Excimer Fluorescence in Polyphosphazenes. 2. Morphology and Dynamics in Polymer Films

Alan S. Yeung and Curtis W. Frank*

Department of Chemical Engineering, Stanford University, Stanford, California 94305-5025

Robert E. Singler

Polymer Research Division, Army Materials and Mechanics Research Center, Watertown, Massachusetts 02172

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ABSTRACT: The effects of substituent on morphology and fluorescence behavior in poly(organophosphazenes) are studied. Side-group and main-chain motions in two representative poly[(aryloxy)phosphazenes], poly(diphenoxyphosphazene) (PBPP) and poly(di-*p*-cresoxyphosphazene) (PBCP), are investigated along with a copolymer, poly[(trifluoroethoxy)phenoxyphosphazene] (PFPP) in both amorphous and crystalline phases in terms of the excimer-to-monomer intensity ratio, I_D/I_M, excimer bandwidth, and excimer band position. The glass transition temperature, T_g, and mesomorphic temperature, $T(1)$, obtained by differential scanning calorimetry, correlate well with transitions observed in I_D/I_M and excimer bandwidth measurements. Multiple excimer-forming sites are found in all polymers, especially in PFPP where isomorphic forms of monoclinic and orthorhombic structures are found. A comparison of fluorescence spectra from solutions and the bulk phase yields qualitative assignments of the excimer bands, whereas the fluorescence spectra for annealed PBPP and PBCP films illustrate the effect of crystal structure. In PBPP, the transformation of the α-form to the β-form of the monoclinic crystal structure upon annealing does not increase the overall excimer emission but causes a blue shift in the composite excimer band. By contrast, the transformation of the α-form to the γ-form of the orthorhombic structure in PBCP results in an increase in excimer emission as well as a red shift of the excimer band. The increase in excimer emission in PBCP upon annealing below $T(1)$ suggests that the orthorhombic structure is more conducive to excimer formation.

Introduction

In recent years, interest in structure–property relationships and phase transitions in polyphosphazenes has expanded. Semicrystalline polyphosphazenes with alkoxy and aryloxy side groups have been found to display two first-order transitions.[1-3] These polymers may exist in a state of partial order above the so-called mesomorphic temperature, $T(1)$, before undergoing true melting to an isotropic state at a higher temperature. Below this mesomorphic temperature, polyphosphazene morphology depends strongly on the substituents as well as thermal and processing history. Useful insights into the morphology and thermal transition behavior of various polyphosphazenes have been provided by X-ray diffraction,[4-16] small-angle and wide-angle X-ray scattering,[17] differential scanning calorimetry (DSC),[1-3,8-10,16,28] nuclear magnetic resonance (NMR),[18-20] electron and optical microscopy,[13,21-23] dilatometry,[12,24] vibrational spectroscopy,[25,26] and viscoelastic[16,24,27] measurements. Alternately, active studies have been pursued in the synthesis and characterization of polyphosphazene copolymers involving the substitution of mixed side groups to inhibit the development of crystallinity.[3,29,30] Despite the wealth of literature available, a clear understanding of the morphology and dynamics of these homo- and copolymers has not been firmly established. In this paper, we introduce a new technique that shows promise for expanding our understanding of these polymers.

Excimer fluorescence has previously been employed to examine the morphology and thermal behavior of polymer blends in which a fluorescent arylvinyl polymer is mixed with a nonfluorescent polymer.[31,32] The ratio of excimer-to-monomer emission intensities, I_D/I_M, has been shown to provide information on conformational features at the local level. As such, it can be utilized to detect changes in segment motions and interactions induced in the polymer as a function of temperature and thermal history.

Although excimer fluorescence depends intimately on the chemical and physical properties of the underlying polymer, the application of this technique to the investigation of semicrystalline polymers has been very limited, perhaps due to the inherently complex photophysics involved.[33] In spite of this difficulty, previous photophysical studies on polyphosphazenes have paved the road for more thorough investigation. Webber et al.[34] examined fluorescence spectra of poly(diphenoxyphosphazene) (PBPP) and reported more facile excimer emission in solution than in films. In a recent communication,[35] we presented some preliminary results concerning the thermal behavior of excimer fluorescence in polyphosphazene films.

In the preceding paper of this series,[36] hereafter referred to as paper 1, we studied the effects of substituent and solvent on the intrinsic fluorescence behavior of phosphazene trimers and polymers in solution. We found that changing substituents from phenoxy to cresoxy groups not only gives rise to a blue shift in monomer and excimer bands but also has a profound effect on the chain conformation and electronic sampling of multiple excimer-forming sites (EFS). Here, we report, in more detail, the first application of photostationary excimer fluorescence to characterize the morphology and dynamics of poly[(aryloxy)phosphazenes] in the solid state.

Experimental Section

Materials. The polymers, poly(diphenoxyphosphazene) (PBPP) and poly(di-*p*-cresoxyphosphazene) (PBCP), were described previously.[2] In addition, we have also included a copolymer, poly[(trifluoroethoxy)phenoxyphosphazene] (PFPP), in our study of the effects of substituent on morphology and fluorescence behavior. The copolymer was prepared by the ring-opening polymerization of hexachlorophosphazene at 518 K,

* To whom correspondence should be addressed.

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followed by reaction of the resulting poly(dichlorophosphazene) with equal amounts of sodium trifluoroethoxide and sodium phenoxide. Spectrophotometric grade tetrahydrofuran (THF) was purchased from Aldrich and used as the casting solvent without further purification.

Sample Preparation. Two types of polymer film were prepared. The thicker films (0.1–0.2 mm), hereafter referred to as as-cast films, were cast from 5–10% solution in THF over mercury and allowed to evaporate to dryness over a 24-h period, followed by further drying under vacuum at 313 K for 24 h.[30] The second set of sample films was prepared from 2% solution in THF by allowing the solvent to evaporate slowly from films cast on clean glass slides at room temperature. The solid films, about 10–20 μm thick, were dried under vacuum at room temperature for 48 h to remove the casting solvent. Subsequent annealing of the solvent cast films was carried out at various temperatures for 60 min and quenched immediately with liquid nitrogen for 5 s. The annealed films were then stored under vacuum for 4 h and allowed to reach room temperature before fluorescence spectra were taken.

Instrumentation. Fluorescence spectra were measured with an excitation wavelength at 250 nm and slit bandwidths of 8 nm to facilitate data collection at low and high temperatures. The spectrofluorometer has been described before.[32] All emission spectra have been corrected for Raman and scattered light and instrument response.

The as-cast films were mounted between two sapphire disks in a sample compartment that was purged with dried, cooled nitrogen gas to provide cooling and prevent degradation. A pair of resistive heaters coupled with a Eurotherm controller and thyrister allowed an average heating rate of 50 K h^{-1}. Fluorescence measurements were made after a steady temperature had been maintained for 15 min. Photostationary spectra of the annealed films were taken with the sample slides mounted in the sample compartment in a front face configuration.

Results

In order to appreciate the complexity of the photophysics involved as well as the difficulty in interpreting the experimental observables, we briefly review some of the fluorescence features in dilute solutions of PBPP and PBCP. In paper 1,[36] we discussed the possibility of three types of EFS found in (aryloxy)phosphazene polymers. Type I EFS, an intramolecular excimer formed between two aryloxy groups bonded to the same phosphorus atom, require bond rotations about the carbon–oxygen and phosphorus–oxygen linkages to achieve a suitable conformation. Although intramolecular interaction between aryloxy groups appended to adjacent phosphorus atoms can lead to excimer formation (type II), such a conformation requires a trans–trans or trans–gauche backbone and eclipsed side-chain conformation, which are energetically unfavorable.[37] Type III EFS include excimer species formed between two aryloxy groups bonded to different polymer chains and groups attached to nonadjacent phosphorus atoms of the same chain. This conformation has no specific requirement for the backbone conformation; however, suitable overlap of phenyl rings is essential.

Excimer fluorescence measurements on the trimers and polymers suggested that more than one type of excimer-forming site exists in the polymer solutions at a concentration of 10^{-4} M repeating units, whereas trimer solutions having the same amount of repeating units showed type I excimer-forming site emission only. The composite excimer bands in the polymer solutions are blue shifted compared to type I EFS in the trimer solutions. Type I excimer-forming site emission has been previously assigned to band maxima at 328 and 338 nm, for phenoxy and cresoxy groups, respectively. Type II and type III EFS, blue shifted relative to type I EFS, were however, not resolved due to significant band overlap. The resulting excimer bands in the polymer solutions, somewhat broadened compared to those for the trimers, do not show any discernible structure.

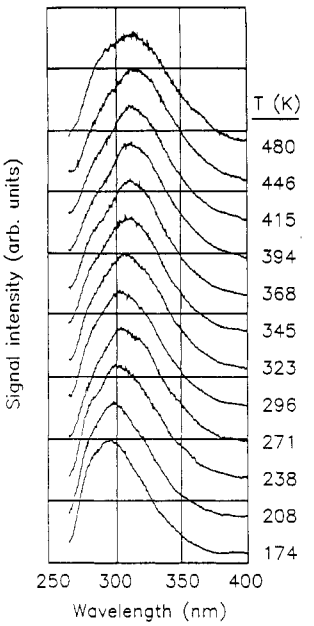

Figure 1. Selected fluorescence spectra for the PBPP film as a function of temperature (all spectra normalized at band maximum).

As-Cast Films. Figure 1 illustrates the normalized fluorescence spectra of PBPP as-cast films measured at various temperatures. Excimer bands in the solid state are generally broader than in solution and, although ill-resolved, strongly suggest the existence of multiple excimer-forming species. For PBPP, the composite excimer band occurs at 303–310 nm in dichloromethane and at 316–320 nm in dioxane,[36] whereas the respective excimer band occurs at 305–315 nm in the bulk phase. Excimer emission, in general, appears to be more efficient in film, contrary to what was reported previously.[32] While more restricted segmental motions are expected to give rise to lower I_D/I_M in the bulk phase, this effect could be offset by an increase in the probability of overlap of phenyl rings as a result of higher local segment density or more efficient energy migration. Increasing the temperature brings about more facile emission and a red shift of the composite excimer band.

Fluorescence spectra for PFPP, not shown, are qualitatively similar to those for PBPP for wavelengths between 250 and 300 nm. This is consistent with the phenoxy group being common to both polymers. A significant difference in PFPP, however, is the appearance at 170 K of a band at 325 nm that grows in to become comparable in intensity to the 305–315-nm band at high temperatures.

Representative fluorescence spectra for PBCP films as a function of temperature are displayed in Figure 2. The hypsochromatic red shifts in monomer and excimer bands for PBCP films relative to PBPP are similar to those in solution.[36] The composite excimer bands found at 320–328 nm for PBCP in dichloromethane and at 324–325 nm in dioxane have been shifted to 317–325 nm for PBCP films. Multiple excimer-forming species appear to dominate the emission spectra at all temperatures, especially at temperatures between 187 and 303 K. This structure in the excimer emission band may be explained in terms of isomorphism; we shall return to this point later. At the present time, no attempt is made to separate the multiple peaks observed in various fluorescence spectra due to their poor resolution.

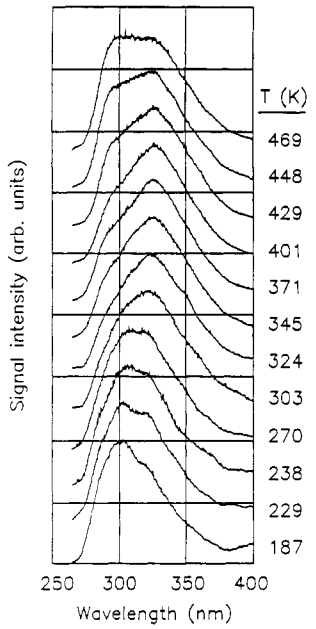

Figure 2. Selected fluorescence spectra for the PBCP film as a function of temperature.

Nevertheless, it is informative to evaluate the extent of excimer emission in terms of I_D/I_M by arbitrarily fitting the composite excimer band to a single Gaussian peak. As in paper 1,[36] the band shape for the monomer band is obtained from the emission spectra of the corresponding trimer solutions at 77 K. The temperature dependences of I_D/I_M for the PBPP, PBCP, and PFPP films are plotted in Figure 3 along with their glass transition temperatures, T_g, and mesomorphic temperatures, $T(1)$, as determined by DSC.[30,38] Also included is the temperature at which the I_D/I_M value begins to increase for PBPP and PBCP, T_{onset}. The PFPP copolymer, however, does not show an onset temperature within the range examined. The interesting feature of these data is that there is a reasonably good correlation between the thermal transitions determined by DSC and the existence of either local (at T_g) or global (at $T(1)$) maxima in the composite I_D/I_M for each polymer. The deviation may arise from the existence of multiple excimer-forming sites.

The temperature dependence of the excimer bandwidth for PBPP, PBCP, and PFPP films provides further information on the dynamics in the bulk phase. Composite excimer bandwidths obtained from the regression analysis are plotted as a function of temperature in Figure 4. The composite bandwidths for PBPP and PBCP films lie in the range of 5100–5300 cm^{-1}, while that for PFPP ranges from about 5200 to about 5800 cm^{-1}. Although the changes of bandwidth in PBPP and PBCP are not as dramatic as in PFPP, the trend of constant bandwidth below T_g, band broadening between T_g and $T(1)$, and band sharpening above $T(1)$ appears universal among all three polymers. This is in contrast to the constant bandwidth behavior observed in dioxane or in trimer solutions, although a general trend of increasing bandwidth is found in dichloromethane solutions.[36]

Figure 5 illustrates the composite excimer band maximum position as a function of temperature. There seems to be no obvious correspondence between the excimer emission band location in solution[36] and in solid films. Indeed, interpretation of the experimental data in films is fraught with difficulties since different conformations can be expected in both amorphous and crystalline phases, in addition to the existence of multiple EFS. At temperatures below T_g, the band position is relatively constant with plateau values of 317, 305, and 307 nm for PBPP, PBCP, and PFPP, respectively. At T_g there is a significant red shift in peak position for all three polymers that persists to the vicinity of $T(1)$ where it appears to level off.

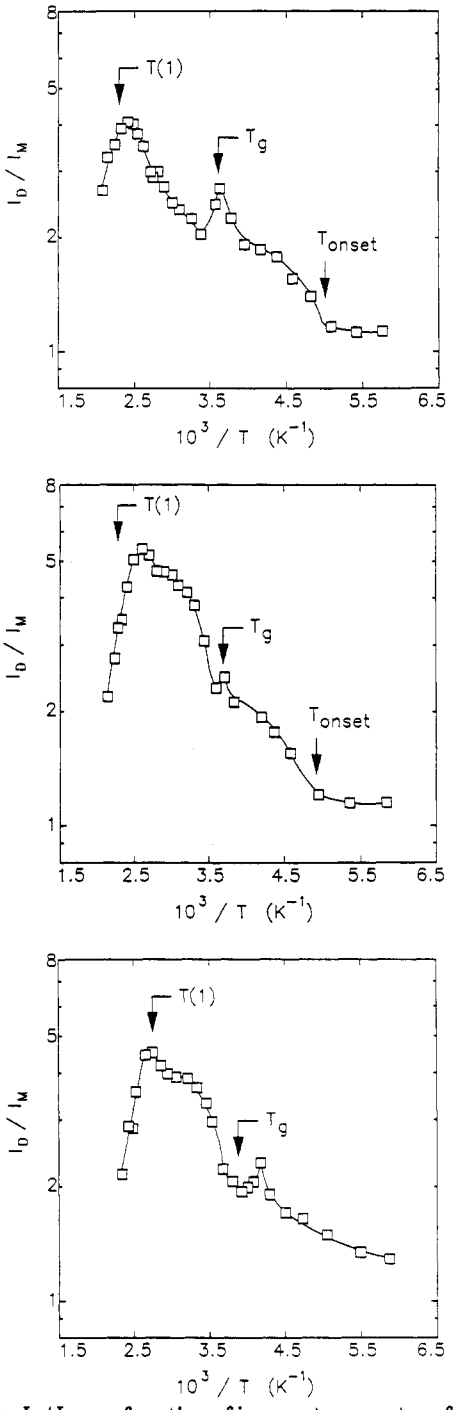

Figure 3. I_D/I_M as a function of inverse temperature for (a, top) PBPP, (b, middle) PBCP, and (c, bottom) PFPP as-cast films. $T(1)$ and T_g as determined by DSC[30,38] and T_{onset} (where appropriate) are also shown.

Annealed Films. In view of the importance of side-group and backbone motions suggested by the thermal dependence of I_D/I_M, we are also interested in investigating the effects of annealing on such motions as reflected by the emission properties. Figures 6 and 7 present the fluorescence spectra of PBPP and PBCP as a function of annealing temperature. Remarkably well-defined structure and band shifts are observed in the excimer peaks, lending support to the existence of multiple emitting species. With increasing annealing temperature, the

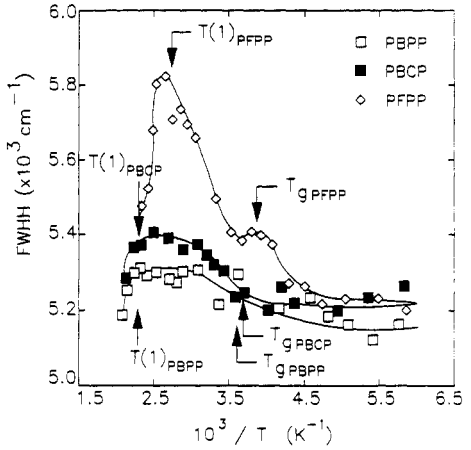

Figure 4. Composite excimer bandwidth as a function of inverse temperature for PBPP (□), PBCP (■), and PFPP (△).

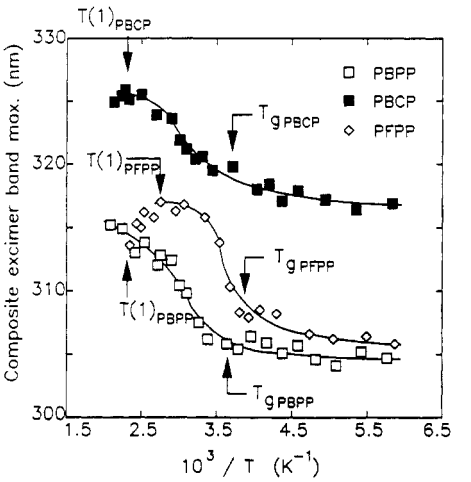

Figure 5. Composite excimer band maximum as a function of inverse temperature for PBPP (□), PBCP (■), and PFPP (△).

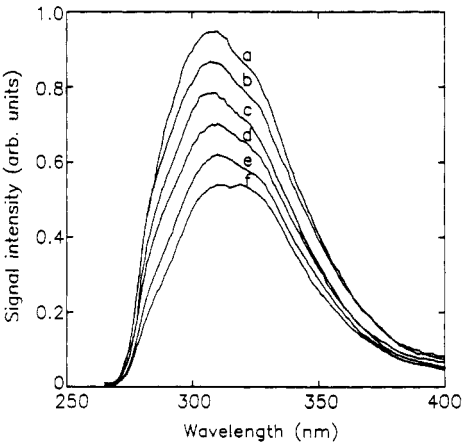

Figure 6. Fluorescence spectra for PBPP films as a function of annealing temperature: (a) 459 K; (b) 450 K; (c) 419 K; (d) 390 K; (e) 365 K; (f) 320 K.

higher energy excimer peak at 305 nm in PBPP grows in magnitude at the expense of the lower energy peak at 317 nm. Conversely, at high annealing temperature, the lower energy excimer peak at 324 nm in PBCP becomes more prominent relative to the higher energy peak at 304 nm in PBCP. Since the annealed films show more well-defined peak separation than the as-cast films, we have attempted to resolve the two peaks by fitting two Gaussian envelopes and a monomer peak to the spectra. The sum of integrated areas of the two peaks is then $I_D = I_{D1} + I_{D2}$, where I_{D1} and I_{D2} are the integrated intensities of the high- and low-

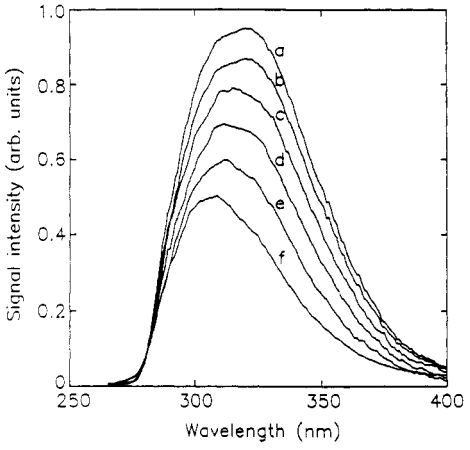

Figure 7. Fluorescence spectra for PBCP films as a function of annealing temperature: (a) 459 K; (b) 450 K; (c) 419 K; (d) 390 K; (e) 365 K; (f) 320 K.

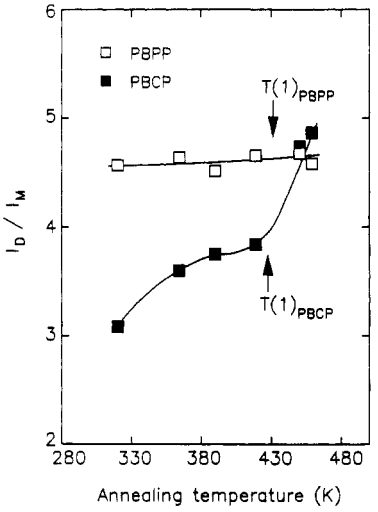

Figure 8. I_D/I_M as a function of annealing temperature for PBPP (□) and PBCP (■). $T(1)$ and T_g as determined by DSC[30,38] are shown.

energy excimer peaks fitted, respectively. For PBPP, the regression analysis yields a satisfactory fit of excimer peaks at 305 and 317 nm with corresponding bandwidths of about 3400 and 4100 cm^{-1}, respectively. Similarly, we obtain a fit of excimer peaks for PBCP at 304 and 324 nm with corresponding bandwiths of about 3400 and 4400 cm^{-1}. These fitted values of bandwidth are considerably lower than those found in type I EFS in PBPP and PBCP, indicating that resolution of such spectra into two excimer bands is still an oversimplification.

Figure 8 shows the change in I_D/I_M as a function of annealing temperature. To highlight the contributions of different excimer peaks to overall excimer emission, I_{D2}/I_{D1} is plotted against annealing temperature in Figure 9. In PBPP, no appreciable change in I_D/I_M is involved as the majority of excimer emission shifted from the low-energy peak to the high-energy peak. This is in contrast to PBCP where I_D/I_M increases gradually with annealing temperature before an abrupt jump when annealed significantly above $T(1)$. The opposite behavior between PBPP and PBCP in terms of I_{D2}/I_{D1} may indicate the profound effect of crystal structure on the excimer peak positions. The dramatic rise of I_{D2}/I_{D1} in PBCP and the modest decline of I_{D2}/I_{D1} in PBPP above $T(1)$ may reflect the subtle morphological changes incurred upon annealing above $T(1)$.

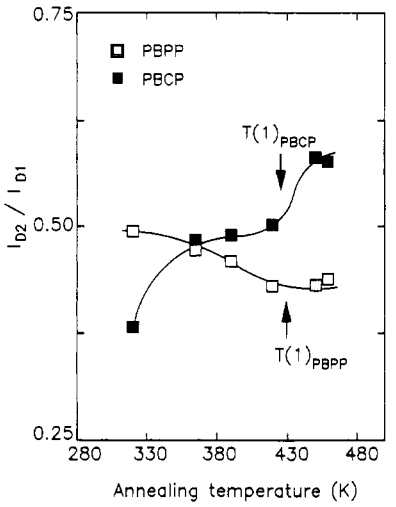

Figure 9. Integrated ratio of the lower to higher energy excimer peaks as a function of annealing temperature for PBPP (□) and PBCP (■).

Discussion

Below T_g. The temperature dependence of I_D/I_M is similar for PBPP and PBCP at temperatures below their corresponding T_g's. In both cases, I_D/I_M remains constant below a certain onset temperature and increases steadily above it. At temperatures below T_{onset}, I_D/I_M is relatively insensitive to temperature because excimer fluorescence takes place primarily via energy migration to a fixed population of preformed EFS that are frozen-in at temperatures below T_g. The number of preformed EFS available for excimer formation will depend on the local chromophore (aryloxy group) concentration and chain conformation, which in turn depend strongly on the chromophore interactions.

As the temperature is raised, local side group motions of the polymer chains become appreciable, causing an increase in free volume and excimer emission due to rotational sampling of excimer-forming sites, i.e., an increase in excimer emission due to bond rotation. This is in agreement with the observation that T_{onset} for PBPP is lower than that for PBCP and can be attributed to the smaller substituents in PBPP. At this point, excimer emission results from a combination of migrational and rotational sampling as preformed excimer sites are still intact.

The lack of onset temperature observed for the PFPP copolymer may be explained in terms of its lower T_g.[38] It is conceivable that the smaller trifluoroethoxy group offers more free volume for the bond rotation of the phenoxy groups such that the onset temperature lies below the temperature range probed.

The fact that I_D/I_M is higher in PFPP than both PBPP and PBCP below T_g and is still higher in PFPP than in PBPP at elevated temperatures is rather intriguing since the number of chromophores in PFPP is only half that for PBPP and PBCP. It is likely that type I EFS, though important in dilute solutions,[36] do not manifest themselves strongly in films, at least not below T_g.

T_g Transition. The drop in I_D/I_M at T_g may be considered to be a consequence of cooperative motions of chain segments, resulting in the thermal breakup of preformed excimer sites previously locked in the amorphous phase of the polymer films. It is surprising that T_g = 259 K for PFPP as determined by DSC does not agree well with the value of T_g = 237 K calculated from the Fox equation,[39] whereas the plot of I_D/I_M vs temperature yields a value of T_g = 241 K, considerably more in line with that predicted by the Fox equation. Although previous studies on phosphazene copolymers have found positive deviations of T_g from the values predicted by the Fox equation,[29,30] their differences are usually less than 10 K. While no previous studies on PFPP have been reported, it is plausible that some block copolymer characteristics may be found in PFPP due to different reactivities of the nucleophiles, and the elevation of T_g for PFPP may be explained by the existence of unequal portions of phenoxy and trifluoroethoxy groups in the amorphous phase. If the amorphous phase is composed of a greater amount of phenoxy groups, the resulting T_g would necessarily be higher and the crystalline phase should therefore be composed of more trifluoroethoxy groups. This is in excellent agreement with the identical values of $T(1)$ observed in PFPP and PBFP.[30,38] Since excimer fluorescence spectra depict only the dynamics of phenoxy groups and the I_D/I_M peak at T_g reflects the thermal breakup of preformed EFS instead of the cooperative motions involved at the glass transition, the use of either I_D/I_M or band maximum position to obtain T_g of phosphazene copolymers may not be feasible, especially when one of the substituents is nonfluorescent.

A further increase in temperature gives rise to a shoulder in the I_D/I_M plot before undergoing the mesomorphic transition. This shoulder is very reproducible and is particularly evident in PBCP and PFPP, though not as obvious in PBPP. To our best knowledge, no indication of any intermediate transition at an intervening temperature between T_g and $T(1)$ has been reported, and the interpretation of such observation is not straightforward. It is tempting to suggest that such a shoulder arises from the deactivation of EFS in the amorphous phase where the excimer-forming site is broken up thermally before excimer emission occurs. If the $T(1)$ transition is indeed responsible for the deactivation of EFS in the crystal phase, it is possible that a similar process may occur in the amorphous phase. However, ^{1}H NMR relaxation studies[18] reveal no abrupt change in spin–spin relaxation time in the amorphous phase of PBFP at all temperatures. Furthermore, the molecular motions of the polymer chains in the mesophase are faster than in the amorphous phase at all temperatures; hence, it is unlikely that such a transition in the amorphous phase occurs at a temperature below $T(1)$. Another possibility is the existence of polymorphs in the crystal phase and such observations of I_D/I_M shoulders and $T(1)$ peaks are similar to the low- and high-temperature endotherms obtained by DSC. This proposal can be rejected on the basis that such endotherms are usually separated by less than 20 K,[28] whereas the temperature differences between the I_D/I_M shoulder and $T(1)$ peak, as shown in Figures 4–6, exceed 70 K for PBPP and PBCP and 40 K for PFPP. Although no abrupt changes in excimer band position at such I_D/I_M shoulders are found, a slight decrease in bandwidth is discernible in PBPP and PBCP. It is possible that such I_D/I_M shoulders are a manifestation of the deactivation of one type of excimer-forming site in the crystal phase. Since the band maximum continues to shift toward the red beyond this point, a dynamic equilibrium region for type II or type III EFS may commence at that point.

$T(1)$ Transition. The abrupt decreases in I_D/I_M and bandwidth at $T(1)$ suggest a morphological change. Increasingly, NMR and dilatometric measurements have indicated that $T(1)$, marked by a lateral expansion[9,10,18] and volume change[3,12,18,24] of the polymers, represents an increase in the degree of freedom. It follows that such

transformation from the crystal phase to a mesomorphic phase creates a dynamic disorder,[3,11,18] which would result in excimer deactivation, especially in the crystal phase. Thus, rapid skeletal and side-group motions are considered to be responsible for excimer dissociation back to the excited monomer at the higher temperatures examined.

The dynamics of chain motions can be probed by considering the kinetics of excimer formation and dissociation. As expected, the increase in I_D/I_M immediately below T_g does not follow the classical diffusion-controlled collision mechanisms as no Arrhenius behavior is found.[40] On the other hand, we observed an Arrhenius behavior of I_D/I_M as a function of temperature above $T(1)$ where thermal decomposition of excimer back to excited monomer in all three polymers occurs. This observation is similar to the classical dynamic equilibrium of PBPP and PBCP in dioxane solutions at high temperatures. The apparent excimer binding energies for the three polymers in the condensed phase are found to be 9.9 kJ mol^{-1}. Identical binding energies for PBPP and PBCP films are in contrast to binding energies of 14.0 and 15.5 kJ mol^{-1} found for PBPP and PBCP in dioxane, respectively.[36] However, these values are higher than the value of 9.5 kJ mol^{-1} reported for type I excimer binding energy in 2-methyltetrahydrofuran (MTHF).[41] Presumably, this thermal deactivation process in the solid state is indicative of an ensemble average of different EFS in both amorphous and crystalline phases and is more complicated than that found in type I EFS in MTHF or a combination of all types of EFS in dioxane.

Degree of Crystallinity and Crystal Morphology. Although regular chain packing in the crystal phase would presumably increase the density and therefore decrease the available free volume for side-group rotations, less chain entanglement and proper alignment of side groups may increase the EFS population and enhance energy migration. To obtain further information on the level of crystallinity in the polymers, it is tempting to quantify the extent of excimer emission from different phases by resolving the various peaks observed in Figures 4–6. In light of the existence of multiple EFS and the oversimplifying data treatment, we are reluctant to carry out such a procedure. However, a measure of excimer emission efficiency may still be possible by inspecting the overall level of I_D/I_M as a function of temperature. For instance, the higher I_D/I_M observed in PBCP compared to PBPP is intriguing considering that the cresoxy groups are presumably more sterically hindered and should therefore afford less excimer formation than observed in solution.[36] It is likely that the efficiency of excimer emission is different in the amorphous and crystalline phases of PBPP and PBCP, because of the different crystal structures in the two polymers. Previous studies on the crystallography of the two polymers have suggested that different crystal structures exist in PBPP and PBCP.[18] PBPP has a monoclinic structure in which the chain sites are closer together, and PBCP has an orthorhombic structure that exhibits two different distances between chain sites rather than one, as in the monoclinic structure.

In different crystal structures, the specific and regular spatial arrangement dictates the chain separation as well as orientation of side chains to a great extent. This restriction may impose constraints that would affect the excimer stability in terms of ring–ring overlap and separation, as well as the extent of energy migration. In paper 1,[36] excimer formation is more facile for PBPP than for PBCP in solution as the more bulky cresoxy groups would necessarily hinder the rotational sampling of EFS in the amorphous phase of PBCP. Hence, PBPP should exhibit a higher I_D/I_M than PBCP if excimer emission arises primarily from the amorphous phase. On the contrary, at temperatures above T_g, significantly higher I_D/I_M is observed in PBCP than in PBPP, suggesting that the probability of excimer emission is different for the differing crystal structures in PBPP and PBCP. The fact that I_{D2}/I_{D1} for PBCP greatly increases with annealing temperature leads us to believe that excimer emission is more facile in the crystal phase of PBCP than in the amorphous phase, whereas the insensitivity of I_{D2}/I_{D1} with annealing temperature in PBPP appears to indicate the contributions from the two phases are comparable in PBPP.

The higher I_D/I_M observed in PFPP at all temperatures indicates that segmental density of chromophores is not as important as segmental mobility and crystal structure for the excimer emission process. Perhaps the crystalline phase in PFPP exhibits more facile excimer emission than PBPP, as PFPP is expected to exhibit isomorphism in which orthorhombic and monoclinic structures coexist.[30,42] This is supported by the significant band widening of PFPP above T_g in comparison with PBPP and PBCP and is indicative of an even broader composition of EFS in PFPP. The appearance of a more well-defined excimer band in PFPP permits us to tentatively assign the excimer band at ca. 325 nm to emitting species in the orthorhombic crystal structure. At the present time, we are unable to delineate the more predominant type of EFS above T_g. However, based on results from excimer band position and bandwidth, as well as comparison between PBPP and PFPP as discussed above, it is likely that type III EFS in the crystalline and amorphous phases represent the most significant excimer sites in the solid state.

To explore further how the fluorescence emission depends upon different crystal morphologies, we focus our attention on the differing annealing behavior of PBPP and PBCP. An inspection of the fluorescence spectra for the annealed films clearly shows that the effect of annealing on the polymer morphology is rather different in PBPP and PBCP, presumably due to the different polymorphic forms found in PBPP and PBCP. Solution-grown crystals of PBPP appear to be best represented by an α-form of the monoclinic crystal structure, which remains stable when annealed below $T(1)$. Upon annealing above $T(1)$, however, the α-para crystal may be transformed into the more ordered crystal structure of the β-form. On the other hand, PBCP has been shown to undergo an irreversible phase transformation from a chain-folded α-orthorhombic texture of moderate crystallinity to an extended (3D) γ-orthorhombic morphology upon heating above $T(1)$.[17]

While the chain conformation in the crystalline phase consists of an ensemble average of different conformations, previous work on oriented films suggests that the distorted cis–trans backbone conformation is most energetically favorable and stacking of aryloxy groups is possible.[6] However, this stacking does not afford an effective overlap of aromatic rings, which is essential in excimer formation. Nevertheless, it is possible that a viable pathway for efficient energy migration exists given sufficient local short-range side-group motions. Without additional studies of the effect of energy migration, conclusions regarding the efficiency of photophysical pathways in different morphologies have to be deferred. Nevertheless, it appears that the excimer emission efficiency of α- and β-monoclinic structures in PBPP is similar, whereas significant improvement in excimer formation efficiency is found when the PBCP morphology changes from the α-form to

the γ-form of orthorhombic structure.

Another illustration of the effect of crystal morphology on spectral observations can be found in PFPP, where two well-resolved excimer peaks can be observed for a broad range of temperature. Although, to our best knowledge, no previous study on this copolymer has been reported, PFPP is expected to exhibit isomorphism and the phenoxy groups in PFPP may be found in either monoclinic or orthorhombic crystal structure. This in turn causes different local side-group separations and interactions in different crystal structures in the polymer. Given the number of possible EFS in crystal structures and in the amorphous phase, we tentatively assign the extra excimer peak for PFPP at about 325 nm to the orthorhombic structure dictated by the trifluoroethoxy groups. The band position of such peak is in excellent agreement with the low-energy excimer band (324 nm) obtained in annealed PBCP films.

Summary

Excimer fluorescence can be used to probe the dynamics of poly[(aryloxy)phosphazenes], which can be related to their structure and morphological changes. Previous photophysical studies on the dilute solutions provide a basis of comparison with the excimer emission process in the solid state and facilitate the elucidation of spectral emission properties in the bulk phase. Rather than attempting to unravel the complexity inherent in the intrinsic fluorescence spectra, where factors such as crystal structure and crystallinity only serve to exacerbate uncertainty and increase the probability of errors in data interpretation, we have chosen to report the values of I_D/I_M, excimer bandwidth, and excimer band maximum position of a composite excimer band. Clearly, this approach provides us with some success in identifying the origin of various transitions based on the side-group motions and in determining the resulting transition temperatures. The annealing experiments afford a qualitative means to assess the influence of crystallinity and crystal structure on excimer fluorescence, whereas a comparison of polymers with different side groups provides us with a better understanding of the effect of substituent size on EFS populations and perhaps energy migration in the amorphous and crystal phases.

To transform excimer fluorescence to a more quantitative technique, several requirements must be met. First, a corroboration of band assignments to different regions is warranted. Recently, alternate synthetic methods have been reported to prepare phosphazene polymers with different substituents.[43-45] It would provide an excellent opportunity to distinguish different EFS if the appropriate polymers are available. Future efforts should be devoted to generalize fluorescence changes that accompany changes in structural and preparative parameters. Second, transient experiments may be used to provide rate constants in the fluorescence process, perhaps in a simplified system where different excimer-forming site contributions can be distinguished. The difficulties involved in measuring the time-resolved fluorescence spectra of the phosphazene polymers include the low quantum yield at extreme temperatures (below T_g and near $T(1)$) as well as the relatively short lifetimes. More work remains to be done in this area.

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