹, whereas the corresponding activation energy for PBCP was not determined since no Arrhenius behaviour was observed. These results suggest that intermolecular excimer forming sites may be pervasive in the polymer solutions and are responsible for part of the diffusive and deactivation processes.

(Keywords: polyphosphazene; phosphazene trimer; excimer fluorescence; chain mobility; solution properties)

INTRODUCTION

Polyphosphazenes comprise a class of inorganic polymers having an alternating phosphorus–nitrogen backbone with two side groups attached to each phosphorus atom. Because of the wide variety of side groups that may be bonded to the polymer chain, many macromolecules with a wide range of properties have been prepared. Indeed, increasing research activities have been directed toward the development of new classes of phosphazene polymers having potential applications as high technology materials, bioactive polymers, catalyst carriers, electrical conductors or semiconductors and memory storage media¹.

Excimer fluorescence has previously been used to examine the photophysics of phosphazene cyclic trimers and polymers. Bortolus and coworkers² studied the temperature dependence of intramolecular excimer emission in aryloxy-substituted cyclotriphosphazene solutions. Their study suggests that the fluorescence behaviour in phosphazenes is strongly influenced by the size of the aryloxy groups. Hargreaves and Webber³ obtained fluorescence spectra of poly[bis(phenoxy)phosphazene] (PBPP) and reported facile excimer emission and a considerably shorter monomer lifetime than polystyrene.

In the present work we focus our attention on the effects of different excimer forming sites and substituents on the fluorescence properties of phosphazene trimers and polymers. Our overall objective is to gain a better understanding of the photophysics of this class of inorganic polymers and to apply this information to the elucidation of their structure and morphology in the solid state. To achieve these goals, we must first establish a reference state wherein effects due to crystal structure, crystallinity and thermal pretreatment are discounted. We begin with the intrinsic fluorescence behaviour of phosphazene trimers in dilute solutions, where the size and nature of substituents are expected to cause an appreciable difference in excimer rotational sampling and stability. Fluorescence work on the cyclic trimers also helps explain complications that arise from multiple excimer forming sites. These results should contrast with the photophysics of polymer solutions under similar conditions. Useful insights into the extent of side group and backbone motions, essential to excimer formation, are obtained from the temperature dependence of the ratio of excimer to monomer emission intensities, excimer bandwidth and band maximum position. We expect these fluorescence observables to depend strongly on the chain conformation of phosphazene polymers with different side groups.

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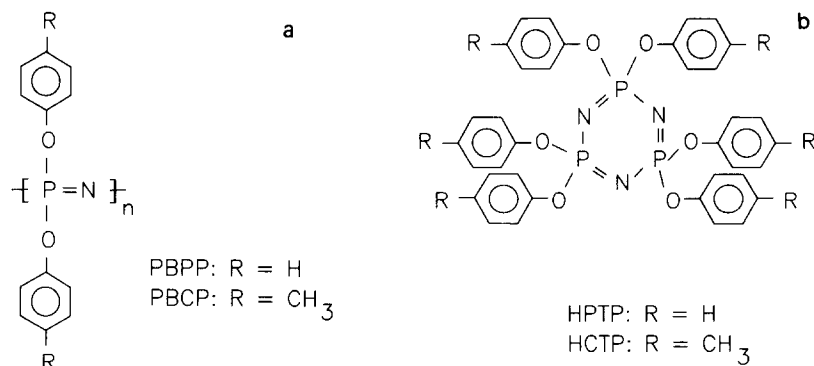


Figure 1 Chemical structures for (a) PBPP and PBCP polymers and (b) HPTP and HCTP trimers

EXPERIMENTAL

Materials

Two representative poly(aryloxyphosphazenes), poly[bis(phenoxy)phosphazene] (PBPP) and poly[bis(*p*-cresoxy)phosphazene] (PBCP), and their corresponding cyclic trimers, hexaphenoxy-cyclotriphosphazene (HPTP) and hexacresoxy-cyclotriphosphazene (HCTP) were investigated. The structures of these polymers and trimers are given in *Figure 1*.

The HPTP and HCTP trimers were prepared by substitution of chlorine in hexachloro-cyclotriphosphazene with the appropriate sodium aryloxide salts, whereas the PBPP and PBCP polymers were synthesized by the ring-opening polymerization of hexachlorophosphazene at 518 K, followed by reaction of poly(dichlorophosphazene) with the corresponding sodium aryloxides. Details of preparation and characterization of the trimers and polymers have been given elsewhere⁴⁻⁵. Spectrophotometric grade dichloromethane and dioxane (Aldrich) were used as solvents without further purification.

Sample preparation

All fluorescence measurements were performed with dilute solutions of 1×10^{-4} M monomer units in dichloromethane or dioxane. These trimer and polymer solutions were subjected to several freeze-pump-thaw cycles before the sample tubes were sealed under vacuum. Special care was taken to avoid thermal degradation during subsequent heating of the samples.

Instrumentation

Fluorescence spectra taken in a right-angle configuration were measured with a data acquisition system that has been described before⁶. A pair of resistive heaters coupled with Eurotherm controller and thyrister were used to provide an average heating rate of 50 K h^{-1} . Measurements were made after a steady temperature had been maintained for 15 min. An excitation wavelength of 250 nm allowed a more complete monomer emission profile in the ultraviolet region of the spectrum. Excitation and emission bandwidths of 8 nm were maintained to ensure that a meaningful fluorescence signal could be obtained when quantum yields became diminished at extreme temperatures. All emission spectra were corrected for Raman and scattered light and instrument response by using an Optronic Laboratories 200 W quartz-halogen Standard of Spectral Irradiance model 220A powered by

an Optronic Laboratories model 65 constant-current power supply. The response function was further checked with secondary standards and compared well with the literature⁷.

RESULTS

The kinetics of intermolecular excimer formation and dissociation in dilute solutions have been developed by Birks⁸. According to this scheme, the ratio of excimer to monomer quantum yields, R , is given by

$$R = \frac{\Phi_{\text{FD}}}{\Phi_{\text{FM}}} = \left(\frac{k_{\text{FD}}}{k_{\text{FM}}} \right) \left(\frac{k_{\text{DM}}}{k_{\text{FM}} + k_{\text{ID}} + k_{\text{MD}}} \right) \quad (1)$$

where k_{FD} and k_{FM} are fluorescence decay rate constants for the excimer and monomer, k_{ID} is the rate constant for deactivation of the excimer by internal conversion, k_{MD} is the rate constant for dissociation of the excimer to excited- and ground-state monomers, and the rate constant for excimer formation is given by k_{DM} .

Two limiting conditions that lead to simplification of the above expression occur at high and low temperatures. In the higher temperature region, known as the dynamic equilibrium regime, the rate of excimer dissociation back to the excited-state monomer is much greater than the deactivation processes due to excimer emission and internal conversion, and equation (1) can be reduced to

$$R = \left(\frac{k_{\text{FD}}}{k_{\text{FM}}} \right) \left(\frac{k_{\text{DM}}}{k_{\text{MD}}} \right) = \left(\frac{k_{\text{FD}}}{k_{\text{FM}}} \right) K \propto \exp \left(\frac{-\Delta H + T \Delta S}{RT} \right) \quad (2)$$

where K is the true equilibrium constant of excimer formation, ΔH is the excimer binding energy, and ΔS is the entropy of excimer formation. Since k_{FD} and k_{FM} are independent of temperature and their ratio ($k_{\text{FD}}/k_{\text{FM}}$) is independent of solvent, measurements of the ratio of excimer to monomer emission intensities in the high temperature regime enable the excimer binding energy to be determined from the slope of an Arrhenius-type plot.

In the low temperature region, known as the diffusion-controlled regime, where the excimer dissociation process becomes unimportant, equation (1) simplifies to

$$R = \left(\frac{k_{\text{FD}}}{k_{\text{FM}}} \right) \left(\frac{k_{\text{DM}}}{k_{\text{FD}} + k_{\text{ID}}} \right) \propto \exp \left(-\frac{E_a}{RT} \right) \quad (3)$$

If the excimer formation kinetics is indeed diffusion-controlled, an Arrhenius plot of the quantum yield ratio

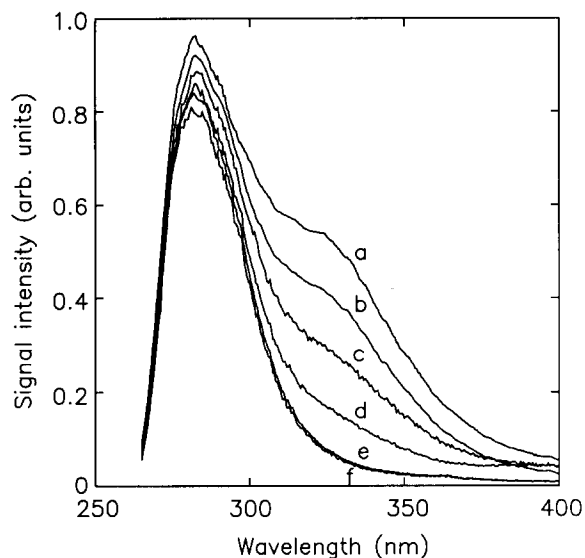


Figure 2 Fluorescence spectra for HPTP in dichloromethane as a function of temperature (K): (a) 293; (b) 262; (c) 238; (d) 216; (e) 197; (f) 182

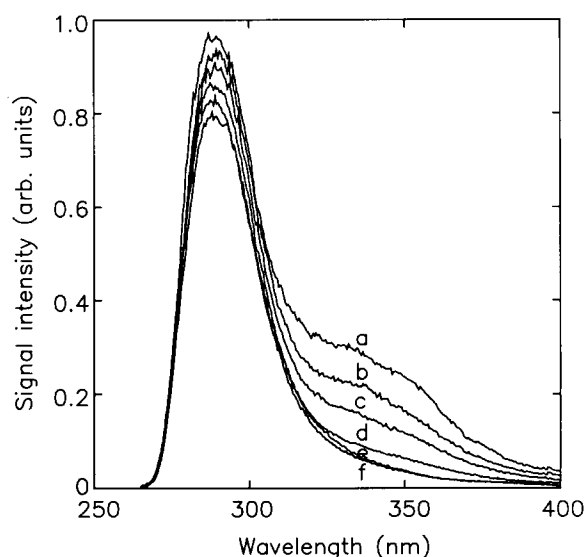


Figure 3 Fluorescence spectra for HCTP in dichloromethane as a function of temperature (K): (a) 293; (b) 262; (c) 238; (d) 216; (e) 197; (f) 182

versus the inverse temperature would yield the activation energy of the diffusion process of excimer formation.

Figures 2 and 3 show representative emission spectra of HPTP and HCTP in dichloromethane as a function of temperature. A typical fluorescence spectrum is composed of a monomer emission band due to a single aromatic side group, and a broad structureless excimer band due to the excited-state dimers of two aromatic rings in a coplanar sandwich configuration. At temperatures near the freezing point of dichloromethane (182 K), the fluorescence spectra are dominated by the sharp monomer emission band at ≈ 283 nm for HPTP and 290 nm for HCTP. Increasing temperature brings forth more efficient excimer emission in both HPTP and HCTP solutions, with the excimer peak occurring at about 328 nm for HPTP and 338 nm for HCTP at sufficiently high temperature. The hypsochromic red shifts of about 7–10 nm in monomer and excimer bands of HCTP relative to HPTP can be attributed to the induction effect

of the methyl group⁹ and are in excellent agreement with those previously reported².

Following the procedure used previously in our studies of aromatic polymers¹⁰, we resolved the fluorescence spectra into a monomer peak based on a model compound and a Gaussian excimer peak on the energy scale. Here, the vibrational envelope of the monomer was taken to be identical to the fluorescence spectrum of the respective trimer solution at 77 K. The excimer band consisted of a Gaussian envelope, wherein the excimer band position, excimer bandwidth at half-height and excimer band maximum intensity were fitted along with the monomer band intensity by a nonlinear regression method. The integrated fluorescence intensity ratio of excimer and monomer emission, I_D/I_M , for HPTP and HCTP, is plotted as a function of the inverse temperature in Figure 4. Excimer emission is relatively unimportant at temperatures below an onset temperature of 182 K and 222 K for HPTP and HCTP, respectively. At higher temperatures, I_D/I_M increases with temperature, suggesting more efficient rotational sampling in solution.

The Arrhenius dependence of I_D/I_M in both HPTP and HCTP solutions suggests that the excimer formation process is indeed diffusion controlled. The activation energies of excimer formation for HPTP and HCTP are listed in Table 1, where the same quantity for HPTP in

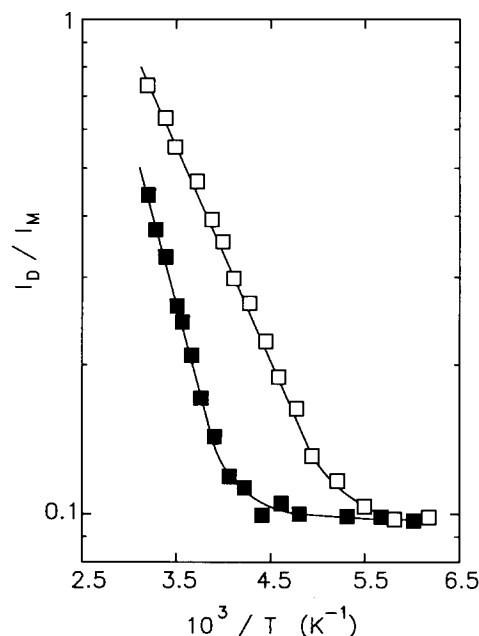


Figure 4 I_D/I_M as a function of inverse temperature for HPTP (\square) and HCTP (\blacksquare) in dichloromethane

Table 1 Activation and binding energies for excimer formation

	E_a (kJ mol ⁻¹)	$-\Delta H$ (kJ mol ⁻¹)
HPTP/MTHF	9.5 ^a	8.2 ^a
HPTP/dichloromethane	7.8	^b
HCTP/dichloromethane	13.4	^b
PBPP/dichloromethane	2.6	^b
PBCP/dichloromethane	^c	^b
PBPP/dioxane	^b	14.0
PBCP/dioxane	^b	15.5

^a Reference 2

^b Not available for temperature range examined

^c Arrhenius behaviour not observed

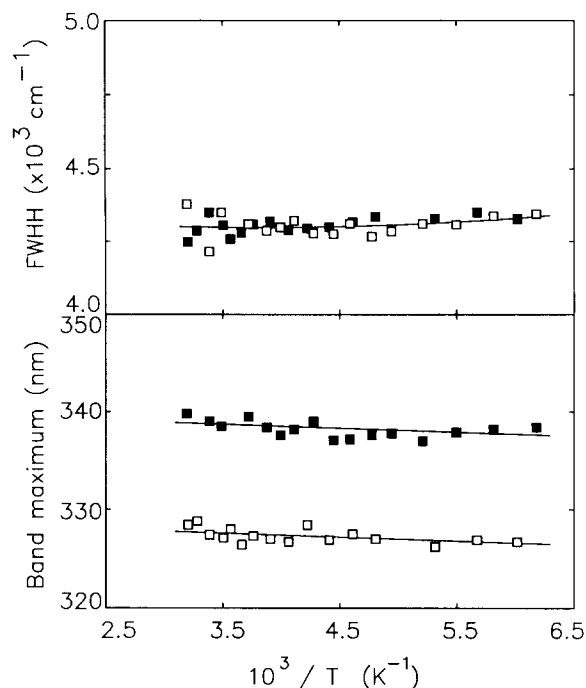


Figure 5 Excimer bandwidth and band maximum as a function of inverse temperature for HPTP (\square) and HCTP (\blacksquare) in dichloromethane

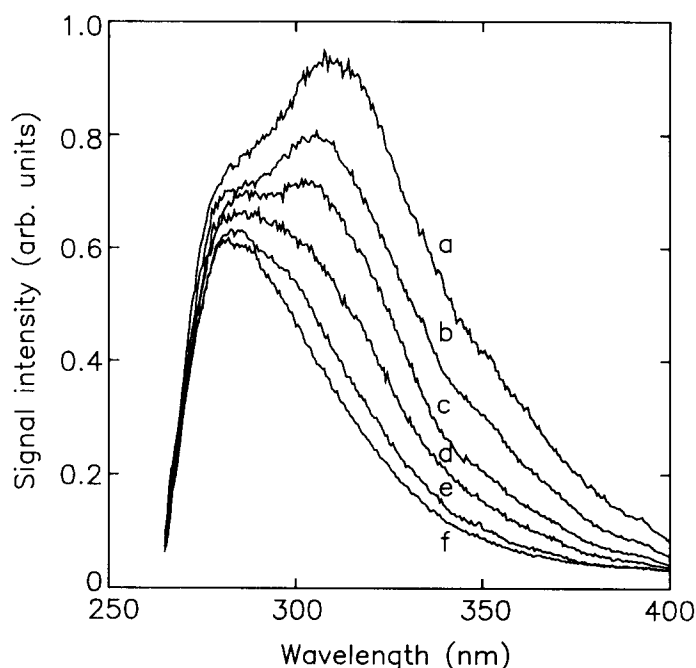


Figure 6 Fluorescence spectra for PBPP in dichloromethane as a function of temperature (K): (a) 293; (b) 262; (c) 238; (d) 216; (e) 197; (f) 182

2-methyltetrahydrofuran (MTHF) is also given for comparison². Although different solvents were used in the two cases, the activation energy for intramolecular excimer formation of HPTP in dichloromethane is in reasonably good agreement with that in MTHF. The higher activation energy for HCTP is believed to be caused by the steric effect due to increased bulkiness of the cresoxy group. From the regression analysis, the temperature dependences of bandwidth and band maximum position of the Gaussian peak are reproduced in Figure 5. Essentially constant bandwidths of 4200–4300 cm^{-1} for both trimers and band positions of

327–330 nm for HPTP and 337–340 nm for HCTP are observed, suggesting no change in excimer stability as a function of temperature for the trimers.

Figures 6 and 7 show typical fluorescence spectra for PBPP and PBCP in dichloromethane, respectively. At low temperatures the fluorescence spectra are dominated by the monomer emission, reminiscent of the spectra observed for HPTP and HCTP. As the temperature is raised, we observe a significant enhancement in excimer emission, which presumably results from an increase in side group mobility. However, the effect of temperature on I_D/I_M for PBPP and PBCP, presented in Figure 8, illustrates some distinct features in the polymer solutions. In contrast to the trimers, where rotation sampling of

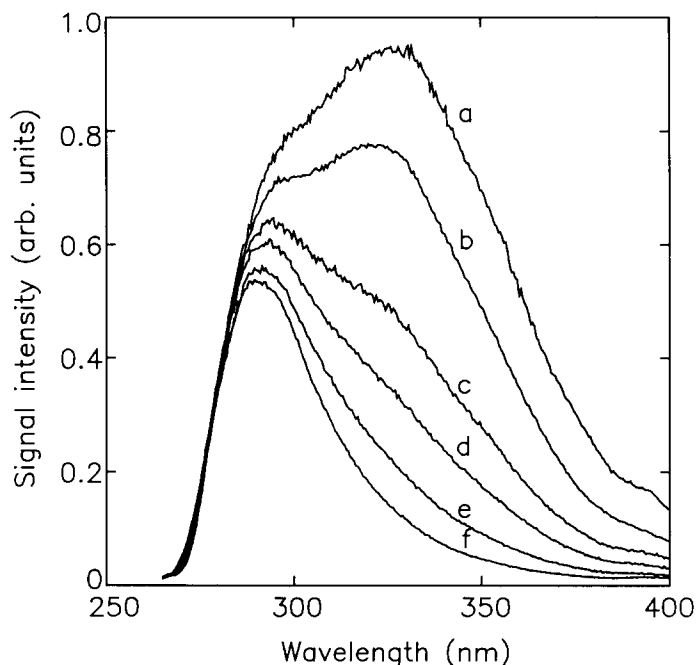


Figure 7 Fluorescence spectra for PBCP in dichloromethane as a function of temperature (K): (a) 293; (b) 249; (c) 240; (d) 235; (e) 216; (f) 192

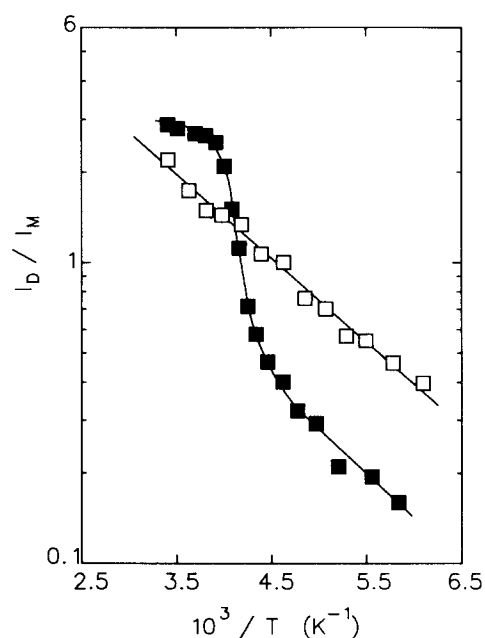


Figure 8 I_D/I_M as a function of inverse temperature for PBPP (\square) and PBCP (\blacksquare) in dichloromethane

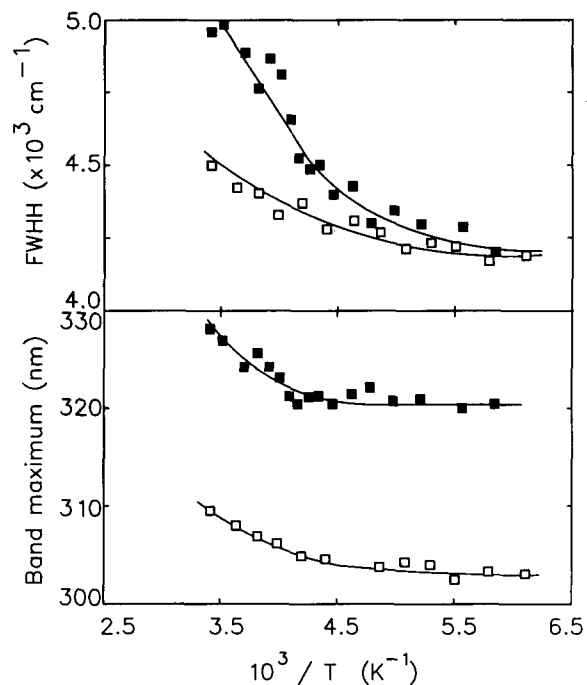


Figure 9 Excimer bandwidth and band maximum as a function of inverse temperature for PBPP (□) and PBCP (■) in dichloromethane

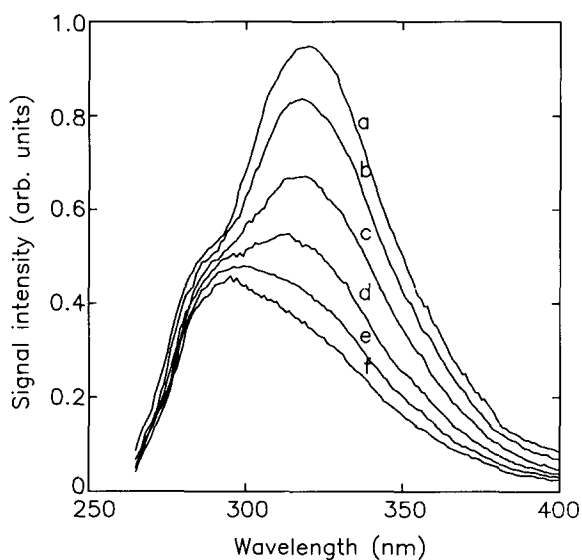


Figure 10 Fluorescence spectra for PBPP in dioxane as a function of temperature (K): (a) 306; (b) 320; (c) 332; (d) 345; (e) 353; (f) 361

EFS begins at some onset temperature, we note that no such onset temperature is observed for the polymers. While the excimer formation process in PBPP may still be characterized as diffusion-controlled, the weak Arrhenius behaviour of I_D/I_M observed in PBPP yields an activation energy of 2.6 kJ mol^{-1} , considerably smaller than that of HPTP. For PBCP, however, the kinetics of excimer formation can no longer be considered diffusion-controlled because serious deviations from an Arrhenius dependence are observed. I_D/I_M for PBCP increases drastically at temperatures above 220 K before levelling off near 300 K.

Figure 9 depicts the change of excimer bandwidth with temperature for PBPP and PBCP in dichloromethane. Both polymers exhibit an increase in bandwidth with increasing temperature, from 4200 to 4500 cm^{-1} in PBPP

and from 4200 to 5000 cm^{-1} in PBCP. The thermal dependence of excimer band maximum positions for PBPP and PBCP, also shown in Figure 9, differs significantly from their trimers. The excimer band shifts from 305 nm at low temperatures to about 310 nm above 310 K for PBPP, and from 320 to 328 nm for PBCP. Evidently, the abrupt increases in band position at 220 K for PBPP and at 240 K for PBCP are related to the similar behaviour in I_D/I_M and bandwidth.

To illustrate further the effects of solvent and temperature on the polymer solutions, we studied the excimer emission of PBPP and PBCP in dioxane in the temperature range 290–360 K. Figures 10 and 11 show typical emission spectra of PBPP and PBCP in dioxane as a function of temperature. As shown in Figure 12, the higher I_D/I_M for PBPP and PBCP in dioxane than for polymer solutions in dichloromethane can perhaps be explained in terms of differences in temperature and

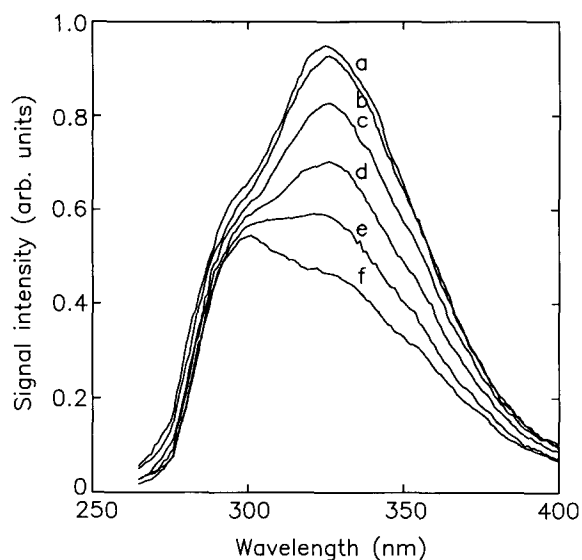


Figure 11 Fluorescence spectra for PBCP in dioxane as a function of temperature (K): (a) 307; (b) 321; (c) 333; (d) 344; (e) 353; (f) 362

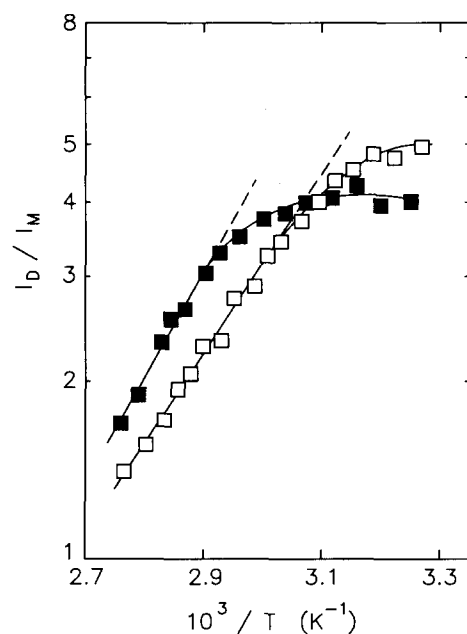


Figure 12 I_D/I_M as a function of inverse temperature for PBPP (□) and PBCP (■) in dioxane

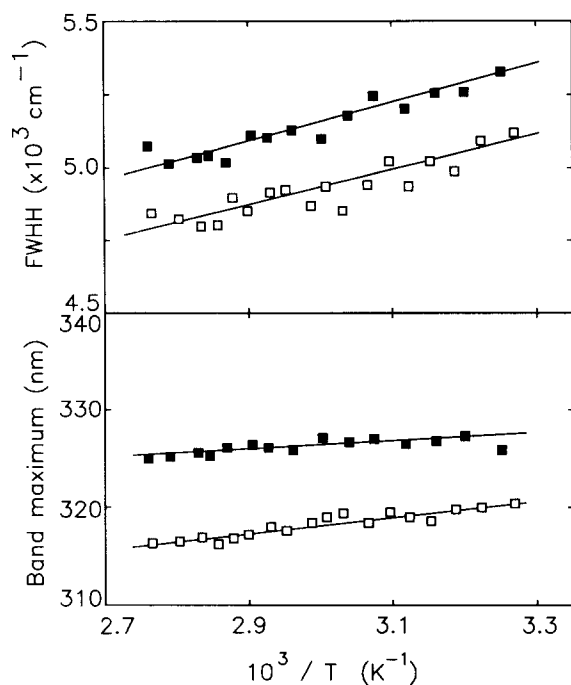


Figure 13 Excimer bandwidth and band maximum as a function of inverse temperature for PBPP (\square) and PBCP (\blacksquare) in dioxane

solvent⁸. Since the solubility parameters for dichloromethane and dioxane are given¹¹ to be 9.88 and 10.13 cal^{1/2} cm^{-3/2},* respectively, the difference in I_D/I_M should not be attributed to solvent quality, but solvent viscosity, which changes from 0.44 centipoise at 293 K for dichloromethane to 1.37 centipoise at 293 K for dioxane¹².

As the polymerization rises, excimer emission is quenched in both PBPP and PBCP solutions, and the resulting decline in I_D/I_M is found to follow a semi-logarithmic behaviour at sufficiently high temperatures, indicating that dynamic equilibrium is attained. The excimer binding energies for PBPP and PBCP, displayed in Table 1, show higher excimer stability than HPTP in MTHF. Equally intriguing are the broadened bandwidths in the dioxane solutions, which decrease from 5100 to 4800 cm⁻¹ for PBPP and from 5300 to 5000 cm⁻¹ for PBCP with increasing temperatures, as illustrated in Figure 13. The excimer band maximum position also manifests differences between polymers in dichloromethane and dioxane. The band maximum positions decrease from 320 to 316 nm for PBPP and 328 to 324 nm for PBCP. These band positions are of lower energy than those in dichloromethane, but of higher energy than those observed in the trimer solutions.

DISCUSSION

Interpretation of the present data requires an examination of possible differences in excimer formation in both trimers and polymers. Indeed, excimer formation in poly(aryloxyphosphazenes) involves a number of different possible conformations, in contrast to that in the trimers. In Figure 14 three types of nominal EFS are displayed. The first is the intramolecular excimer formed between two aryloxy groups bonded to the same phosphorus atom (type I). This type of EFS, also found in phosphazene trimers, requires bond rotations about the carbon–oxygen

and phosphorus–oxygen linkages to achieve a suitable conformation. The second type results from intramolecular interactions between aryloxy groups appended to adjacent phosphorus atoms. An examination of the spatial arrangement of the chromophores reveals that such a conformation requires a *trans-trans* or *trans-gauche* backbone and eclipsed side chain conformation (type II), and can only occur in phosphazene polymers. The third EFS, also absent in dilute trimer solutions, is the intermolecular excimer composed of two aryloxy groups bonded to different polymer chains or, equivalently, groups attached to non-adjacent phosphorus atoms of the same chain (type III). This conformation has no specific requirement for the backbone conformation but suitable overlap of phenyl rings is essential.

In HPTP and HCTP different substituent sizes can only affect the excimer rotational sampling through its bond rotation since only type I EFS is possible. In polymer solutions, however, altering the size of the chromophores not only affects the side group bond rotation, but can also change the polymer chain conformation as a whole¹³. Since the molecular weight of the phosphazene polymers studied is rather high ($M \approx 10^6$), it is conceivable that all three types of EFS are present in the polymer solutions. This is supported by the apparent excimer emission in the polymer solutions at low temperatures, whereas no such excimer emission is observed for the trimers. While excimer emission due to type I excimer can be probed in the trimer solutions, the present data do not allow us to distinguish unambiguously contributions to excimer emission from different EFS in the polymer solutions. In particular, we are not able to compare contributions to excimer emission from intramolecular excimer sites involving adjacent phosphorus atoms (type II) and intermolecular excimer sites or

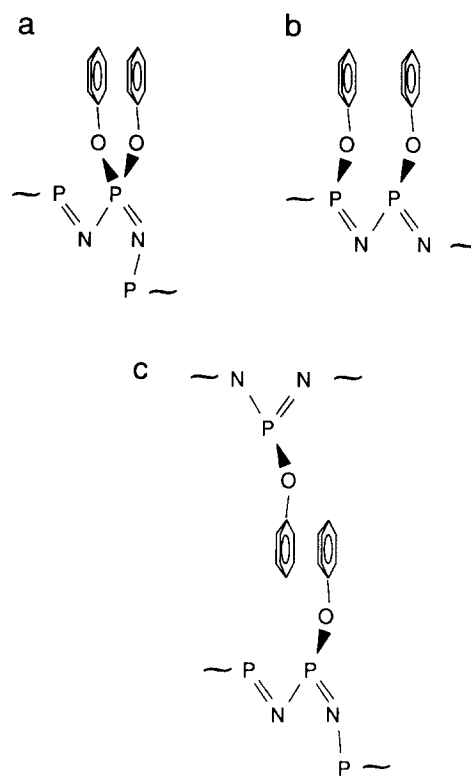


Figure 14 Possible excimer forming sites: (a) type I, intramolecular (same P atom); (b) type II, intramolecular (adjacent P atoms); and (c) type III, intermolecular or intramolecular (non-adjacent P atoms)

* 1 cal = 4.184 J

intramolecular excimer sites involving non-adjacent phosphorus atoms (type III). Previously, conformational¹³, osmometry and viscosity studies¹⁴ have indicated that, at room temperature, an extended *cis-trans* conformation is preferred in dilute solutions and that a *trans-trans* or *trans-gauche* conformation required for type II EFS is not particularly favourable. However, these and other studies^{15,16} have suggested that the energy barriers for rotation along the phosphorus-nitrogen backbone are relatively low and that no significant deviations from a randomly coiled configuration are observed.

If the onset temperature of increasing I_D/I_M in trimers can be regarded as the beginning of rotational sampling of type I EFS, the absence of onset temperature for PBPP and PBCP in dichloromethane provides further evidence that types II and III EFS may be inherently important for the polymers in the temperature range examined. The lower onset temperature for HPTP than for HCTP is consistent with the current proposal that less bulky phenoxy groups in HPTP should experience less steric hindrance. Although the higher I_D/I_M for the polymers than for the trimers gives a qualitative measure of the type II and type III EFS populations, a more quantitative approach could be quite involved given the possibility and extent of energy migration in the EFS sampling.

For the trimers, the constant bandwidth and band maximum position suggest that the electronic properties of the excimer are unchanged with temperature. The increase in bandwidth with temperature for the polymers in dichloromethane could therefore be interpreted as resulting from the emergence of multiple excimer sites. The excimer bandwidth for the polymers at low temperatures, where only types II and III EFS are important, is identical to that for the trimers, suggesting that the bandwidth of a combination of types II and III excimer bands is similar to that of type I. Although bandwidths for the three types of EFS are expected to be similar due to the restrictive requirements for excimer formation, an excimer peak originating from a combination of types II and III EFS will exhibit bandwidths similar to type I only if the bandwidth and band maximum positions for types II and III are similar. This is unlikely given the difference in excimer equilibrium separations. Indeed, an examination of the valence bond linkages gives a ring-ring separation of 2.4 \AA^* for the type I EFS and 2.8 \AA for the type II EFS in the phenoxy or cresoxy groups, while no fixed ring-ring separation is dictated for type III. These separations are considerably less than the van der Waals equilibrium separation of $3.5\text{--}3.7 \text{ \AA}$ ordinarily found in polystyrene excimers. The fact that type I EFS exhibits a bandwidth and maximum position similar to polystyrene can be attributed to the electron-withdrawing effect of the oxygen in the aryloxy groups. On the other hand, the decrease in bandwidth with temperature in dioxane can be attributed to the thermal deactivation of all EFS, perhaps more significantly for type I in consideration of the slight blue shift involved.

The excimer band shifts with increasing temperature in the polymers are also well explained in terms of the combination of more than one excimer band. In comparing the band maximum positions in the trimers and polymers, we observe an apparent blue shift of excimer bands in PBPP and PBCP. It follows that excimer bands

originating from the combination of types II and III EFS must be blue-shifted with respect to type I EFS. Corresponding to the change in bandwidth, the significant red shift in excimer band with temperature for the polymers in dichloromethane suggests that the type I EFS becomes more prominent as the temperature increases. In dioxane solutions we also observe a slight blue shift of band position compared to the trimers. Similar to the decrease in bandwidth for the polymers in dioxane at high temperatures, the blue shift is attributed to the thermal deactivation of predominantly type I EFS.

The fact that the activation energy for PBPP is considerably lower than that for its trimer, HPTP, is interesting, as both trimer and polymer solutions have an equal number of chromophores within their systems. However, if one takes into account the presence of types II and III EFS, whose population may not be as sensitive to temperature changes as type I, the difference is easily explained. The increase in I_D/I_M further corroborates the importance of types II and III EFS in the polymer solutions, despite the relatively dilute solutions.

We were surprised by the fact that PBCP does not follow a diffusion-controlled collision mechanism. It is possible that the addition of a methyl group onto the phenoxy group leads to the failure of one or both of the underlying assumptions for a diffusion-controlled process of excimer formation. For the process to be Arrhenius, the local environment perceived by the chromophores should be represented by the macroscopic viscosity, and Stokes' law should be applicable to the diffusion of these side groups. Because the activation energy depends on the ease with which two aromatic rings approach each other to achieve the necessary sandwich configuration, an additional methyl group attached to the phenoxy species would necessarily hinder this approach. Since this steric effect does not cause a non-diffusive contribution to the type I excimer formation process in HCTP relative to HPTP, it is conceivable that the increase in bulkiness of side group in PBCP affects only the conformation of the polymer in solution and, therefore, this non-diffusive behaviour in PBCP should be attributed to changes induced in main chain conformation.

Excimer binding energies for PBPP and PBCP in dioxane also show distinct differences from HPTP in MTHF. Usually, the excimer binding energy is expected to be independent of the nature of the solvent as the excimer has a definite steric configuration⁸. A higher binding energy indicates that the EFS are more stable in the polymer solutions. This disagreement further confirms that types II and III EFS may be pervasive in the polymers and are responsible for part of the deactivation process. The higher binding energy in PBCP than in PBPP is best visualized by using the potential energy diagram proposed by Birks⁸. The attachment of the methyl group to the phenoxy species tends to balance the electron-withdrawing influence of the oxygen atom, thereby lowering the attraction potential curve. However, there is probably a concomitant upward shift in the repulsive potential as well.

SUMMARY

We have studied the effect of substituents on the photophysics of trimers and polymers at various temperatures. We conclude that the size of substituent plays an important role in the diffusion process of excimer

* $1 \text{ \AA} = 10^{-1} \text{ nm}$

formation, excimer stability and polymer conformation in solution. These data obtained from dilute solutions should provide an information platform from which a photophysical study on the effects of substituent, crystal structure and crystallinity on polymer morphology can be launched. More specifically, band assignment for type I EFS is possible from a comparison between trimers and polymers. Although types II and III EFS cannot be resolved here, we believe that type III plays a more important role and therefore the amorphous intermolecular EFS (type III) can be assigned qualitatively. These results suggest that further study of the temperature dependence of I_D/I_M could improve our understanding of the structure of these inorganic backbone polymers.

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REFERENCES

- 1 Allcock, H. R. *Chem. Eng. News* 1985, 18 Mar., 23
- 2 Gleria, M., Barigelletti, F., Dellonte, S., Lora, S., Minto, F. and Bortolus, P. *Chem. Phys. Lett.* 1981, **83**, 559
- 3 Hargreaves, J. S. and Webber, S. E. *Polym. Photochem.* 1982, **2**, 359
- 4 Singler, R. E., Hagnauer, G. L., Schneider, N. S., LaLiberte, B. R., Sacher, R. E. and Matton, R. W. *J. Polym. Sci., Polym. Chem. Edn.* 1974, **12**, 433
- 5 Singler, R. E., Schneider, N. S. and Hagnauer, G. L. *Polym. Eng. Sci.* 1975, **15**, 321
- 6 Frank, C. W. and Gashgari, M. A. *Macromolecules* 1979, **12**, 163
- 7 Berlman, I. B. 'Handbook of Fluorescence Spectra of Aromatic Molecules', Academic Press, New York, 1965
- 8 Birks, J. B. and Christophorus, L. G. *Proc. Roy. Soc. Lond.* 1964, **A277**, 571
- 9 Becker, R. S. 'Theory & Interpretation of Fluorescence & Phosphorescence', Wiley, New York, 1969
- 10 Gelles, R. and Frank, C. W. *Macromolecules* 1983, **16**, 1448
- 11 Riddick, J. A., Bunger, W. B. and Sakano, T. K. 'Techniques of Chemistry', Vol. II: 'Organic Solvents', Wiley, New York, 1986
- 12 Burdick & Jackson Solvent Guide, 1984
- 13 Allen, R. W. and Allcock, H. R. *Macromolecules* 1976, **9**, 956
- 14 Andrady, A. L. and Mark, J. E. *Eur. Polym. J.* 1981, **17**, 323
- 15 Hagnauer, G. L. and LaLiberte, B. R. *J. Polym. Sci., Polym. Phys. Edn.* 1976, **14**, 367
- 16 Singler, R. E., Hagnauer, G. L. and Sicka, G. W. 'Elastomers and Rubber Elasticity', *Am. Chem. Soc. Symp. Ser.* 1982, **193**, 229