Effects of temperature and CO₂ pressure on the emission of N,N'-dialkylated perylene diimides in poly(alkyl methacrylate) films. Are guest-host alkyl group interactions important?

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MS received 29 July 2015; revised 20 October 2015; accepted 14 November 2015

Abstract. Static and dynamic fluorescence measurements have been made on four *N*, *N'*-dialkylated perylene diimides in films of poly(alkyl methacrylate)s (PAMAs) with 5 different alkyl groups and in a 'model solvent', *n*-butyl acetate, over wide temperature ranges. The results indicate that the excited singlet states of the perylene guest molecules are controlled primarily by chain relaxations rather than hole free volumes in the polymer matrixes. The short singlet lifetimes of the perylene molecules require that the guest molecules respond primarily to the environments experienced by their ground states within the PAMA matrixes; each of the PAMAs offers slightly different locations in which the guest molecules can reside as a result of interactions between the *N*-alkyl substituents on the imide groups of the perylenes and the alkyl groups on the PAMA side chains. PAMAs with branched side chains were found to have a larger influence than PAMAs with linear side chains on the fluorescence properties of the guest molecules. The results are compared to those employing pyrenyl derivatives (with much longer excited singlet lifetimes) in the same PAMA films. The overall results indicate that the perylenes can be used as a complementary probe of local polymer chain dynamics, but they are less sensitive to their environments than are pyrenyl groups. However, they offer some distinct advantages: (1) a much wider range of *N*, *N'*-disubstituted perylene diimides can be synthesized easily; (2) those substituents can be designed to allow a greater or lesser interaction with an anisotropic host matrix. Also, rapid conformational changes of a bis-peryene derivative appear to be restricted in the polymer matrixes. Those restrictions appear reduced when the polymer films are placed under high pressures of the plasticizing gas, CO₂, but not when they are under equal pressures of a much less intervening gas, N₂.

Keywords. Perylene Diimides; fluorescence; conformational changes; polymer matrixes; excited singlet states.

1. Introduction

Here, we compare the dependence of the photophysical properties of four *N*, *N'*-dialkylated perylene diimides (referred to as 'perylenes' here for convenience; figure 1) to those of pyrene in films of 5 poly(alkyl methacrylate)s (PAMAs). Such a study is important because a wide range of dialkylated perylenes is much easier to synthesize than the corresponding pyrenes, and many perylenes exhibit near-unity fluorescence quantum yields, high stability to UV radiation and heat, strong electron-accepting ability, and a propensity to π -type aggregation.^{1–3} As well, we were interested to study the intramolecular electron transfer of the diamino derivative of perylene, (*N*, *N'*-di(2-*N''*, *N''*-dimethylamino)ethyl)peryene-3,4:9,10-tetracarboxylic

diimide) in *n*-butyl acetate and PAMA films. However, it exhibited an excited state lifetime, ~ 4 ns, comparable to those of the 3 mono perylenes, in *n*-butyl acetate in spite of a very low fluorescence quantum yield. (Similar observations were reported by Wu *et al.*⁴). A detailed analysis leads us to suggest that a small amount of impurity is responsible for the fluorescence detected; because our efforts to separate the impurity from the desired diamino derivative were unsuccessful, no further studies of the latter in solution or in the PAMA films were conducted. In addition, because the pyrenyl excited singlet state lifetimes are ~ 50 -100 times longer than those of the perylene diimides, the two sets of results yield information about relaxation processes in different time domains. Three of the perylenes have a single core and *N*-alkyl groups that vary from short to long alkyl chains (i.e., butyl (PERBUT) and 8-pentadecyl (PERPDA)) or bulkier, more rigid cyclohexyl groups (PERCYA); one has a

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Figure 1. Structures of perylene diimide guest molecules.

bis-peryene core (TP; also with 8-pentadecyl groups attached to the imide functionalities) in which the optimal 90° angle between the aromatic groups can be changed rather easily in its ground and excited singlet states.

Neat PAMAs are anisotropic on the micrometer scale because they consist of regions enriched in more polar ester groups and less polar alkyl groups. Both the bulk and microscopic properties of PAMA films are dependent on the size and branching of the alkyl side groups attached to the carboxyl moieties, as well as the tacticity of the main chains.^{5,6} PAMAs with short or branched alkyl groups are amorphous materials, whereas those with long (12 or more carbon atoms) *n*-alkyl ester groups contain micro-crystalline domains at lower temperatures.⁷ As the length of alkyl side groups increases, the main chains are moved farther apart, which decreases the energy needed for their movement in the rubbery state. Also, the preferred locations, conformations, and orientations of guest molecules inside the polymer matrixes depend on the magnitudes of intimate probe–polymer and polymer–polymer interactions.^{8,9} Others^{10–12} and we^{13–15} have observed interesting properties of different PAMAs based on the comportment of photochemical and photophysical probes in ensemble average measurements; a cartoon representation of the most probable site locations within the PAMAs is presented in figure 3 of ref 14. These studies differ from single molecule excitations in which stochastic measurements can be made multiple

times to generate ensemble averages. An interesting example of this technique has been reported in the glassy phase of poly(methyl methacrylate) using several perylene derivatives as the probe.^{16,17} In our previous photophysical and photochemical investigations with 5 different PAMAs, it was found that they can be placed in three different categories, depending upon the nature of the dynamic and structural characteristics of the alkyl side groups:^{13–15} (i) in PAMAs with short, linear alkyl chains, such as poly(ethyl methacrylate) (PEMA) and poly(butyl methacrylate) (PBMA), the sizes and shapes of the alkyl groups allow guest molecules to approach closely the ester functionalities and the main chains; (ii) In PAMAs with more rigid and bulkier side-chains, such as poly(isobutyl methacrylate) (PIBMA) and poly(cyclohexyl methacrylate) (PCHMA), the nature of the alkyl groups forces guest molecules to reside farther from the ester functionalities and main chains of the polymer; (iii) in PAMAs with long *n*-alkyl side chains, such as poly(hexadecyl methacrylate) (PHDMA), guest molecules are excluded from the volume segments of the micro-crystallites, but can enter those regions after chain melting.

Photophysical probes, such as pyrene, are known to be sensitive to the polarity,^{18–21} correlated motions^{22,23} and chemical nature^{24,25} of their microenvironments. In that regard, we have shown that the size and length of side-chain alkyl groups in PAMAs play an important role in determining the rates of inter- and intramolecular photophysical processes of pyrenyl guest molecules.^{13,14} It was concluded that the dynamics of the pyrenyl-guest molecules in these media are controlled primarily by side chain relaxation rates of the polymer chains. However, based on both photophysical and photochemical studies, the most important factor in polyethylene films was found to be ‘hole’ free volume.¹⁵

The subtle changes in the fluorescence properties of the perylenes in the PAMA films, over temperature ranges that include the glass (or crystalline)-to-rubbery transitions, have been analyzed carefully to discern how the interplay between the natures of the alkyl chains on the perylenes and on the PAMAs alter the average locations and the ease of movement of the guest molecules within the polymer films. In addition, we have explored the effect of CO₂ and N₂ pressure on the luminescent properties of the perylenes in the PAMA films; the swelling caused by imbibed CO₂ has the same effect as increasing temperature (*but manifested isothermally*) on the ability of the polymer chains to undergo specific motions that affect the perylene excited singlet state dynamics.

2. Experimental

2.1 Materials and Methods

Poly(butyl methacrylate), poly(hexadecyl methacrylate), poly(ethyl methacrylate), and poly(cyclohexyl methacrylate) were purchased from Scientific Polymer Products, Inc. Poly(isobutyl methacrylate) was obtained from Aldrich. Some of their characteristics are reported in Supporting Information. They were purified as reported in the literature.¹³ Perylene-3,4,9,10-tetracarboxylic dianhydride (Aldrich, 97%), cyclohexylamine (Aldrich, $\geq 99\%$), 1-butylamine (Aldrich, 99.5%), anhydrous toluene (EMD Chemicals, Inc. 99.8%), and methanol (Aldrich, 99.8%) were used as received. Anhydrous dichloromethane (Aldrich, 99.8%) was placed overnight over anhyd. CaCl_2 , decanted into CaH_2 , and distilled onto dried molecular sieves (Type 3A) under nitrogen, where it was stored in a brown bottle until being used.²⁶ All flattened capillaries were from Vitro Dynamics, Inc.

2.2 Synthesis

Detailed procedures for the syntheses and characterization of PERBUT and PERCYA are described in Supporting Information. Syntheses of TP and PER-PDA are reported elsewhere.^{27,28} They were $>99\%$ pure according to HPLC analyses.

2.3 Preparation of Doped Films

All doped films (except those of PHDMA) were prepared by dissolving PERBUT, PERCYA, PER-PDA or TP and a PAMA polymer in anhydrous dichloromethane and pouring the solution onto a Teflon plate. The initial concentrations in the dichloromethane solutions were adjusted so that the ultimate perylene concentrations in the films were $\sim 10^{-6}$ mol/kg of PAMA. After most of the solvent had evaporated at room temperature, the films were washed with methanol and then dried under vacuum (0.25 torr) for 10 h. They were cut into pieces of desired sizes, and flame-sealed in flattened, 4 mm pathlength, Pyrex capillaries under vacuum (0.19 torr) on a mercury-free vacuum line. The film thicknesses were determined to be 0.4–0.9 mm using a Mitutoyo Vernier.

Doped PHDMA films were prepared by adding appropriate amounts of a perylene and polymer in dichloromethane solutions into flattened Pyrex capillaries of ~ 0.6 mm pathlength. A drying tube was affixed and the solvent was removed by placing the capillaries

first in a water bath at 343 K and then under vacuum (0.25 torr) for 24 h. Thereafter, the Pyrex capillaries were flame-sealed under vacuum (0.19 torr) using a mercury-free vacuum line.

2.4 Instrumentation and Procedures

^1H NMR spectra were recorded on a Varian 400 MHz spectrometer in either CDCl_3 (TMS as the internal standard) or $\text{CF}_3\text{CO}_2\text{D}$ (residual proton peak at ~ 11 ppm as standard) with 64 scans. MestReNova v5.2.4-3924 software by Mestrelab Research was used to analyze the spectra. Elemental analyses were performed on a Perkin-Elmer Model 2400 Elemental Analyzer. The purities of the perylenes were determined by high-performance liquid chromatography (HPLC) using an Agilent Technologies (Hewlett Packard Series 1100) liquid chromatograph with a Phenomenex silica column (250X4.60 mm, 5 micron) using CHCl_3 as eluent. UV/Vis absorption spectra were recorded on a Varian UV-visible (Cary 300 Bio) spectrophotometer.

Steady-state emission and excitation spectra were recorded on a Photon Technology International fluorimeter (SYS 2459) with Felix 32 software for data analysis (linked to a personal computer) and a 150 W high-pressure xenon lamp with a Quantumwest temperature controller and an Omega temperature probe. Quantum yield measurements were performed on solutions in 1.0 cm pathlength quartz cuvettes that were purged with N_2 for 30 min and closed with rubber stoppers. The fluorescence quantum yields were calculated using eq 1.^{29,30}

$$\Phi_f = \Phi_r (A_r F_s / A_s F_r) (\eta_s^2 / \eta_r^2) \quad (1)$$

A_s and A_r are the absorbances of the sample and reference solutions, respectively, at the same excitation wavelength, F_s and F_r are the corresponding areas of the fluorescence spectra (intensity versus wavelength), and η is the refractive index of the solvents. Rhodamine 6G ($\Phi_f = 0.95$ in ethanol)³¹ was used as the reference compound.

Fluorescence decay histograms were obtained with an Edinburgh Analytical Instruments single photon counting system (model FL900) using H_2 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. The solution samples for dynamic decay measurements were placed in 0.4 mm thickness flattened glass capillaries and were degassed by ≥ 5 freeze (liquid nitrogen)-pump-thaw cycles at ~ 0.15 torr and flame-sealed.

For solution phase studies, the temperature probe and a flattened Pyrex capillary (7 mm (length) $\times$ 4 mm (width) $\times$ (0.4 or 3 mm (i.d.)) were placed inside a 1 cm cuvette filled with decane. For studies with films, 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. For CO_2 and N_2 pressure-dependent fluorescence studies, polymer films were affixed to a side of a triangular quartz cuvette that was placed inside a high pressure chamber³² which, in turn, was placed in the sample compartment of the fluorimeter.

2.5 Quantum calculations

The ground state geometry of the N, N' -dimethyl analogue of TP was optimized using the M06/6-31(d) program in the Gaussian09 suite³³ with the dielectric constant of butyl acetate, 5.0, as the 'solvent', as modeled by the polarizable continuum model (PCM) function. Potential energy surfaces for rotation about the central N—N bond of the optimized structure (figure S1 in Supplementary Information) in the ground and excited singlet states were constructed at increments of 5 degree angles of twist using the same program.

3. Results and Discussion

3.1 Solution state absorption and emission studies

At room temperature, absorption spectra of the 3 mono perylenes (10^{-6} M) in butyl acetate, a solvent which can be viewed as a monomeric, low-viscosity analogue of the PAMAs, showed a vibronic progression of peaks at 518, 482 and 452 nm (figure S2a, in SI) that is characteristic of the $S_0 \rightarrow S_1$ electronic transitions.^{34,35} Peaks at 527, 567 and 614 nm were observed in the emission spectra for the same solutions (figure S2b in SI). Not surprisingly, given the coupling between the two

chromophoric groups of TP,^{36–38} its absorption and emission spectra were shifted bathochromically by ~ 8 nm compared to the other perylenes. Also, the intensity ratio of the $0 \rightarrow 0$ to $0 \rightarrow 1$ peaks ($I_{0-0}/I_{0-1} = 2.4$) in TP was larger than in the other perylenes (1.6), and the corresponding emission ratios were 3.5 and 2.4 (table 1). The I_{0-0}/I_{0-1} ratios in absorbance or fluorescence are known to be a monitor of aggregation³⁹ and local environments of perylene diimide derivatives⁴⁰ when the changes are pronounced.^{41,42} Also, the fluorescence quantum yields for the 4 perylenes were near unity and their excited singlet-state lifetimes were ~ 4 ns (table 1 and figures S18–S20 in SI).

3.2 Effect of temperature on fluorescence intensities and decay times in butyl acetate

A small (but perceptible) decrease in fluorescence intensity with increasing temperature, probably due to increased rates of non-radiative decay, was observed for 10^{-6} M PERBUT, PERCYA and PERPDA in butyl acetate (figure S3a in SI). However, the intensity of fluorescence from TP increased and then decreased with increasing temperature (figure S3b in SI). Unlike the other probe molecules investigated here, TP is able to undergo conformational changes about a central N—N bond (twisting and/or bending motions) that can affect profoundly the degree of interaction between the two perylene groups.^{35–37} The initial increase in emission intensity with increasing temperature is probably linked to conformational changes, and the decrease at higher temperatures to a greater importance of non-radiative decay processes. However, within the resolution limits of our measurements, the fluorescence decay rates showed no discernible changes over the temperature ranges investigated. In this regard, the perylenes are less sensitive probes than pyrenes.

In both its ground and excited singlet states, deformation of the lowest energy conformation of the dimethyl

Table 1. Photophysical characteristics of perylene guest molecules in n -butyl acetate and PIBMA ($\sim 10^{-6}$ mol/kg of perylene in PIBMA) at 295 K. Fluorescence quantum yields (Φ_f) and excited singlet state lifetimes (τ) of the perylenes are in n -butyl acetate ($\lambda_{\text{em}} = 530$ nm).

Perylene diimide	n - Butyl acetate		PIBMA		Φ_f^b	τ (ns) ^c	I_{0-0}/I_{0-1} (abs)		I_{0-0}/I_{0-1} (em) ^b	
	λ_{abs} (nm)	λ_{em} (nm) ^a	λ_{abs} (nm)	λ_{em} (nm)						
PERBUT	518, 483	527, 566	523, 486	529, 569	0.97 ± 0.03	4.0	1.6 ^d	1.2 ^e	2.4 ^d	2.3 ^e
PERCYA	519, 482	527, 566	522, 485	530, 570	0.96 ± 0.03	4.0	1.6 ^d	1.2 ^e	2.4 ^d	1.8 ^e
PERPDA	520, 484	528, 569	523, 486	529, 569	0.97 ± 0.03	4.4	1.6 ^d	1.2 ^e	2.3 ^d	2.3 ^e
TP	527, 490	534, 574	532, 494	537, 578	0.99 ± 0.01	3.4	2.4 ^d	1.7 ^e	3.5 ^d	3.0 ^e

^a $\lambda_{\text{ex}} = 480$ nm; ^b $\lambda_{\text{ex}} = 489$ nm; ^c $\chi^2 \leq 1.2$ and residual plots exhibited no systematic deviation from zero; ^d in n -butyl acetate; ^e in PIBMA.

Figure 2. Ground and excited singlet state potential energy surfaces from single point calculations of twisted *N, N'*-dimethyl bisperylene diimide starting from the optimized ground state geometry.

analogue of TP, where its two aromatic moieties are perpendicular to each other, requires only $1.5 \text{ kcal mol}^{-1}$ to twist by 15° (i.e., from 90° to 75°); a 30° twist increases the energies by ca. 7 kcal mol^{-1} (figure 2 and table S2 in SI). The energies of TP conformers must be virtually the same as those of the model compound.

3.3 Dynamic emission studies in PAMA films

Fluorescence intensity decay histograms from time-correlated single photon counting experiments of the three mono perylenes in the PAMAs at 10^{-6} mol/kg were mono-exponential. At 298 K, the lifetimes, $\sim 4 \text{ ns}$, were comparable to those in butyl acetate (table S3 in SI), and they remained virtually unchanged over ranges of temperatures from below to above the glass or melting transition temperatures. Representative decay histograms for the samples reported in table 1, with residual plots that demonstrate the lack of deviation of the curves to best fits, are shown in figures 3 and 4. Films of TP in the PAMAs also yielded mono-exponential decays with lifetimes $\sim 3 \text{ ns}$ throughout the temperature ranges investigated. Thus, the dynamic measurements offer very little insights into the intimate perylene interactions with its polymer hosts (or in solution with butyl acetate).

3.4 Spectroscopic properties of the perylenes in PAMA films

At room temperature, PEMA, PCHMA and PIBMA are in their glassy state, and PBMA and PHDMA are in

their rubbery state (table 2). The initiation or cessation of main chain motions (i.e., α -relaxations) occur close to the glass transition or melting temperatures. The absorption, excitation and emission spectra of perylenes in the PAMA films were similar in shape and position to the corresponding spectra in butyl acetate, and the emission spectra were independent of excitation wavelength. However, the absorption and emission spectra were red-shifted by ~ 5 and $\sim 3 \text{ nm}$, respectively, in the PAMAs with respect to those in butyl acetate. No aggregation of the perylene moieties was expected at the very low concentrations employed, and the spectral data are consistent with that being the case (figure 5). The I_{0-0}/I_{0-1} ratios from the perylene absorption spectra were 1.2 and 1.7 in the PAMAs, and in butyl acetate, respectively. Except in PHDMA, where the emission ratios of the mono perylenes, 2.5, were similar to those in butyl acetate, and the ratio for TP, 4.0, was higher than in butyl acetate, the emission ratios in the PAMAs were also slightly lower—1.8 for PERCYA and 2.3 for PERBUT and PERPDA (table 1).

We interpret these differences as a consequence of PERCYA being located in a slightly different environment than PERBUT and PERPDA in the polymer matrixes (vide infra).

3.5 Effect of temperature on fluorescence intensities in the PAMA films

The fluorescence intensity changes of the perylenes were compared in temperature ranges from below to above the glass transition/melting temperatures. Due to the more rapid relaxation processes above the transition temperatures, movement of guest molecules between and within sites is enhanced in films of the PAMAs. Fluorescence intensities of PERBUT and PERPDA decreased as temperature was increased in all of the PAMAs except PHDMA. Also, no large changes in fluorescence intensity were observed near the glass transition temperatures of the 3 glassy PAMAs, but a large change was observed near T_m of PHDMA, due to a change in the refractive index of the polymer medium rather than a photophysical effect experienced by the probe.

Cooling the films to their initial temperature after heating above their T_g or T_m reestablished the original fluorescence intensity; the polymer systems are reversible and the perylenes are thermally stable within the temperature range investigated. Contrary to the other two mono perylenes, the fluorescence intensity of PERCYA, the perylene derivative with the bulkiest *N, N'*-substituents, cyclohexyl, increased

Figure 3. Decay histograms ($\blacklozenge$) of $\sim 10^{-6}$ M PERBUT (a), PERCYA (b), PERPDA (c) and TP (d) with best fit lines (—) in butyl acetate at 295 K and lamp profiles ($\blacksquare$); ($\lambda_{\text{ex}} = 480$, $\lambda_{\text{em}} = 530$ nm). The residual plots are below each decay panel and χ^2 values are reported in table 1.

with increasing temperature in the four glass-forming PAMAs. The different compartment in the fluorescence changes can be ascribed to the PERCYA molecules residing preferentially in a location whose polarity and chain mobility are somewhat different from those experienced by PERBUT and PERPDA.

The response of the fluorescence intensity of TP to increasing temperature in the PAMA films, a decrease, was very different from that found in butyl acetate (a rise followed by a fall; figure S3b in SI). As mentioned, the angle between the planes defined by its two perylene groups determines the degree and nature of their interactions. Although the angle experienced by TP molecules in their ground state may be very similar

in the polymer matrixes and in butyl acetate (based on the absorption spectra), its ability to change during its excited singlet state lifetime can be vastly different as a result of the very high microviscosity in the PAMAs and the very low one in butyl acetate: very little structural change is expected of TP in the films during its very short excited singlet-state lifetime (*vide infra*). As a means to compare the general behavior of fluorescence changes with temperature, the normalized fluorescence intensities $\{[I(T) - I(T_g)]/I(T_g)\}$ were plotted as a function of reduced temperature ($T - T_g$) (figure 6). The plots can be divided into regions below ($T - T_g < 0$; i.e., the glassy state) and above the glass transition ($T - T_g > 0$; i.e., the rubbery state). As can be seen, the temperature

Figure 4. Decay histograms (♦) of $\sim 10^{-6}$ M PERBUT (a), PERCYA (b), PERPDA (c) and TP (d) with best fit lines (—) in PIBMA at 295 K and lamp profiles (■); ($\lambda_{\text{ex}} = 480$, $\lambda_{\text{em}} = 530$ nm). The residual plots are below each decay panel and χ^2 values are reported in table 1.

induced changes are larger in the branched polymers, PIBMA and PCHMA, than in the unbranched ones with short alkyl chains, PBMA and PEMA, where the perylenes are expected to reside more closely on average to the polymer backbones.

Table 2. Transition temperatures of PAMAs.^a

Polymer	Glass (g) or melting (m) temperature (K)	T_{α} (K) ^a
PHDMA	281 (m)	330
PBMA	290 (g)	322
PIBMA	322 (g)	330
PEMA	342 (g)	290
PCHMA	368 (g)	280

^aData from ref.⁴³

3.6 Effects of CO_2 and N_2 pressure

The influence of high pressures of CO_2 on the emission characteristics of the perylenes in the PAMA films was also investigated. At a particular temperature, increasing the CO_2 pressure may conceptually have two counteracting effects on the mechanical properties of the polymer films: (1) dissolved gas may plasticize the films^{44,45} and, thus, lower glass transition temperatures; (2) increased hydrostatic pressure on the polymers may increase glass transition temperatures as a result of decreased free volume.^{46–48}

As shown in figure 7a, increasing the pressure of CO_2 decreased the fluorescence intensities of the perylenes in PIBMA films at 295 K. The changes were comparable for PERCYA, PERBUT and PERPDA, and smaller,

Figure 5. Normalized (a) excitation ($\lambda_{em} = 570$ nm) and (b) emission ($\lambda_{ex} = 480$ nm) spectra of ca. 10^{-6} mol perylene/kg PIBMA at 293 K: PERBUT (—), PERCYA (---), PERPDA (.....), and TP (-·-·-).

but discernible, for TP. At 324 K (i.e., slightly above T_g), the onset pressure where decreases in the intensity occur, are much lower (figure 7b).

Comparison of changes in the fluorescence intensity of PERCYA in various PAMAs at 295 K (figure S16 in SI) demonstrates that polymers with higher T_g 's require a higher pressure to initiate the fluorescence intensity changes. Although the optical density and spectral features of PERBUT in a PBMA film at 295 K ($T_g = 290$ K) were indistinguishable at 1 and 40 atm of CO_2 , a decrease in fluorescence intensity was noted at >10 atm pressure. However, significant changes were noted only

above ~ 30 atm CO_2 pressure in PIBMA ($T_g = 322$ K) and PEMA ($T_g = 342$ K). These data and those in figure S16 demonstrate clearly that the degree to which CO_2 pressure affects the polymer matrix depends on the proximity of the temperature to T_g (i.e., side and main chain polymer mobility), and that the decreases in fluorescence intensity are related to photophysical aspects of perylene-polymer interactions.

At 295 K, the PIBMA film expanded visually up to 40 atm of CO_2 ; above that pressure, the film broke into pieces. At 324 K, 30 atm was the maximum pressure at which no deformation of the PIBMA films was

Figure 6. Fluorescence intensity changes at emission maxima of (a) PERBUT, (b) PERCYA, (c) PERPDA and (d) TP in the PAMA films ($\sim 10^{-6}$ mol/kg; $\lambda_{ex} = 480$ nm) in four of the PAMA films as a function of reduced temperature ($^{\circ}\text{C}$).

Figure 7. Emission intensities at the emission maxima of perylenes in PIBMA films ($\sim 10^{-6}$ mol/kg): PERBUT (●), PERCYA (■), PERPDA (▲), and TP (★) as a function of CO₂ pressure at (a) 295 K and (b) 324 K ($\lambda_{\text{ex}} = 480$ nm). Note that $T_g = 322$ K for PIBMA at one atm of pressure.

detectable. Contrary to the effect of CO₂, even 40 atm of N₂ did not lead to noticeable changes in the fluorescence intensity of PERCYA in PBMA at 295 K (figure S17 in SI).

3.7 What controls PAMA host-guest interactions?

The temperatures at which the fluorescence intensities were recorded are far above the onset of the γ relaxation (involving rotations of side chains; $T_\gamma = 120$ –160 K) and β relaxation (involving rotation of the ester side groups; $T_\beta = 220$ –270 K) processes for all the PAMA polymers,^{15,44,45,49,50} but they span a range that includes the α -relaxation processes (involving movement of the polymer backbones), which are near to and associated with the glass transition temperatures, T_g .^{44,45,51,52} Both the β - and α -relaxations are strongly coupled in acrylates like the ones employed here.⁵³ Also, motional changes of the polymer segments associated with these two relaxation processes may couple with transitions of the singlet excited states of the perylenes.^{51,52} When that occurs, both the quantum yield and intensity of the

perylenes can decrease when fundamental vibrations and harmonics of their excited singlet states are coupled with vibrational modes of the PAMAs.^{54,55} Thus, the observed decreases in the fluorescence intensity of PERBUT and PERPDA with increasing temperature may be related to the larger segmental motions of the PAMAs that enhance non-radiative deactivations or to effects induced in the ground states by the alkyl chains of PERBUT and PERPDA.

Perylene guest molecules can experience lower-polarity (near the alkyl groups) or higher-polarity (near to the ester functionalities) local environments in the PAMAs that are mediated by van der Waals interactions. In that regard, carboxy groups of polyacrylates are known to interact with the π -electrons of aromatic^{56,57} and carbonyl groups⁵⁸ of guest molecules. The interaction energies between carbonyl groups of polyacrylates and polycyclic aromatic hydrocarbons like perylenes are consequential to determining where the perylenes prefer to reside within the PAMA matrixes:⁵⁹ the calculated binding energy between formaldehyde and benzene is 1.86 kcal mol⁻¹.⁶⁰ Although the corresponding magnitudes of the interaction energies between carbonyl groups and 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 of the perylenes than in their ground states. Furthermore, because the interactions must be orientationally selective and sensitive to the intermolecular separation distances, any static or dynamic change of the side chains within the PAMA films, caused by a phase transition or even different temperatures within a phase, must affect the degree of carbonyl-erylene excited state interactions (and, thus, the fluorescence properties). Therefore, from the structural features of the guest molecules in the present study, it is reasonable to expect that the perylenes prefer to reside near the main chains of the PAMAs, as well, and will do so to the extent that steric factors permit.

The fluorescence from pyrene-based probes has also been used to report on the size, shape, and flexibility of the cavity walls of the guest sites in polyethylene and poly(alkyl methacrylate) films.^{8,9} Although changes in the fluorescence properties of the perylenes are less influenced by the polarity of the medium than pyrenyl guests (because the perylene core is less sensitive to the polarity of its environment⁶¹), the fluorescence intensity ratios can still be used to differentiate among the environments offered by the PAMAs based primarily on their proximity to sites of host relaxations. The similarity among the I_{0-0}/I_{0-1} fluorescence intensity ratios indicate that PERBUT, PERPDA, and PERCYA reside in similar locations within the polymer

Table 3. I_{0-0}/I_{0-1} emission ratios for the perylenes ca. 10°C below and above the glass or melting temperatures of the PAMAs.

	PEMA (T _g = 342 K)		PIBMA (T _g = 322 K)		PBMA (T _g = 290 K)		PCHMA (T _g = 368 K)		PHDMA (T _m = 281 K)	
	333K	353K	313K	333K	283K	303K	363K	373K	273K	293K
PERBUT	2.0	2.0	2.3	2.3	2.2	2.2	2.0	2.0	2.6	2.7
PERCYA	1.9	1.9	1.8	1.8	2.0	2.0	1.8	1.7	2.6	2.7
PERPDA	2.0	2.2	2.3	2.3	2.2	2.2	2.3	2.3	2.4	2.5
TP	3.1	3.1	3.0	3.0	3.1	3.1	2.9	2.9	4.2	4.0

matrixes of all of the glass-forming PAMAs (i.e., excluding PHDMA), and that those locations do not change appreciably in the glassy and rubbery states (table 3). Although these ratios are similar to those found in *n*-butyl acetate (table 1), there are small and systematic differences that are consistent with these perylenes occupying slightly different average locations within each of the glass-forming PAMAs. Specifically, the I_{0-0}/I_{0-1} ratios for PERCYA, the perylene with the bulkiest *N*-alkyl group, cyclohexyl, are consistently lower than those of PERBUT and PERPDA within each PAMA. In that regard, both the intensity ratios and the aforementioned increase in overall fluorescence intensity of PERCYA with increasing temperature may be ascribed to the steric effect of its rather rigid and bulky cyclohexyl groups, which impede its ability to reside as near the polymer main chains as the other mono perylenes.

As noted, guest molecules are excluded from the microcrystalline regions of the hexadecyl chains below the melting temperature, T_m , of PHDMA, but they still can and do reside within low polarity regions that are constituted by the non-crystalline portions of the chains. Above T_m , the low-polarity, highly-viscosity region is expanded to include all of the region of the melted hexadecyl chains.^{5,6,62} As a result, the major changes in the observed absolute intensities occur for optical rather than physical reasons, and the values below and above T_m are not useful indicators of perylene locations. *However, the I_{0-0}/I_{0-1} ratios do remain physically useful indicators.* For the mono-perylenes (including PERCYA) in PHDMA those ratios, ~2.4-2.7, are almost the same both above and below T_m , but are significantly higher than in the glass-forming PAMAs; the perylenes remain in locations that appear physically to be very similar throughout. Of special note are the very high ratios for TP in PHDMA: the I_{0-0}/I_{0-1} ratios are ~3 in all of the glass-forming PAMAs and ~4 in PHDMA. Whereas the ratios from the other perylenes are only slightly higher in PHDMA than in glass-forming PAMAs, the difference for TP is much larger, and it reflects its greater sensitivity to local

environment. The temperature dependence on the fluorescence intensity of the mono perylenes is larger in the PAMAs than in butyl acetate. Below the glass transition temperatures, the guest molecules are able to move only very slowly between sites. The rate of their movement and their redistribution between different site types is facilitated by increasing temperature, especially when the increases involve a transition from glassy to rubbery states. However, whether the intensities increased or decreased with increasing temperature depended on the specific structures of the *N*-alkyl groups on the perylenes and the PAMAs. Thus, the *decrease* in the emission intensity from PERBUT with increasing temperature in the other PAMAs follows the order, PIBMA > PCHMA > PBMA > PEMA, and that of PERCYA, containing 2 cyclohexyl groups, *increased* in the order, PIBMA > PCHMA > PEMA > PBMA. Interestingly, and indicative of the relationship between the nature of the alkyl chains on the perylenes and the side chains on the PAMAs, PERPDA and TP, both with 8-pentadecyl chains, showed similar trends in their emission intensities that differed from those of PERBUT or PERCYA (i.e., (PCHMA > PIBMA > PBMA > PEMA)).

Furthermore, comparisons among the reduced temperature plots in figure 6 show that the 3 mono perylenes exhibit larger changes in their fluorescence intensities with temperature in PCHMA and PIBMA (i.e., the polymers with bulkier ester groups) than in PEMA and PBMA (i.e., the polymers with less bulky ester groups). The small side chains of PEMA and PBMA attenuate movements of segments of the main chains, leading to higher activation energies for α -relaxations.⁷ As a result, the perylene molecules are less mobile in PEMA and PBMA than in the comparable phases of PCHMA and PIBMA at comparable temperatures. The long alkyl side chains of PHDMA increase the average distance between neighboring main chains, allow the formation of 'voids',⁶⁰ and facilitate short-range translational mobility, even in the solid state. The side groups of PIBMA and PCHMA restrict guest mobility⁶³ in the glassy states, but their guest sites are sufficiently flexible to permit short-range

Scheme 1. Cartoon representations of possible preferred locations of perylene solutes (green objects) in the different PAMA matrixes: (a) PERBUT and PERPDA in PEMA or PBMA. (b) PERBUT and PERPDA in PIBMA or PCHMA. (c) PERCYA in PEMA or PBMA. (d) PERCYA in PIBMA or PCHMA.

conformational changes, especially in the rubbery states. Accordingly, the PAMAs can be placed into the same three categories that were based upon results with pyrene reporter molecules.^{13,14} These considerations and concepts are illustrated in scheme 1 as cartoon representations of the predicted, preferred solubilization sites of the different perylenes in the 5 PAMAs.

Given that both the microviscosities of the polymers and the average locations of the perylenes change continuously with temperature, nonlinear slopes like those found in figure 6 were expected. Note also that there are no abrupt discontinuities in the fluorescence intensities at the α - transition temperatures; they would be expected if void volume changes were responsible for the observed changes in the fluorescence intensities rather than relaxation phenomena.

The primary factor influencing the fluorescence properties of probe molecules in polyethylene films appears to be hole free volume. Guest molecules are restricted to reside in the non-crystalline (amorphous) and interfacial (i.e., along the surfaces of microcrystallites) within these matrixes.⁶⁴ During the long excited singlet-state lifetimes of the pyrene molecules (~ 200 ns), the distance traversed in polyethylene is estimated to be < 1 Å. However, as noted above, the results presented here and in previous studies with PAMAs^{12–14} indicate that the fluorescence properties of aromatic guest molecules depend much more on chain segment relaxation rates

and micro-diffusion than on hole free-volume. Thus, the nature of the side chains in the PAMAs is a very important parameter in understanding the behaviors of the different perylenes.

As mentioned, plasticizing and hydrostatic effects can act in potentially opposite ways on the properties of the fluorescence of the perylene guest molecules when PAMA films are placed under high pressures of gases such as CO_2 and N_2 .^{50,65} The results indicate that the lowering of T_g , caused by large amounts of CO_2 (but not N_2) dissolved within the PAMA films, plays the more important role here; the observed decreases in fluorescence intensity of the perylenes in the PAMA films above a particular pressure of CO_2 under isothermal conditions is most easily attributed to relaxation of motional constraints on the guest molecules by their hosts. In essence, the ‘walls’ constituting the local host cavities are softened. The solubility of the less polar gas, N_2 , is known to be much lower than that of CO_2 in poly(methyl methacrylate), PEMA and, presumably, the other PAMAs employed here.^{63,66} Whereas both molecules have zero dipoles, the quadrupole moment of CO_2 ($(-14.27 \pm 0.61) \times 10^{-40} \text{ C m}^2$) is more than 3 times as large as that of N_2 ($(-4.65 \pm 0.08) \times 10^{-40} \text{ C m}^2$).⁶⁷ Thus, N_2 pressure is sensed primarily as a hydrostatic force on the PAMA films, and it exerts a much less effective influence on the perylene emissions.

4. Conclusions

A detailed examination of the influences of structural changes in four *N,N'*-dialkylated perylene diimides on their fluorescence properties in 5 poly(alkyl methacrylate)s has been explored, and the data are compared with those in a model liquid solvent, *n*-butyl acetate. The temperature ranges over which the measurements have been made include either the glass-to-rubber or crystalline-to-melt (rubber) transitions of the polymers. In addition, the influence of high pressures of a polar, more soluble gas (CO₂) and a less polar, less soluble gas (N₂) on the emission characteristics of the perylenes in the polymer films has been investigated. From the data, we conclude that the subtle changes in the average locations of the perylenes within the polymers as a function of temperature, perylene alkyl substituents, and polymer side chains are responsible for the observed changes in the intensities and intensity ratios of the fluorescence from the four perylene guest molecules. Although similar conclusions have been reached from studies employing the fluorescence of pyrene-based probes in the same 5 PAMAs, the nature of the coupling between the excited states of the perylene and pyrenyl guests are different and the former can be modulated in subtle and synthetically easier ways by changing the type of alkyl groups attached to the nitrogen atoms of the imide functionalities; for example, the distinctly different temperature dependences of the I_{0-0}/I_{0-1} emission intensity ratios from PERCYA and either PERBUT or PERPDA demonstrate that the nature of the *N*-alkyl groups on the imide ends of the perylene cores has a discernible effect on the positions of the guest molecules in the PAMA matrixes. Also, the much shorter excited singlet lifetimes of the perylene molecules requires that their emissions be much more dependent on their ground-state environments within the PAMA matrixes.

Finally, the results employing TP have allowed us to examine the influence of the polymer matrixes on the ability of the two perylene units to twist with respect to each other, and the manifestations of that twisting are clearly manifested, especially in a comparison of the I_{0-0}/I_{0-1} emission ratios in the glass-forming PAMAs and in PHDMA. The dissimilar behavior of TP in the PAMAs and in *n*-butyl acetate demonstrates that the high micro-viscosity of the polymer matrixes restricts rapid conformational changes of the linked ring system. Those restrictions are decreased when the polymer films are placed under high pressures of the plasticizing gas, CO₂, but not when they are under equal pressures of a much less intervening gas, N₂.

In summary, the results presented here develop a useful set of probes to investigate detailed interactions occurring in the nanometer distance scale within polymer matrixes, and to follow the changes that they undergo as a result of various macroscopically applied stimuli. They offer complementary information to that from pyrenyl probes. In principle (and in practice), the range of substituents that can be placed *easily* on a perylene diimide far exceeds that for pyrene. For this reason, the ability to tune structural interactions between a perylene diimide and a host matrix is greater than with pyrene. At the same time, the electronic interactions are generally more sensitive between the excited singlet state of a substituted pyrene and its local environment than those of a perylene diimide. Thus, each system has advantages and disadvantages. We emphasize that the approach and probes employed here are applicable directly to many other types of polymer matrixes.

Supplementary Information (SI)

Electronic Supplementary Information (ESI) available: Details of synthetic procedures of PERBUT and PERCYA, characterizations, purification methods for PAMAs, and instrumentation details and procedures. Energies of conformations from single point and optimized geometry calculations of *N,N'*-dimethyl bisperylene diimide, fluorescence decay curves and excited state lifetimes and additional fluorescence data of PERCYA, PERBUT, PERPDA and TP, fluorescence intensities versus temperature plots, and fluorescence intensity versus pressure plots of films. These data are also available at www.ias.ac.in/chemsci.

Acknowledgements

Prof. Russell Schmehl of Tulane University and Prof. Sridhar Rajaram of the Jawaharlal Nehru Centre for Advanced Scientific Research in Bangalore are thanked for stimulating discussions. Also, we are extremely grateful to Prof. Rajaram for generously supplying two of the perylene diimides used in these studies. Prof. Miklos Kertesz is thanked for his help with the quantum calculations. The US National Science Foundation is gratefully acknowledged for its financial support through grants CHE-1147353 and -1502856.

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