Effects of Temperature and Alkyl Groups of Poly(Alkyl methacrylate)s on Inter- and Intramolecular Interactions of Excited Singlet States of Pyrenyl Guest Molecules

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Temperature-induced changes in the static and dynamic characteristics of the fluorescence from pyrene and N,N-dimethyl-3-(pyren-1-yl)propan-1-amine (PyC3NMe2) have been used to determine the locations and mobilities of these probes in the anisotropic environments provided by films of 5 poly(alkyl methacrylate) (PAMA) polymers in which alkyl is ethyl, butyl, isobutyl, cyclohexyl, and hexadecyl. Whereas emission from pyrene reports on the polarity of the guest sites and the ability of molecules to diffuse translationally between sites, emission from PyC3NMe2 yields information about the fluidity and the shape of the guest sites. Data have been obtained from 20 to >400 K, a range that spans the onsets of several relaxation processes in the hosts. Those data indicate that the pyrenyl groups reside near to ester functionalities in most of the PAMAs, although the distance from them (and the main chains) depends upon the bulkiness of the alkyl groups. Among the most important conclusions derived from this research is that the rates of segmental relaxation phenomena near the probe molecules—and not free volume, as was concluded previously from fluorescence measurements in polyethylene films—are the dominant contributors to the fluorescence changes. Of practical importance, changes in those rates have permitted the onset temperatures of many of the relaxation phenomena occurring in the vicinity of the probes to be located.

1. Introduction

Polymers contain "voids" as a result of packing constraints on their chains.¹ These spaces facilitate chain segmental motions and diffusion and, in some cases, aid in forming "templates" that affect the reactivity of a guest molecule.² In addition, the reactions or spectroscopic responses of environmentally sensitive guest molecules can be used to probe the microstructural features of polymer matrixes³ and, especially, the sites in which the guests reside.^{4–6} For example, fluorescence from pyrene (PyH) and its derivatives is sensitive to temperature, polarity, and the presence of various types of excited state quenchers,⁷ and the relaxations of polymer chains can have a marked influence on the luminescence of PyH molecules. Thus, the intensity ratios of the third most energetic and the most energetic vibronic bands in the fluorescence spectrum of PyH (I_3/I_1) and decay constants of its excited singlet state have been shown to depend upon the exact composition of ethylene-co-vinyl acetate copolymers as well as to identify olefinic segments as the loci for preferential attachment of the PyH molecules.8 In addition, the amount of void space surrounding a guest molecule during the course of its photoreactions in constraining polymer matrixes can lead to products (or intermediates) that are totally different from those formed in solution state reactions.⁹

Because the lifetimes of the "cages" in which guest reactions reside in isotropic solvents are very short (i.e., comparable to the times needed for the substrates to change to product structures), substantial cage-escape of substrate fragments and minimal spatial templating by the cage are expected.¹⁰ In polymer matrixes, the guest molecules template the conformations and orientations of the neighboring polymer chain seg-

ments that constitute their cages, but slow relaxation of these chains can impede translational, rotational, and conformational motions of guest molecules so that they occur on time scales that are longer than necessary for reactants to move to products.¹¹ In this regard, chain relaxation processes, especially in the glassy states of neat polymers, such as a poly(alkyl methacrylate) (PAMA), can be very slow and locally anisotropic.^{12,13} For example, PAMAs with long *n*-alkyl groups have nanosegregated regions enriched with either low polarity alkyl or higher polarity ester groups¹⁴ that provide potentially very different environments to guest molecules.

The rates of relaxation of polymer segments for rotation of the ester (-COOR) side groups (β -relaxation) and movements of the backbone chains (α -relaxation) in several PAMAs are available over wide temperature ranges.¹⁵ As the length of an alkyl side group (R) increases, neighboring backbone chains are pushed further apart, causing "internal plasticization" and decreasing the barriers to movement of the chains.¹⁵ Therefore, the activation energy of the α -relaxation process decreases with increasing alkyl chain length, whereas that of the β -relaxation decreases to a negligible extent:¹⁵ the activation energy for α -relaxation decreases from ~419 kJ mol⁻¹ for poly(methyl methacrylate) to 205 kJ mol⁻¹ for poly(*n*-propyl methacrylate); the corresponding values for β -relaxation in both polymers are ~88 kJ mol⁻¹.^{15,16}

Here, we investigate the dependence of the optical properties of two luminescent guest molecules, PyH and *N*,*N*-dimethyl-3-(pyren-1-yl)propan-1-amine (PyC3NMe2), on the length and size of alkyl side chains of five different PAMA hosts above and below their glass or melting transition temperatures. Both intermolecular excimer formation (i.e., static from ground-state aggregation or dynamic from translational diffusion) and intramolecular exciplex formation (i.e., from conformational changes) have been monitored. From correlations of the static

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 TABLE 1: Phase Transition Temperatures, Densities, And

 Average Molecular Weights of the PAMAs Employed in

 This Study

polymer	phase transition temperature ^a (K)	density ^{b,c} (g cc ⁻¹)	${ m mol\ wt}^c$ $(M_{ m w})$
PCHMA PEMA PIBMA PBMA	368 342 322 290	1.10 1.11 1.05 1.07	65 000 350 000 70 000 180 000
PHDMA	281	0.87	200 000

^{*a*} Glass transition temperatures (T_g) of the PAMA, except PHDMA, for which the melting temperature of crystallized side chains (T_m) is given (vide infra), from DSC measurements. ^{*b*} At 298 K. ^{*c*} Data from suppliers.

and dynamic fluorescence properties of the two probe molecules, we have discerned how the structures of the alkyl chains and phases of PAMA influence intimate solutematrix interactions. Specifically, we have examined translational and microdiffusional motions of PyH molecules and conformational preferences and labilities of PyC3NMe2 molecules within the PAMA matrixes using steady-state and time-resolved fluorescence. We find that hole-free volumes (which are related to the sizes of the cavities in which the probe molecules reside) of the PAMAs are much less important than the rates of relaxation of their various chain segments (which are related to the rates of size and shape changes of the guest cavities¹⁷) in mediating the fluorescence properties of the probe molecules. This conclusion was unexpected because changes in the fluorescence of different probe molecules indicate that hole-free volumes are the more important factor in polyethylene matrixes.^{4,18}



2. Experimental Section

2.1. Reagents/Materials. Poly(butyl methacrylate) (PBMA), poly(hexadecyl methacrylate) (PHDMA), poly(ethyl methacrylate) (PEMA), and poly(cyclohexyl methacrylate) (PCHMA) were purchased from Scientific Polymer Products, Inc., and poly(isobutyl methacrylate) (PIBMA) was from Aldrich. They were purified as described in the Supporting Information. Some characteristics of these polymers are included in Table 1. PyH

(Aldrich, 99%) was recrystallized twice from ethanol (mp 425-426 K (lit.^{19,20} mp 425-426 K)).

2.2. Syntheses. PyC3NMe2 was synthesized as shown in Scheme 1.21 Details of experimental procedures and characterizations are described in the Supporting Information. PyC3NMe2 was stored as its hydrochloride salt, N.N-dimethyl-3-(pyren-1yl)propyl-1-ammonium chloride hydrate: mp 456-472 K (dec). ¹H NMR (CDCl₃, 400 MHz), δ 2.46–2.50 (m, 2H), 2.71–2.72 (m, 6H), 3.02-3.05 (m, 2H), 3.50-3.53 (t, 2H, J = 7 Hz), 7.86-7.88 (d, 1H, J = 7.6), 8.0-8.19 (m, 8H). Elemental analysis: calcd for C₂₁H₂₂ClN•H₂O: C, 73.78%; H, 7.08%; N, 4.10%. Found: C, 74.12%; H, 7.29%; N, 4.10%. In a typical procedure to regenerate PyC3NMe2, N,N-dimethyl-3-(pyren-1-yl)propan-1-ammonium chloride hydrate (2 mg) was stirred with 10 mL of diethyl ether and 5 mL of 30% aqueous NaOH for 5 min under a nitrogen atmosphere. The mixture was extracted with diethyl ether (3 \times 20 mL), and the combined extracts were washed twice with 20 mL of water and dried over anhydrous Na₂SO₄. The volatile liquid was concentrated under reduced pressure in a rotary evaporator to obtain PyC3NMe2 (~99% pure by GC analysis) as a viscous liquid. ¹H NMR (CDCl₃, 400 MHz): δ 1.99–2.07 (m, 2H), 2.27 (s, 6H), 2.42–2.45 (t, 2H, *J* = 7.2 Hz), 3.36–3.40 (t, 2H, *J* = 7.8 Hz), 7.87-7.89 (d, 1H, J = 8), 7.96-8.17 (m, 7H), 8.29-8.31 (d, 1H, J = 9.6). MS-EI: m/z observed, 288; calculated, 287.4 (M⁺, $C_{21}H_{21}N$).

2.3. Instrumentation. UV/vis absorption spectra were recorded on a Varian UV-visible (Cary 300 Bio) spectrophotometer. Steady-state excitation and emission spectra were obtained on a Photon Technology International Fluorometer (SYS 2459) with a Quantumwest temperature controller and an Omega temperature probe. The probe was placed in decane liquid that filled the cuvette in which the sample container, a 7 mm (width) \times 4 mm (length) \times (0.4 or 3 mm (i.d.)) flattened Pyrex capillary (Vitro Dynamics, Inc.) was placed. Spectra were recorded front-face at an angle of $\sim 45^{\circ}$ with respect to the incident beam, and the emission was collected at 90° with respect to the excitation source. Fluorescence measurements of PyH in the PAMAs were carried out at 20–420 K at intervals of 10° using a SPEX 0.5 m spectrograph. Excitation was with the 325 nm line of a Kimmon model IK helium-cadmium laser. Fluorescence rise and decay histograms were obtained with an Edinburgh Analytical Instruments time-correlated single photon counter (model FL900) using H₂ as the lamp gas. An "instrument response function" was determined using Ludox as scatterer. Data were collected in 1023 channels. Deconvolution was performed by nonlinear least-squares routines that minimize χ^2 using software supplied by Edinburgh. Fits were considered acceptable when $\chi^2 \leq 1.3$, and residual plots exhibited no systematic deviations from zero. Differential scanning calorimetric measurements were carried out on a TA Instruments differential scanning calorimeter (Q 200) under a nitrogen atmosphere with a heating/cooling rate of 10 °C/min. Glass



transition temperatures were determined using Universal Analysis 2000 software supplied by TA Instruments from the onset of intersection of the first and second tangents of the baseline displacements in thermograms.

2.4. Preparation of Doped Films. Doped films, 0.2–0.8 mm thick, of all PAMAs except PHDMA were prepared by dissolving PyH or PyC3NMe2 and a polymer in dichloromethane or chloroform and pouring the solution onto a Teflon plate. The film was dried by evaporation at room temperature, and the surfaces were washed with methanol. Doped PBMA, PIBMA, PCHMA, and PEMA films were heated to their glass transition temperatures and cut to the desired sizes.

Doped films of PHDMA were prepared by placing dichloromethane solutions of it and PyH or PyC3NMe2 into flattened Pyrex cuvettes (~0.4 mm thickness). The solvent was evaporated by warming the solutions on a water bath (~345 K), with a drying tube filled with anhydrous CaSO₄ connected to the cuvette and then in a desiccator at ~0.2 Torr for 6–12 h (dynamic vacuum) and 12–24 h (static vacuum).

Concentrations of dopant molecules in the solvent-free films $(\sim 10^{-4} \text{ mol/(kg of polymer}))$ were calculated from absorption spectra using Beer's law and film thicknesses that were averages of at least five different positions.²² The films were flame-sealed in flattened glass capillaries after being degassed at least 5 times by freeze-pump-thaw cycles at <10⁻⁵ Torr in a mercury-free vacuum line.

3. Results

3.1. Melting or Glass Transitions in PAMAs. Although main chain tacticity and molecular weight influence the nature and temperature of the glass or melting transitions in PAMAs, the type of alkyl group attached to the carboxy moieties is the most important factor when the average main chain lengths are in the range of the polymers described in Table 1.²³ Increasing the length of alkyl side chains decreases the glass transition temperatures of PAMAs.24,25 For example, when the alkyl chain length increased from ethyl (PEMA) to butyl (PBMA), the glass transition temperature decreased by 52°. On the other hand, replacing a linear *n*-alkyl side chain by a branched isomeric one is known to increase the glass transition temperature:¹⁵ the glass transition of PIBMA is 32° higher than that of PBMA, and the glass transition temperature of PCHMA, 368 K, is much higher than those observed for the *n*-alkyl derivatives. When the *n*-alkyl side chain is ≥ 12 carbon atoms in length, the PAMAs form crystallized regions that undergo a first-order melting transitions:²³ in PHDMA, $T_{\rm m} = 281$ K, and the crystalline hexadecyl chains form microdomains that separate the noncrystalline main chains.¹⁵

3.2. PyH-Doped PAMAs. *3.2.1.* Absorption and Emission Studies of Doped Polymers. Films of the PAMAs are transparent above 300 nm so that the structured $\pi - \pi^*$ absorption bands from PyH and PyC3NMe2 at 300–350 nm and fluorescence at 360–450 nm (or to >450 nm for excimers or exciplexes) were clearly discernible (Figure 1). The excitation spectra were similar in shape and position to the corresponding absorption spectra but were offset or broadened slightly in some cases. These differences may result from the nonuniformity of sites in which the guest molecules reside or to slight differences between the electronic characteristics of isolated and aggregated pyrenyl groups.³

3.2.2. I_3/I_1 Ratios and Changes in Fluorescence Intensities as a Function of Temperature. As mentioned, PAMAs consist of more polar ester groups and less polar alkyl groups that tend to aggregate into nanosegregated spaces. Therefore, guest



Figure 1. (A) Absorption (solid line) and excitation (λ_{em} 400 nm, dashed line) spectra and (B) emission (λ_{ex} 340 nm) spectra of PyH in PHDMA (9 × 10⁻⁵ mol/(kg PHDMA)) at 293 K.



Figure 2. I_3/I_1 ratios from ~10⁻⁴ mol PyH/(kg PAMA) (λ_{ex} 325 nm) recorded from low to high temperatures: PEMA (\bigtriangledown), PBMA (\square), PHDMA (\triangle), PIBMA (\bigstar), and PCHMA (\bigcirc). Arrows refer to melting or glass transition temperatures measured by differential scanning calorimetry.

molecules may experience more or less polar environments, depending upon their locations within the polymer matrixes. Preferential confinement of guest molecules to a specific type of environment can be expected in these polymers, especially in their glassy states. Regardless, guest molecules are excluded from the nanocrystalline regions of hexadecyl chains in PHDMA^{2,26} so that PyH and PyC3NMe2 reside in regions of higher polarity, on average, below $T_{\rm m}$ than above it. Movement of guest molecules between and within sites is facilitated in films of the PAMAs above their T_g 's as a result of more rapid relaxation processes. The same is true for PHDMA above its $T_{\rm m}$ because of increased rates of polymer relaxation and, additionally, the ability of the guests to access the regions where the hexadecyl chains are melted. Thus, steady-state fluorescence measurements and I_3/I_1 intensity ratios are indicative of the ensemble averages of sites in which guest molecules reside in the PAMAs.

The 0–0 electronic transition associated with the I_1 band from PyH is more strongly coupled than the I_2 or I_3 band to vibronic aspects of the medium;²⁷ the I_1 band is the most sensitive, and I_3 is the least sensitive to solvent polarity. For that reason, only I_3/I_1 ratios in the PAMA matrixes are discussed in detail here. Both temperature and solvent polarity can affect I_3/I_1 ratios.^{7,28} However, the changes induced by temperature alone are smooth and continuous; abrupt excursions of I_3/I_1 values over small temperature increments indicate large changes in the probe environment and, thus, the onset or cessation of a relaxation process in the polymer film.

The I_3/I_1 ratios from PyH in the PAMAs did not change appreciably at temperatures below ~100 K (Figure 2). Similar effects were observed for I_2/I_1 ratios in PEMA, PBMA, and PCHMA; the intensities of the I_2 band from PyH in PHDMA, and PIBMA were too weak to allow precise I_2/I_1 ratios to be calculated (Figure S1 of Supporting Information). Above 100 K, I_3/I_1 increased slightly up to the glass transition (or melting)



Figure 3. Effect of temperature on (A) the emission spectra (λ_{ex} 325 nm) of $\sim 10^{-4}$ mol PyH/(kg PBMA): black line, 20 K; red line, 120 K; green line, 180 K; blue line, 210 K; cyan line, 250 K; magenta line, 280 K; and orange line, 420 K; and (B) the intensity of the 366 nm fluorescence band of $\sim 10^{-4}$ mol PyH/(kg PAMA): PHDMA, \triangle ; PBMA, \Box ; PIBMA, \bigstar ; PEMA, \bigtriangledown ; and PCHMA, \bigcirc . The inset in A shows the isoemissive point region within the rectangle. Arrows in B refer to bulk melting or glass transition temperatures from differential scanning calorimetry.

temperatures. For example, I_3/I_1 from 8×10^{-5} mol PyH/(kg PBMA) increased from 0.75 at 120 K to only 0.89 at 270 K (near the glass transition temperature, 290 K) but rose to 0.96 at 290 K and 1.82 at 420 K. The lack of an exact correspondence between the I_3/I_1 inflection temperature and T_g (or T_m) can be explained by how the two phenomena are measured: I_3/I_1 ratios are monitors of *local* environments where PyH molecules reside; glass or melting transitions are *bulk* properties of the polymers that are almost impervious to local disturbances caused by the very low PyH concentrations employed here.

Similar increases in I_3/I_1 were observed in the other glass forming PAMAs as temperature was increased (Figure 2). In heated films of PHDMA, a different behavior was observed: I_3/I_1 increased abruptly near 290 K and then *decreased* at a slightly higher temperature. We suspect that this excursion is related to the onset of relaxation processes in the PHDMA chains. The general trend of the I_3/I_1 ratios, to increase slightly below the T_g (or T_m) temperatures and then to increase rapidly above them, is indicative of an average environment that is more polar below the glass (or melting) transition temperature (i.e., PyH molecules reside closer to the ester groups). This conclusion is supported by observations in other media that I_3/I_1 ratios are less sensitive to temperature in low polarity environments than in more polar ones.²⁸

As with the I_3/I_1 ratios, the overall PyH fluorescence intensities in the PAMAs do not change with temperature in a regular fashion. Instead, small but perceptible slope changes are observed that, in many cases, can be associated with the onsets on heating (or cessations on cooling) of host relaxation processes. Although the overall intensities decrease with increasing temperature, a small band centered at 366 nm and to the blue of the 0-0 (I_1) emission band, first *increases* (above ~ 100 K in all of the PAMAs, except PHDMA, for which the break commences at lower temperature) and then decreases with increasing temperature (Figure 3); rotations of side chains (or γ -relaxations) are known to commence near 100 K (T_{γ} = $102-125 \text{ K}^{29}$). Thus, the increase in the 366 nm band intensity may be related to enhanced electron-phonon coupling,³ whereas the subsequent decrease is probably a consequence of enhanced competing matrix-related decay processes (i.e., main-chain mobility associated with α -relaxations that accompany transitions from the glassy to melted states;^{30,31} vide infra) becoming dominant. The observed decrease in the intensity of the 366 nm band from 40 to 80 K in PHDMA may be due to increased mobility of short segments of flexible alkyl side chains.

Hot bands in emission have been observed in a number of organic lumophores in which upper vibronic levels are populated or excited state energies are split by coupling with a host.^{32–34}

A 365 nm hot band from emission of PyH in polyethylenes (PEs) has been attributed to guest molecules located in the interfacial regions (i.e., between melted and crystalline domains).³ In PAMAs, the presence of an isoemissive point at 368 nm (or at 369 nm in PCHMA) for PyH indicates that the increased population of vibronically excited excited singlet states is at the expense of excited singlets in their zeroth vibronic level. The difference in maxima between the hot band and 0–0 band for PyH in the PAMAs, ~485 cm⁻¹ (0.06 eV), is similar to the energies of vibrations of methylene chains; thus, the intensity changes at 366 nm may be related to vibronic coupling between PyH singlet states and alkyl groups of the PAMA that constitute the cavity walls.³⁵

3.2.3. Monomeric and Excimeric PyH Emissions in PAMA Films. As expected, increasing the PyH concentration at one temperature increased the intensity of excimer emission (centered near 480 nm) relative to that of the monomeric emissions (Figure 4). Excimer emission was observed at much lower concentrations in both solid and melted states of PHDMA than in the other polymers. The excitation maxima of excimer and monomer are not affected by PyH concentration in PHDMA, although the spectra were broader at higher concentrations. (see Figure S2 of the Supporting Information). As mentioned, spectral differences observed in PHDMA at different PyH concentrations may result from inhomogeneities (i.e., different site types) in the polymer matrix.³

The independence of the shapes of the absorption and excitation spectra to PyH concentration below $\sim 10^{-3}$ mol/(kg PAMA) as well as to emission wavelength for the excitation spectra are suggestive of very little ground state aggregation and a dominance of dynamically formed excimers in PHDMA. Moreover, the peak-to-valley (P-V) ratios^{7b} for PyH excitation spectra at a concentration of 1.5×10^{-3} mol/(kg PHDMA) were similar when acquired at emission wavelengths of 480 (excimeric emission) and 380 nm (monomeric emission). At much lower concentrations ($<10^{-3}$ mol/(kg PHDMA)), the excitation spectra collected at emission wavelengths \geq 450 nm were too weak to make realistic P-V ratio comparisons. Consistent with the presence of ground state PyH aggregates in the other PAMAs,³⁶ the absorption and excitation spectra were red-shifted with respect to those in PHDMA. These results indicate that the presence of long alkyl chains in PHDMA, even below its $T_{\rm m}$, allow dynamic processes leading to excimers, whereas the shorter or branched chains in the other more rigid PAMAs decrease diffusion within the excited singlet lifetimes of the PyH molecules. Thus, most of the excimer-like emission emanates from excitation of ground state aggregates in glass forming PAMAs.



Figure 4. Intensity-normalized (at 376 nm) emission spectra at different concentrations of PyH in PAMA films at 293 K (λ_{ex} 340 nm): (A) 9 × 10⁻⁵ (-) and 1.5 × 10⁻³ (- -) mol/(kg PHDMA; (B) 10⁻⁴ (-), 9.6 × 10⁻³ (- -), and 0.215 (····) mol/(kg PBMA).



Figure 5. Emission spectra (λ_{ex} 340 nm) of PyH in PAMA films: (A) 1.5×10^{-3} mol/(kg PHDMA) (-, 263 K; - - -, 293 K; ..., 323 K; - - -, 343 K) and (B) 0.215 mol/(kg PBMA) (-, 263 K; - - -, 298 K; ..., 331 K; - - -, 341 K).

Reabsorption of the emitted light (and significant aggregation) at 0.215 mol PyH/(kg PBMA) is evidenced by a relative decrease in the intensity of the I_1 band (Figure 4B) and distortion of the emission spectrum. Therefore, no attempt has been made to analyze data from this sample quantitatively. However, additional analysis of these results, based upon dynamic measurements, will be presented later.

Above $T_{\rm m}$ in PHDMA films, the intensity of the red-shifted excimer emission was considerably reduced relative to the monomer emission (Figure 5A). This comportment suggests a decrease in intermolecular interactions among guest molecules at the higher temperatures or increased dissociation of the excimers.³⁷ In PBMA at temperatures both below and above the glass transition, no excimer emission was observed when PyH was $\sim 10^{-3}$ mol/(kg PBMA); at an exceedingly high PyH concentration, 0.215 mol/kg, excimeric emission was observed, and its intensity increased with increasing temperature (Figure 5B) as a result of ground state aggregation and the need for much less motion for a ¹PyH to encounter a ground state PyH molecule. In PBMA films at this very high PyH concentration, there was a relative increase in excimer fluorescence as the temperature was increased and an isoemissive point at 428 nm. The preference for monomer \rightarrow excimer emissions at higher temperatures is consistent with increased mobility or reorientations of the PBMA chains. Above the glass transition temperature, the mobility of chains may facilitate excimer formation by bringing PyH molecules into the appropriate proximity and orientation. Similar temperature-induced orientational changes have been reported for methyl 4-(1-pyrenyl)butanoate doped into polystyrene matrixes.¹²

3.3. PyC3NMe2 in PAMA Films. *3.3.1. Absorption and Static Emission Studies.* PyC3NMe2 is known to form intramolecular exciplexes whose emission intensity depends upon factors that include solvent polarity and temperature.^{38,39} In all of the PAMA films, the ratios of monomer to exciplex emission



Figure 6. Emission spectra (λ_{ex} 345 nm) of 10⁻⁴ mol PyC3NMe2/(kg PIBMA) at 293 K (--), 327 K (---), and 360 K (····).

intensities were much lower than those in isotropic solvents of similar polarity, such as ethyl acetate.⁴⁰ These lower ratios are attributed to the very high microviscosities in the films that inhibit the motions of the propylene spacer that are necessary to bring the 1-pyrenyl and dimethylamino groups into the correct exciplex orientation.^{20,41,42}

In PIBMA and PCHMA, the emission spectrum of PyC3NMe2 consisted of 1-pyrenyl peaks at 379, 399, and 420 nm, and a broad exciplex emission centered near 450 nm (Figures 6 and S3 of the Supporting Information). The intensities of the monomeric and exciplex emissions decreased and increased, respectively, as temperature was increased (Figure S4 of the Supporting Information). These changes were accompanied by an isoemissive point at 429 nm (Figure 6) and were reproducible when the temperature was increased or decreased (Figures S5 of the Supporting Information). In the PAMAs with the unbranched alkyl side chains, PHDMA, PBMA, and PEMA, the exciplex emission intensities were small and changed very little with increasing temperature (Figure S6 of the Supporting Information). We attribute these differences in the exciplex

TABLE 2: Decay Components (τ_i), Their Percentages (in parentheses), and Preexponentials (A_i) from Analyses of Histograms from $\sim 10^{-4}$ mol/(kg PAMA) Films at 298 K^a

lumophore	polymer	$\lambda_{\rm em}$, nm	τ_1 , ns	A_1	τ_2 , ns	A_2	χ^2
$PyH^{b,c}$	PEMA	380	310				1.2
	PCHMA	380	318				1.2
	PIBMA	380	329				1.1
	PBMA	380	333				1.2
	PHDMA	380	366				1.2
PyC3NMe2 ^{c,d,e}	PEMA	380	184 (93)	0.566	50(7)	0.158	1.2
		450	191 (84)	0.096	51 (8)	0.032	1.2
		450	184 (87)	0.102	36 (5)	0.031	1.3
	PBMA	380	208 (93)	0.350	77 (7)	0.070	1.3
		450	202 (89)	0.095	24 (7)	0.062	1.3
		450	208 (88)	0.091	30 (8)	0.060	1.3
	PHDMA	380	186 (92)	0.116	56 (6)	0.024	1.1
		450	166 (79)	0.023	33 (12)	0.018	1.1
		450	186 (73)	0.020	51 (17)	0.017	1.1
	PIBMA	380	200 (75)	0.210	115 (25)	0.122	1.1
		450	175 (61)	0.092	64 (34)	0.139	1.2
		450	200 (47)	0.063	85 (44)	0.140	1.2
	PCHMA	380	190 (80)	0.213	91 (20)	0.109	1.2
		450	182 (80)	0.096	56 (14)	0.054	1.2
		450	190 (75)	0.087	66 (18)	0.061	1.1

^{*a*} PHDMA and PBMA are in their melted states at this temperature, and the other PAMAs are in their glassy states. ^{*b*} $\lambda_{ex} = 340$ nm; percentage of one decay component was >98%; the second minor component is not included. ^{*c*} $A \le 1$ ns component (presumably from scattered excitation radiation) is not included. ^{*d*} $\lambda_{ex} = 345$ nm. ^{*e*} 450 nm decays were fitted by either allowing all components to change or keeping constant the τ_1 component at the 380 nm excitation value (shown in italics) while optimizing the total curve fit.

emission to conformational preferences of PyC3NMe2 and to variations in the rates of the side-chain relaxations in PAMAs (vide infra).

3.4. Dynamic Emission Studies. At 298 K, time-correlated single-photon counting histograms from films of $\sim 10^{-4}$ mol PyH/(kg PAMA) were monoexponential decays (>98%) with lifetimes of >300 ns (Table 2) whose magnitudes parallel the expected PAMA polarities: faster decays were observed in the higher polarity PEMA (310 ns) than in the lower polarity PHDMA (366 ns). At higher PyH concentrations ($\sim 0.2 \text{ mol}/$ (kg PAMA)) in all of the PAMAs except PHDMA, the lifetimes remained near 300 ns (Table S1 of the Supporting Information). In PHDMA, the decay constants were 155 and 366 ns in 1.5×10^{-3} and $\sim 10^{-4}$ mol PyH/kg, respectively (Table S2 and Figure S7 of the Supporting Information). These results are consistent with much more rapid diffusion of PyH in PHDMA (above $T_{\rm m}$) than in the other PAMAs (vide ante).

Films of $\sim 10^{-4}$ mol PyC3NMe2/(kg PAMA) yielded decay histograms that were biexponential, with the major component (>75%) having a 186–200 ns decay constant (Table 2). The shorter decay component may be from excitation of ground state molecules, which are in a conformation close to that necessary to form an exciplex.⁶ Because decay constants from histograms monitored at longer emission wavelengths did not possess a negative pre-exponential factor (Table 2), it is likely that intramolecular formation of exciplexes is occurring from partially folded conformers on a very rapid time scale (<1 ns) that is unresolvable with our instrumentation. Consistent with this hypothesis, the amount of the shorter decay is higher in the glassy states of the two polymers with the branched alkyl groups, PIBMA and PCHMA.

4. Kinetic and Spectral Analyses

4.1. Monomer Fluorescence. Changes in monomer fluorescence intensity at $\leq 10^{-4}$ mol PyH/(kg PAMA) (i.e., where no excimeric emission could be detected) were used to determine the activation energies for nonradiative processes. Under these conditions, the quantum yield for monomer fluorescence of PyH

 $(\Phi_{\rm M})$ is expressed by eq 1, where $k_{\rm M}$ is the rate constant for radiative decay and is independent of temperature within the range explored here,¹⁹ and $k_{\rm iM}$ is the rate constant for the sum of internal conversion and intersystem crossing. Because $\Phi_{\rm M}$ is directly proportional to the total intensity of monomer fluorescence ($I_{\rm M}$), the quantum yield and intensity ratios are equal at two different temperatures when the sample position and instrumental parameters are unchanged. Under these conditions, eq 2 applies; see Supporting Information for a derivation.

$$\Phi_{\rm M} = \frac{k_{\rm M}}{(k_{\rm M} + k_{\rm iM})} \tag{1}$$

$$\ln\left(\frac{I_0}{I_F} - 1\right) = \text{constant} - \frac{E_a}{RT}$$
(2)

In eq 2, I_0 and I_F are areas under the fluorescence curves at very low temperatures (where k_{iM} is constant) and at a higher temperature, respectively. In the present study, integrated fluorescence areas (from emission spectra of intensity versus wavenumber) are plotted as a function of temperature from 20 to 420 K; I_0 was estimated from the average area of fluorescence intensities over a range of temperatures from 20 K to a higher temperature at which the area remained almost constant. If, at least in part, changes in k_{iM} are a consequence of coupling between the vibronic modes of the PyH excited singlet state and relaxation modes of nearby polymer chains, the energy of activation (E_a) in eq 2 includes the contributions from relaxations of polymer chains near the lumophores.

4.2. Dynamic and Static Formation of PyH Excimers. Because the dissociation of [PyH + PyH] should be very slow in the PAMA polymer films, the florescence intensity ratios for excimer and monomer emissions, I_{480}/I_M , under photostationary state conditions are related to the rate constants in Scheme 2 by eq 3;⁴³ the second term on the right side of the equation needs to be included only when excitation of the ground state

SCHEME 2: Kinetic Steps for Formation of PyH Excimer, ¹Py_D, via Static and Dynamic Pathways^a



 a PyH + PyH is the ground state dimer, and " α " is the fraction of light absorbed by non-aggregated PyH molecules.



Figure 7. Arrhenius plots of the ratio of excimer to monomer fluorescence intensities of 1.5×10^{-3} mol PyH/(kg PHDMA)) (λ_{ex} 325 nm). Activation energies (E'_a) are calculated for temperature ranges below and above T_m (indicated by the vertical dashed line).

aggregates contributes to the emission intensity at 480 nm; see the Supporting Information for details.

$$\frac{I_{480}}{I_{\rm M}} \approx \frac{\alpha^2 k_{\rm DF} k_{\rm D} [\rm PyH]}{k_{\rm M} (k_{\rm DF} + k_{\rm iD} + k_{-\rm D} + k'_{-\rm D})} + \frac{\alpha (1 - \alpha) k_{\rm DF} k'_{\rm D} [{}^{1}\rm PyH + \rm PyH]}{\frac{\alpha (1 - \alpha) k_{\rm DF} k'_{\rm D} [{}^{1}\rm PyH + \rm PyH]}{k_{\rm M} (k_{\rm DF} + k_{\rm iD} + k_{-\rm D} + k'_{-\rm D}) [{}^{1}\rm PyH]}} \quad (3)$$

No evidence for ground state aggregation is observed in $\leq 10^{-4}$ mol PyH/(kg PAMA) films at all temperatures examined here. Thus, in these films, the second term on the right side of eq 3 can be neglected because all of the excimer formation is presumed to be dynamic (i.e., no [PyH + PyH] is present) and the activation energy of excimer formation (E'_a) can be obtained from the slope of an Arrhenius plot of I_{480}/I_M , provided radiative the decay constants (k_M and k_{DF}) are temperature-independent and k_{iD} and k_{-D} are smaller than k_{DF} .

In PBMA, PEMA, PIBMA, and PCHMA, a considerable amount of PyH ground state aggregation was indicated by an instantaneous component in excimer rise times (Table S1 of the Supporting Information) at higher PyH concentrations necessary to observe its emission. Thus, the simplified form of eq 3 can be applied only to PHDMA, in which dynamic excimer formation with a growing-in excimer component (Table S2 of the Supporting Information) is observed at a relatively low concentration, 1.5×10^{-3} mol PyH/(kg PHDMA). An Arrhenius plot of excimer—monomer emission in PHDMA is shown in Figure 7, along with the activation energies (E'_a) calculated in two different temperature regimes. The values suggest similar deactivation pathways of ¹PyH in both the solid and melted states of PHDMA.

4.3. Intramolecular Exciplex Formation from PyC3NMe2. Motions of the propylene chain of PyC3NMe2, especially those emanating from its two principal conformations, are known to





SCHEME 4:46



influence significantly the rates of intramolecular exciplex formation.^{38,45} Exciplex formation by PyC3NMe2 requires the lone-pair orbital on nitrogen to reside over and be approximately perpendicular to the π -orbitals of the pyrenyl group.¹⁹

For purposes of analysis, we assume that the two principal conformers of PyC3NMe2 (A and B in Scheme 3), present in mole fractions, f_A and f_B ,^{38,46} have similar extinction coefficients. The excited singlet state of A, ¹A, becomes the exciplex (¹E) after a shape change that involves two C–C bond rotations and overcoming a small energy barrier; to become ¹E, ¹B must undergo a larger shape change (that may or may not include formation of the ¹A conformation) unless inversion about nitrogen or rotation around the H₂C–N bond occurs very rapidly with respect to C–C rotations. The steps associated with interconversions among these conformers and the formation of their exciplex-like conformation (E) are shown in Scheme 4.

In low-viscosity liquid solutions, PyC3NMe2 exists mostly in its A conformer and interconverts with the B conformer on time scales of ${\sim}10~\text{ns.}^{38}$ In glassy and melted PAMA films, fluorescence decays of the locally excited pyrenyl singlet states of PyC3NMe2 are biexponential (Table 2), suggesting the presence of more than one kinetically indistinguishable family of PyC3NMe2 conformers. In addition, in the glassy states of the more rigid PIBMA-and especially in PCHMA films (and probably in the glassy and even melted states of the other polymers)-dissociation of the exciplex is expected to be very slow (i.e., k_{-A} or $k_{-B} \ll k_4$). Although, C–N rotation or nitrogen inversion in acyclic amines have similar energy barriers in solution (<30 kJ mol⁻¹);^{47–49} inversion (being less volume demanding) is more facile in polymer cavities.⁴⁸ On these bases, a mixture of A and B conformers appears to be present in the PAMA films. Thus, if $k_A = k_B = k$, quantum yields of monomer (Φ_M) and exciplex (Φ_E) emissions (or corresponding fluorescence intensities, $I_{\rm M}$ and $I_{\rm E}$) can be related to the rate constants in Scheme 4 by eq 4.38,46

$$\frac{\Phi_{\rm E}}{\Phi_{\rm M}} = \frac{k_{\rm E}k}{k_{\rm M}(k_{\rm E} + k_{iE})} \cong \frac{I_{\rm E}}{I_{\rm M}} \tag{4}$$

Furthermore, assuming the same temperature dependence for $k_{\rm E}$ and $k_{\rm M}$,^{38,44} the difference between the activation energies



Figure 8. Arrhenius plot of the ratio of exciplex ($I_{\rm E}$) to monomer ($I_{\rm M}$) fluorescence intensities for 1×10^{-4} mol PyC3NMe2/(kg PIBMA) ($\lambda_{\rm ex}$ = 345 nm). Activation energies ($E'_{\rm ac}$) are calculated for temperature ranges below and above $T_{\rm g}$ (indicated by the vertical dashed line).

 (E''_{a}) from exciplex formation (E''_{ae}) and the apparent activation energy contribution from radiative and nonradiative components of the exciplex (ΔE_e) can be obtained from Arrhenius plots using eq 4 (see the Supporting Information); E''_{ae} and ΔE_e are two temperature-dependent variables in eq 4.^{38,44} An Arrhenius plot of the exciplex-monomer fluorescence ratio for PyC3NMe2 in PIBMA is shown in Figure 8.

5. Discussion

For the fluorescence from any probe to report on changes in its host properties, it must be located in the proximity of where the changes are occurring, and it must interact with the host matrix, perturbing the emission in some way. In neat anisotropic polymers, such as the PAMAs investigated here, there may be more than one type of guest site, and changes may occur to the polymer matrix at locations that are far removed from the guest sites or at them. Thus, although it is not always possible to discern host transitions or relaxations from the emission of a probe molecule, it is sometimes possible to detect subtle changes in the host matrix that are very difficult to detect using bulk measurements. Like any other technique, fluorescence from guest molecules is useful only when its limitations are kept in mind.

The two probes used in the present study are designed to report on the size, shape, and nature of the cavity walls of the occupied guest sites and their changes with time: PyH can provide a measure of translational diffusion and rates of segmental chain motions in its local environment; conformational motions of PyC3NMe2 can sense the lability of the walls of the occupied sites and, therefore, the rates of segmental chain motions. In addition, the length and shape of the alkoxycarbonyl side groups in PAMAs are known to influence the structural and conformational order of the main chains,^{50,51} and our studies demonstrate that the nature and mobility of the side chains affect the fluorescence properties of the guest molecules. Furthermore, the temperature dependence of fluorescence of the pyrenyl probes suggests that the five PAMAs can be broadly classified into three categories: (1) those with linear, short side groups (PBMA and PEMA); (2) that with a long n-alkyl group (PHDMA); and (3) those with a more rigid, branched alkyl group (PCHMA and PIBMA).

The small side chains of PEMA and PBMA attenuate movements of segments of the main chains and increase the activation energies for α -relaxation.¹⁵ As a result, guest molecules are less mobile than in the comparable phases of the other PAMAs at comparable temperatures. In PHDMA, the long alkyl side chains increase the average distance between neighboring main chains, facilitate the formation of voids,¹⁵ and allow short-range translational mobility, even in the solid state. The side groups in the glassy states of PIBMA and PCHMA restrict guest mobility,⁵² but their cavities are sufficiently flexible to permit short-range conformational changes at higher temperatures (i.e., especially in the rubbery states).

Hole free-volume can be a useful parameter to understand the structural and dynamic properties guest molecules in some polymer matrixes,^{6,53} such as those afforded by PEs.⁴ In these polymers, alkyl chains are folded into crystalline regions with interfacial regions at their borders and more disordered chains in amorphous regions.⁵⁴ Guest molecules are excluded from entering the crystalline regions, but do divide themselves between the interfacial and amorphous regions.² The largest mean void volume in any of the PAMAs investigated here as determined by positron annihilation spectroscopy, 213 Å³, is smaller than the van der Waals volume of even a PyH molecule, 322 Å^{3,22,55} Thus, the polymer components that make up the cavity walls are expected to be in close contact with the pyrenyl guest molecules.

However, the results presented here indicate that microdiffusion and the fluorescence properties of guest molecules in the PAMAs depend much less on hole free volume than on chain segment relaxation rates, and those rates are very dependent upon the nature of the PAMA side chains. We find no direct correlation between the photophysical properties of our probes and void free volumes, although a strong correlation exists between optical properties of the guests and the microstructural features of the polymers. If the photophysical properties of the guest molecules were affected only by free volume changes, similar trends should have been observed in the five PAMAs because their void volumes always increase with increasing temperature. Our temperature-dependent positronium lifetime annihilation spectroscopy measurements⁵⁶ and those by others⁵⁷ show a gradual increase in free volume with increasing temperature in four of the 5 PAMAs; there is no discernible slope change in the free volumes in the temperature range from below to above $T_{\rm m}$ (or $T_{\rm g}$). Because they do not show such a slope discontinuity, although there is a noticeable correlation between polymer chain relaxation parameters and the fluorescence properties of both PyH and PyC3NMe2 (vide infra), we discount free volume changes as being the primary cause for the excursions in our fluorescence measurements. As will be shown, the large, abrupt changes in fluorescence properties, most pronounced in the temperature ranges encompassing $T_{\rm m}$ (or $T_{\rm g}$), appear to be caused by coupling with polymer chain-segment interactions (i.e., the structure type and mobility (or relaxation) of polymer chains in PAMAs, as well as temperature).

5.1. Information Derived from PyH Fluorescence. 5.1.1. From Monomer Intensities. At 20 K, the shapes of both the guest molecules and polymer chains are virtually "frozen", and the high fluorescence intensities can be attributed to very little vibronic coupling between the guest molecules and the polymer matrixes. Except in PIBMA, PEMA, and PCHMA, the fluorescence intensity of PyH is not significantly affected up to ~ 100 K in the PAMAs (Figures 9 and S8 of the Supporting Information). Consistent with the assumption that matrix—guest interactions are minimal in this range of temperatures, the relative intensity of the emissive hot band from PyH does not change up to ~ 100 K in three of the PAMAs; in PIBMA and PHDMA, initial decreases are observed, probably as a consequence of small movements of the alkyl groups (δ -relaxations).⁵⁸ For example, rotations of the ester methyl group in PEMA occur



Figure 9. Effect of temperature on the total area of fluorescence intensity (from 360 to 470 nm, but calculated from integration of fluorescence intensity vs wavenumber plots; $\lambda_{ex} = 325$ nm) and activation energy plots from $\sim 10^{-4}$ mol PyH/(kg PAMA): (A, B) PEMA, (C, D) PHDMA, and (E, F) PIBMA. Relaxation temperatures indicated in the graphs with arrows are based upon slope changes. Temperature regions used to calculate the activation energies are delineated with red lines. Dashed lines represent glass transition or melting temperatures. I_0 values are taken as the average intensities at 20–40 K in PEMA, 20–50 K in PHDMA, and 20–30 K in PIBMA. Slope changes in the integrated intensity curves were reproducible at least within the limits of the symbol sizes in films of the same type (see Figure S9 in Supporting Information); they are not due to instrumental artifacts or specific placement of the samples in the spectrometer.

at ~40 K,¹⁵ and rotations of isopropyl groups in PIBMA commence at ~60 K.⁵⁹ Care must be taken in assigning the origin of small excursions in fluorescence intensities, especially at lower temperatures. For example, the small (but reproducible) perturbations in the fluorescence intensity of PyH near 40 K in PEMA (Figure 9A) may be a result of rotations of the methyl group or to a heretofore unidentified relaxation process. In either case, our techniques are incapable of identifying its origin.

Substantial decreases in the fluorescence intensities of PyH occur in the PAMAs above ~100 K as a result of increased guest-matrix interactions, attributed to the onset of polymer chain relaxations that can be identified as excursions in the slopes of intensity-temperature plots. For PEMA, two lower-onset temperatures are noted: the one at 100 K is associated with small rotations of the lateral segments, and the one at 150 K is attributed to rotations of the ester groups.¹⁵ The 150 K excursion agrees with the literature value for a γ -relaxation (T_{γ}) .^{29,60} For the other acrylates with longer and larger lateral groups, these processes are observed at 130 K for PHDMA, 140 K for PIBMA, 150 K for PBMA, and 160 K for PCHMA.^{29,58,60} The small changes in the fluorescence intensities of PyH in PAMAs at the onsets of γ -relaxations are not

surprising, given the large differences between the rates of γ -relaxations and vibronic modes associated with pyrenyl excited singlets.

As mentioned, the rates of radiationless decay and, therefore, the fluorescence quantum yield and intensity of PyH molecules can change when fundamental vibrations and harmonics of the excited singlet state are coupled with vibrational modes of the PAMAs.⁶¹ PyH in its B_{1u} electronic state has vibrations in the range 498–3102 cm⁻¹,³ and vibrational modes of chain segments of PAMAs are in the range ~700–3000 cm⁻¹.^{35,62} In this regard, the temperature dependence of IR spectra of polyethylenes has shown that low-energy vibrations (<2700 cm⁻¹) are less populated at low temperatures.³ Similarly, the absence of energy-matched "electron–phonon pairs" may be responsible for inefficient quenching of PyH excited singlet states at the onset of γ -relaxations in PAMAs.

However, strong coupling between pyrenyl excited singlets and surrounding polymer chains at higher temperatures is evidenced by larger decreases in the fluorescence intensity at the onsets of β - and α -relaxations. Obviously, chain mobility and translational diffusion of guest molecules increase with increasing temperature and become significantly larger above

TABLE 3:	Temperature	Ranges of	Increasing	Hot-Band (36	66 nm) Intens	sity ($\Delta T_{\rm hot \ band}$	K) and	$T_{\rm g}$ (and $T_{\rm g}$	m) Values from
Spectra Red	corded from L	low to High	Temperat	ures on ${\sim}10^-$	⁴ mol PyH/(k	g PAMA) Fili	ns ^a	-	

		γ ($E_{\rm a}$)		β (E _a)		α (E _a)		
polymer	$\Delta T_{\mathrm{hot} \ \mathrm{band}}{}^{b}$	present work	lit.	present work	lit.	present work	lit.	$T_{\rm g(DSC)}$
PEMA	120-300	150^{c} 159^{d} (2.9)	$118 - 141^{29,60}$ $(2-6)^{29,60}$	260^{c} 269^{d} (11.7)	179-225 $(12-25)^{29}$	330^{c} 322^{d} (27.3)	294-305 $(45-77)^{29}$	342
PBMA	120-282	150 ^c	$102 - 125^{29}$	240 ^c	152-208 $(15-32)^{29}$	$\frac{290^c}{280^d}$	245-275 $(62-67)^{29}$	290
PHDMA	100-281	(3.6) 130^{c}	(4-7)	(6.4) 220 ^c 215 ^d		(30.8) 280^{c}		281 ^e
РСНМА	120-310	(1.8) 160°		(8.7) 260 ^c 256 ^d	$\sim 200 - 300^{60}$	(17.8) 330^{c} 324^{d}		368
PIBMA	110-260	(5.0) 140 ^c	$\sim 150 - 200^{60}$	(12.1) 210-240 ^c 233 ^d		(30.1) 330^{c} 322^{d}		322
		(2.6)		(10.5)		(19.7)		

^{*a*} The onset temperatures of the relaxation temperatures and activation energies (E_a (kJ mol⁻¹) in parentheses) within the temperature regions specified in Figure 9 are included with available literature values. ^{*b*} Intensities were nearly constant below the lower temperature and decreased above the higher temperature in each range. ^{*c*} From plots of integrated fluorescence areas versus temperature. ^{*d*} From Arrhenius plots. ^{*e*} T_m .

the glass transition temperatures. Closer to the glass transition (i.e., α -relaxation) or melting temperatures, the significant increases in main chain motions^{15,30,31} lead to large decreases in the fluorescence intensities.

Both β - and α -relaxations involve movements of larger chain segments than those of the γ -relaxations,⁵⁸ and in some cases, they are not well resolved in our fluorescence plots.⁶³ In general, β -relaxtions (involving the side groups) and α -relaxations (involving the main chain) in acrylates are strongly coupled processes.⁵² Consequently, the high temperature part of the β -relaxation dominated temperature range can be strongly overlapped by the lower temperature part of the α -relaxation temperature range.⁶⁴ This indicates that motions of smaller chain segments are weakly coupled to the singlet excited states of pyrenyl in acrylates. Thus, the small amplitude motions induce less nonradiative deactivation than the motions of larger segments when the pyrenyl groups are equidistant from both.

Above the glass (melting) transitions, the emission intensities decreased monoexponentially with temperature, as expected for a lumophore in a liquid-like medium. Therefore, the temperature of the glass transition in the proximity of the pyrenyl groups was determined spectroscopically by the onset of the exponential decrease of the fluorescence intensity. For example, the β -relaxation of PEMA has a well-defined onset temperature at T_{β} = 260 K according to measurements of the integrated fluorescence area (Figure 9). The area under the fluorescence curve decreases faster above T_{β} , and only a smooth change of slope can be observed at the α -relaxation, estimated from the beginning of exponential decay to be at 330 K; the bulk glass transition temperature, determined by DSC, is (as expected) at a slightly higher temperature, 342 K. The difference between these T_{β} and T_{α} values and those reported in the literature, 294-305 K,^{29,60} are consistent with local perturbations caused by the PyH probes (Table 2).

With the exception of PCHMA, for which T_{α} by fluorescence was 320 K and $T_g = 368$ K, T_{α} from spectroscopic measurements and glass transition temperatures from DSC thermograms are similar. For PCHMA, the difficulty to define the onsets of the β - and α -relaxations using fluorescence may result from the bulkier cyclohexyl side groups excluding PyH molecules from the immediate vicinity of the main chains. These results with the other PAMAs indicate that a significant fraction of the PyH molecules reside in sites that are near the polymer main chains.

To the extent that the activation energies (E_a in eq 2) determined from the Arrhenius plots of PyH in the PAMAs (Figure 9) are affected by quenching induced by coupling with chain relaxations, they should correlate with the energies required for the latter. However, they are not expected to be the same magnitude because more than one process can influence coupling of PyH singlet modes within one temperature range, and a fraction of the PyH molecules may be in sites far from where the potentially strongest coupling might occur. Apart from changes in chain mobility, electronic properties of the medium, such as its dielectric and index of refraction,^{26,65} are also affected by temperature and, therefore, will influence the dynamics of the ¹PyH states, but they are expected to change smoothly with temperature.

For example, the E_a obtained from the fluorescence intensity measurements of a film of $\sim 10^{-4}$ mol PyH/(kg PEMA) is ~ 0.6 kJ mol⁻¹ for the temperature range 110–140 K. Only γ -relaxations are known to operate for PEMA in this temperature region.¹⁵ Fluorescence intensity changes were larger at higher temperatures, and E_a values increased to 2.9 kJ mol⁻¹ for the PyH-doped PEMA in the range 160–260 K. The E_a values from PyH fluorescence in PBMA, PIBMA, and PHDMA in their γ -relaxation regions are also very low, $\leq 5 \text{ kJ mol}^{-1}$ (Table 3), and the values for PEMA and PBMA are lower than those determined from measurements with smaller fluorophores, such as xanthone and benzophenone,²⁹ probably as a result of the less effective interactions between the segmental motions of the polymer chains and the PyH molecules in the PAMA cavities. E_a values of PyH fluorescence in PEMA in the 270-330 K range, associated with β -relaxations,^{29,60} and above 340 K, from α - relaxations, are 11.7 and 27.3 kJ mol⁻¹, respectively (Figure 9), and are larger than the E_a from the slope in the γ -relaxation region. However, they, too, are much lower than the activation energies obtained for neat PEMA from bulk dielectric or NMR measurements,^{15,66} although the trend toward increasing activation energies in the higher temperature ranges is consistent with the changes in the activation energies for PAMA relaxations from NMR studies.66

Another probe of the local environment is the temperature dependence of the I_3/I_1 fluorescence band ratios of PyH molecules. The effects of temperature on I_3/I_1 and on the total fluorescence intensities of PyH in PAMAs follow similar trends: I_3/I_1 ratios increased slightly above T_{γ} and more so above T_{β} and T_{α} . For example, the I_3/I_1 ratio in $\sim 10^{-4}$ mol PyH/(kg PEMA) is ~ 0.7 at T_{γ} , increased slightly to ~ 0.9 at T_{α} , and increased more above T_{α} (to 2.1 at 390 K; Figure 2). The temperature dependence of the PyH I_3/I_1 ratios in the PAMAs and their similarity to the I_3/I_1 ratios at 277 K in butyl acetate²⁸ (~ 0.8 and ~ 1 in the PAMAs) suggest that the average local environment experienced by the PyH molecules in the PAMAs is near the ester groups and, therefore, near the main polymer chains.

It is known that the interaction energies of carbonyl groups in acrylates and polycyclic aromatic hydrocarbons are similar to those of $\pi - \pi$ interactions between aromatic groups:^{67,68} the calculated binding energy for formaldehyde-benzene and benzene-benzene (plane-to-edge) interactions are 1.86 and 1.78 kcal mol⁻¹, respectively.⁶⁹ Similar interaction energies are expected in PAMAs if PyH molecules are near the methacrylate carbonyl groups. Although the magnitude of similar interaction energies of carbonyl groups with excited singlet states of aromatic molecules are unknown, it is reasonable to assume that they will be stronger in the more-polarizable excited singlet states than in the ground state. If the interactions are spatially specific within the PAMAs, any change in the orientation or relaxations of the side chains would affect ¹PyH-carbonyl interactions (and thus, the fluorescence properties). In the glassy (or solid) states of the PAMAs, these interactions would have a significant impact on translational diffusion of PyH molecules.

The observed temperature dependence of the fluorescence intensity and I_3/I_1 ratio may be related strongly to variations of these matrix—guest interactions, as mediated by changes in chain relaxation types and rates. This appears to be the case for the intensity fluctuations of the hot band at 366 nm, where its increased intensity within the β - and γ -relaxation regions can be explained by increasing electron—phonon coupling. At temperatures close to the glass transition or melting temperatures (α -relaxations), the observed decreases in the hot-band intensity are consistent with diminished carbonyl—aromatic interactions.^{30,31}

5.1.2. From Excimer Fluorescence Data. The dynamics of excimer formation or decay can be used to probe microdiffusion of PyH in the PAMAs. Because the local viscosity in the PAMAs is very high (and translational diffusional rates are low), dynamic excimer formation can take place only over short distances. When low concentrations and rigid cavity walls in PAMAs keep the pyrenyl moieties isolated from one another, no dynamic or static excimer emission occurs. In this work, static excimer emission was not used to probe chain dynamics because it pertains to PyH solubility rather than its diffusion in the PAMAs. Only in PHDMA could significant dynamic excimer formation be confirmed by TCSPC experiments: there was a protracted rise component to the histograms monitored at the excimer emission wavelengths (Figure S7 of the Supporting Information) and the ratio of pre-exponentials for the decay constants was -1 (Table S2 of the Supporting Information).

Below T_{α} , PyH molecules are excluded from regions in PHDMA where alkyl side-chains are crystalline. Thus, the *effective* PyH concentrations are higher than those calculated from the total polymer volume, and the (statistically) enhanced proximity of PyH molecules in the amorphous parts facilitates dynamic excimer formation during the ¹PyH lifetimes. When

the microcrystallites of PHDMA melt, the volume that the PyH molecules can occupy expands (increasing the average separation between PyH molecules), but the microviscosity decreases, as well. The observed decreases in excimer fluorescence intensity above the melting point in PHDMA indicate that the "dilution effect" is more important than the increased rates of diffusion. Even for concentrations somewhat higher than the $\sim 10^{-3}$ mol PyH/(kg PAMA) employed for PHDMA, no static or dynamic excimer emission was detected in the glassy or rubbery states of the other PAMAs. Thus, we conclude that the PyH molecules are better dispersed in these matrixes than in PHDMA and that their local viscosities are significantly higher. Only at much higher PyH concentrations could excimer emissions be detected (Table S1 of the Supporting Information), and the lack of a negative pre-exponential (or its appearance only at elevated temperatures) in analyses of our TCSPC histograms for PyH fluorescence leads us to conclude that these excimers are formed predominantly by excitation of ground state aggregates.

The activation energy for dynamic excimer formation (E'_{a} , Scheme 2) in 1.5 × 10⁻³ mol PyH/(kg PHDMA) increased slightly from 10 kJ mol⁻¹ in the temperature region below T_{α} to 11 kJ mol⁻¹ above it (Figure 7). These values are close to those found in low-viscosity solvents (e.g., PyH in ethyl acetate⁴³). They support our contentions that the melted polymer chains in PHDMA are very mobile and that the average distance between PyH molecules below T_{α} is smaller than would be expected in a normal "solution".

5.2. Information Derived from PyC3NMe2. PyC3NMe2 is a probe of the "stiffness" of the cavity walls in the PAMAs. Its dimethyl amino group permits intramolecular exciplex formation if the appropriate conformation can be achieved during the excited singlet lifetime of the pyrenyl moiety. As mentioned in the Results section, the initial conformations of the PyC3NMe2 molecules determine whether intramolecular exciplex formation is static and the ease of its formation if it is dynamic. In an attractive hypothesis, the stiffer chains in PIBMA and PCHMA (based on the activation energies for α -relaxations in the glassy state: 188 kJ mol⁻¹ for PIBMA and 222 kJ mol⁻¹ for PCHMA¹⁵) may force the amino donor group of PyC3NMe2 to reside closer to the pyrenyl group, on average (and, thereby, make easier dynamic exciplex formation), than in the other PAMAs. Increasing temperature would accelerate exciplex formation further by softening the cavity walls.

NMR studies have also shown that side group mobility depends upon the nature of alkyl chain and temperature in PAMAs.^{52,70} For example, the rates of β -relaxations that involve 180° flips of the ester groups remain almost constant in poly(methyl methacrylate) from room temperature to 370 K⁶³ but increase with increasing temperature in PEMA, PIBMA, and PCHMA.52,70 Combining these NMR results with the photophysical data reported here, we believe that side group rotations modify the cavity walls and, thus, the conformations of the PyC3NMe2 molecules. Thus, in the less rigid PAMAs, the PyC3NMe2 molecules may be able to adopt less "constrained" conformations that are less prone to fold into the exciplex geometry. This hypothesis is consistent with the temperature dependence of PyH fluorescence in the PAMAs, in which a strong correlation between side-chain mobility and guest fluorescence intensity was observed. The temperatureinduced conformational changes are evident in the larger relative amounts of exciplex emission from PyC3NMe2 in the glassy and rubbery states of PIBMA than in PHDMA, PEMA, or PBMA. The lower activation energy for exciplex formation (E''_a) , eq 4) in glassy PIBMA, 13.4 kJ mol⁻¹, than in its rubbery state, 16.9 kJ mol⁻¹, also supports our contention that the matrixes of PHDMA, PEMA, or PBMA favor conformations of PyC3NMe2 that are less conducive to exciplex formation and attenuate motions from those conformations to the exciplex geometry.

6. Conclusions

We conclude that polymer chain relaxations within five poly(alkyl methacrylate) host polymers are primarily responsible for changes observed in the luminescent properties of two fluorescence probes, PyH and PyC3NMe2. This finding is contrary to what was concluded from studies of luminescence from similar fluorophores in polyethylene matrixes,^{6,71} where hole-free volume changes were the primary controlling factor.

Furthermore, the nature and relaxation rates of the side chains of the PAMAs modulate the photophysical properties of the guest molecules. Subtle (but reproducible) changes in plots of fluorescence intensity versus temperature, attributed to strong coupling between excited guest molecules and relaxations of nearby chain segments, have allowed us to identify the onset temperatures of some of the chain relaxation processes in the PAMAs. The vibronic modes of the fluorescence from PyH and the dynamic properties of the fluorescence from both probes indicate that they prefer to reside near the polar ester side groups (i.e., near the main polymer chains) in the PAMAs when steric considerations permit.

The dynamic PyH excimer formation observed in the solid and melted states of PHDMA suggests that its cavity walls are "soft", permitting some translational diffusion of PyH molecules on time scales compared to the excited singlet lifetimes. The more rigid polymer side chains in the other four PAMAs restrict translational diffusion and dynamic excimer formation much more. Intramolecular exciplex emission from PyC3NMe2 indicates that the branched side chains of PIBMA and PCHMA afford guest sites that either impose conformations on PyC3NMe2 molecules that either are close to the exciplex geometry or permit rapid conformational changes leading to such conformations. The more flexible side chains of the other three PAMAs appear to support more extended conformations of PyC3NMe2 or slow attainment of the exciplex geometry from them.

Future studies in the PAMAs are planned to investigate this hypothesis further by monitoring the temperature and phase dependence of the fluorescence of probes structurally similar to PyC3NMe2, but with one of the amino methyl groups replaced by a longer alkyl chain. In addition, we are exploring in the same PAMAs whether selected photochemical reactions respond primarily to relaxation of the polymer chains (as was found for the photophysical processes investigated here) or to free volume within the reaction cavities.

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Supporting Information Available: Details of derivations of equations, material sources, synthetic procedures of PyC3NMe2 and characterizations, purification methods of PAMAs and instrumentation details. Additional fluorescence spectra of PyH and PyC3NMe2, lifetime data of PyH in PAMAs, and integrated florescence intensities versus temperature plots from duplicate

films are also provided. This material is available free of charge via the Internet at http://pubs.acs.org.

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