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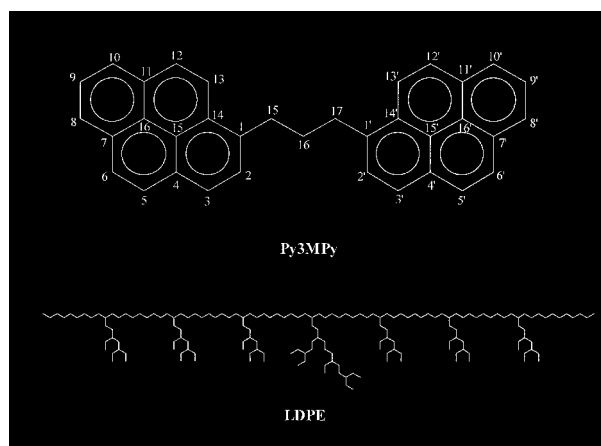
Host/Guest Simulation of Fluorescent Probes Adsorbed into Low-Density Polyethylene, 1

Excimer Formation of 1,3-Di(1-pyrenyl)propane

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Full Paper: Molecular dynamics and Rotational Isomer State/Monte Carlo techniques with a Dreiding 1.01 Force Field are employed to study the excimer formation of isolated 1,3-di(1-pyrenyl)propane and the probe adsorbed into a low-density polyethylene (LDPE) matrix model. The probability of formation of each molecular conformer at several temperatures was calculated using these theoretical techniques. Conformational statistical analysis of the four torsion angles (ϕ_1 , ϕ_2 , θ_1 , θ_2) of Py3MPy showed that the angles $\text{—C—C}^{\text{ar}}\text{—}$ (ϕ_1 , ϕ_2) present two states $c^{\pm} = \pm 90^{\circ}$; and the angles —C—C— (θ_1 , θ_2), the three *trans* states = 180° , $g^{\pm} = \pm 60^{\circ}$. The correlation of $\theta_1\text{—}\theta_2$ torsion angles showed that the most probable pairs were g^+g^- and g^-g^+ for the excimer-like specimens, although these angles are distorted because of interactions with the polymer matrix. The temperature dependence of the excimer-formation probability revealed that this process was thermodynamically controlled in the isolated case. When the probe was adsorbed into the LDPE matrix, the excimer formation process was reversed at $T = 375$ K. At $T > 375$ K, the behavior was similar to the isolated case but, at $T < 375$ K, excimer formation probability increased with temperature as found experimentally by steady-state fluorescence spectroscopy. This temperature was coincident with the onset of the LDPE melting process, determined experimentally by thermal analysis.



Initial structures of Py3MPy (top) and of LDPE (bottom).

Keywords:

1,3-di(1-pyrenyl)propane; fluorescence; Monte Carlo simulation; molecular dynamics; polyethylene (PE)

Introduction

The photochemical and photophysical properties of dyes adsorbed into polymer matrices has influence on areas of research which are interesting from both technological and fundamental perspectives.^[1] These studies are usually performed with the dyes chemically bonded to the polymer chains (molecular labels) or with the dyes adsorbed into the polymer matrix (molecular probes). Both the properties of the adsorbed molecules and the polymer can be investigated.^[1] One particular type of study using

molecules adsorbed into polymer matrices is the determination of polymer relaxation processes using photoluminescence of several types of probes or labels.^[2]

In a previous work we reported that the excimer formation of 1,3-di(1-pyrenyl)propane (Py3MPy) adsorbed in low-density polyethylene (LDPE) was strongly affected by temperature that was simultaneously interfering with both the dynamics of the intramolecular excimer reaction and the polymer relaxation processes. We also detected that there was an onset temperature above which the molecular conformation was adequate for excimer formation; this temperature was coincident with the LDPE β -relaxation process (ca. 270 K). In addition, we observed a

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higher offset temperature where a maximum excimer fluorescence emission was detected.^[3] This offset temperature was coincident with the onset of the LDPE melting process (370 K). These results were qualitatively analyzed assuming a convolution of the available free volume in the polymer matrix and the intrinsic excimer dynamics of the Py3MPy molecule. Both are temperature-dependent phenomena: the change in free volume results from the polymer relaxation processes and the excimer-like conformation of the probe may be a thermally activated process. In any case, it should be elucidated if intramolecular excimer formation in this restricted medium is driven by the available free volume or by polymer–probe interactions.

Photophysical properties of *n*-alkyl bispyrene molecules were described in several studies using different theoretical and experimental approaches.^[4,5] Several of these studies concerned the excimer formation mechanism for these molecules in fluid media. Nevertheless, the mechanism of excimer formation is still controversial. In some cases, it has been suggested that the intramolecular excimer dynamics of bis(1-pyrenyl)alkanes involves a distribution of several conformers while other works suggest that only some specific conformations are able to participate in the process. Regardless of the dynamic processes intrinsically related to the molecule in fluid media, other pathways may arise when the probe is adsorbed in a solid polymer matrix. For example, the dynamic process for the excimer formation of *n*-alkylbispyrene molecules adsorbed in solid matrices was controlled by the size and the shape of the polymer cavity.^[6]

Calculations based on the equilibrium treatment approach using Tripos Force Field from Sybyl 6.0, allowed the identification of all conformations that were responsible of the formation of face-to-face complexes.^[7–10] Using these calculations we studied the conformations produced by the overlap of one, two, three and four six-member rings belonging to pyrene units. Similar studies for the excimer-formation calculations were performed using Molecular Dynamic (MD) simulations.^[11–13]

In the present work we evaluate the probability of achieving a suitable excimer-like conformation of 1,3-di(1-pyrenyl)propane (Py3MPy) in both the isolated state and adsorbed into LDPE matrix, in an attempt to explain the influence of the solid matrix on the molecular conformation. The probability and free energy for each conformation, and the enthalpic and entropic contributions are also theoretically calculated using Rotational Isomer State (RIS)/Monte Carlo (MC) by the Theodorou and Suter technique.^[14]

Calculation Methodology

Dynamic information of the host/guest system requires molecular dynamics simulations in the temperature range

of interest, around 300 K. In the case of a relatively large molecule such as Py3MPy inserted in a LDPE matrix, simulation time should be large enough to allow a number of conformational transitions, some of them giving rise to excimer-forming events. The problem is that as a result of the dense nature of the system and the large molecular volume of Py3MPy, any attempt to do so will fail within normal computation times. As an alternative, the simulation of the host/guest ensemble may be performed using the RIS/MC method. Therefore, two methods were used to calculate the conformational probability of (Py3MPy) intramolecular excimer formation: i) MD simulation was applied for the isolated molecule using the Cerius2 3.5 package^[15] and ii) RIS/MC^[14] was applied for Py3MPy adsorbed into a model LDPE matrix. The Dreiding 1.01 Force Field was used for all the calculations.^[16] Charges over the atoms were computed by QEq_CHARGED 1.1 that was included in Cerius2 3.5.^[15]

Polymer Model

For calculating the probability of the possible conformers of Py3MPy adsorbed into the polymer matrix, it was assumed that Py3MPy was located in the LDPE amorphous-phase matrix. This assumption was based on previous experimental studies by X-ray diffraction,^[17,18] which demonstrated that the LDPE crystalline phase was not modified by the presence of a fluorophore.

Although LDPE is an extensively studied polymer, only average molecular details are described. For example, the number of branches, the branch length or the polymer density, are average magnitudes. Since the polymer model should reflect the properties of polymer used in experimental work^[19] (a LDPE), the selected value for density was $0.92 \text{ g} \cdot \text{cm}^{-3}$ at 298 K.^[20] The density at other temperatures was evaluated according to the well-known ratio between specific volume and desired temperature. Concerning the branched structure of LDPE, it is reported that typical commercial polymers contain, on average, about 50% of all carbon atoms in small branches.^[20] Considering these assumptions, we have built a model polyethylene chain formed by 50 ethylenic units containing six lateral branches randomly located along the main chain. The number of out main chain atoms was 88, that is equivalent to 44%. Figure 1 shows the molecular schematic structures of Py3MPy and LDPE.

Molecular Dynamics

The geometrical parameters such as bond lengths, bond angles and torsion angles were taken as variables in the simulations. Each of the trajectories was 1 ns long with a time step of 1 fs. The initial temperature was twice the working temperature and the molecule was thermally equilibrated for 100 ps at each specific temperature

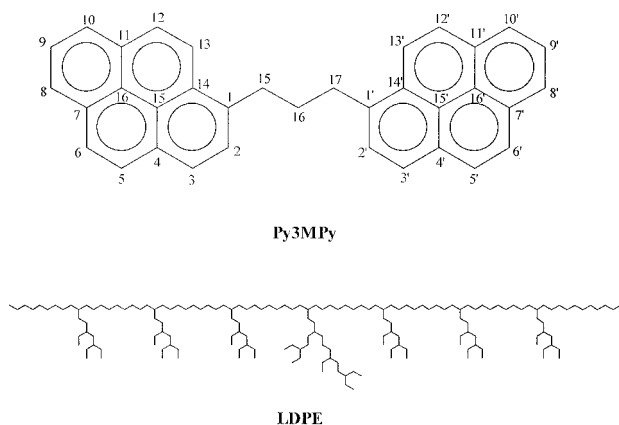


Figure 1. Initial structures of Py3MPy (top) and of LDPE (bottom).

before data collection. Velocities were recalled at intervals of 50 fs. Conformations were saved at intervals of 200 steps for subsequent analysis, yielding 5000 different conformations for each trajectory. Simulation started with an initial conformer with all the internal torsion bonds oriented in the *trans* conformation. The total energy of this state was minimized by the conjugate gradient method with $1 \text{ cal} \cdot \text{mol}^{-1}$ as the termination criterion, and was calculated for six temperatures within the range 600–1100 K.

RIS/MC

Similar calculation was performed for a Py3MPy molecule adsorbed into the polyethylene bulk by RIS/MC. The conformation was built by the Theodorou and Suter technique.^[15] This process consists of the generation of an initial host/guest system using a RIS/MC scheme. Temperature factors enter the procedure only in setting the system density and in the statistical weights used in the RIS generation. The initial values for the temperature and the density used in the simulations are presented in Table 1. The second calculation step involved the energy minimization by conjugate gradient as termination method ($3 \text{ kcal} \cdot \text{mol}^{-1}$).^[21] 2000 conformations were selected for the subsequent analysis.

Table 1. Initial conditions of density and temperature used for RIS/MC calculations for Py3MPy in a LDPE matrix.

Temperature K	Density $\text{g} \cdot \text{cm}^{-3}$ a)
238	0.94
300	0.92
333	0.89
375	0.84
390	0.80
423	0.78

a) See ref. ^[26]

Excimer Model

The geometrical parameters used for the calculation of Py3MPy intramolecular excimer-like structures are: the distance between the aromatic ring centroids, d , and the angle between the ring planes, ψ . Therefore, a given conformation was considered as an excimer-like conformation if the geometrical parameters fulfilled the following criteria:^[8–13] the values of these two parameters were taken from experimental data on pyrene excimers with coplanar rings,^[22] $3 \leq d \leq 4 \text{ \AA}$ and $\psi \leq 40^\circ$. Although excimer is an excited state, its geometry is similar to the ground-state sandwich dimers and thus, for the purpose of molecular simulation, this important photophysical difference is considered irrelevant. Therefore, in this work, the excimer term should be understood as a sandwich-coplanar complex.

The probability of excimer formation was defined as:

$$P_E = \sum_{i=1}^N \varepsilon_i p_i \quad (1)$$

where the summatory is extended to N conformations, p_i is the probability of the i^{th} conformation, and the weight factor ε_i is 0 when the excimer is not formed and 1 when the excimer conditions are fulfilled.

Results and Discussion

Conformational Study of Py3MPy

Two types of torsion angles are involved in the Py3MPy excimer where the flexible aliphatic spacer between the two pyrenyl moieties participates. Those nominated as ϕ_1 and ϕ_2 involve the carbon atoms 14-15-16 and 16-17-1'-14', and, θ_1 and θ_2 are formed by 1-15-16-17 and 15-16-17-1' carbon atoms, respectively (Figure 1). The probability for each conformer was calculated for different combinations of torsion angles pairs (ϕ_1 - ϕ_2 and θ_1 - θ_2) for Py3MPy in a vacuum, and adsorbed into the LDPE matrix, using the different approaches described previously.

Py3MPy in a Vacuum

Rotational Angles of Py3MPy

Figure 2 shows the probability values of the torsion angles calculated at the temperature of ca. 1000 K. The conformations with highest probability correspond to those for which torsion angles ϕ_1 and ϕ_2 have the values of ca. $c^\pm = \pm 90^\circ$, and the angles θ_1 and θ_2 have the values of ca. $t = 180^\circ$ (*trans*) and $g^\pm = \pm 60^\circ$ (*gauche*). The conformational probability as a function of ϕ_1 , ϕ_2 , θ_1 and θ_2 was calculated at 600, 700, 800, 900, 1000 and 1100 K. No differences were observed between these temperatures. The probability of all angles approximately obey

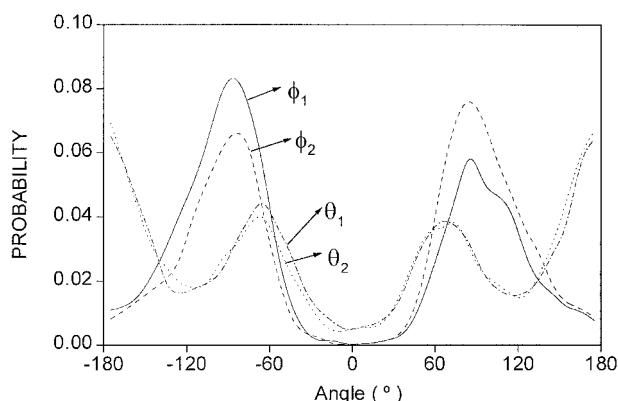


Figure 2. Probability of the torsion angles of Py3MPy in vacuum and at 1000 K: ϕ_1 (—), ϕ_2 (- - -), θ_1 (- · - ·) and θ_2 (· · · ·).

the ratio $p(\varphi) = p(-\varphi)$. This condition shows that the system are at equilibrium.

Correlation between the Angles $\theta_1-\theta_2$ and $\phi_1-\phi_2$

Figure 3 shows the probability maps calculated for all Py3MPy conformers (Figure 3a and 3b) in vacuum and at 1000 K and for those conformers that form excimer (Figure 3c and 3d). Although the angles $\theta_1-\theta_2$ may adopt the nine possible combinations that give rise to the states t , g^+ and g^- , only the g^+g^- and g^-g^+ pairs cause with significantly high probability. These results agree with NMR studies reported by Zacharisse et al.^[23,24] In addition, the angles ϕ_1 and ϕ_2 can adopt all possible combinations of states c^+ and c^- on the excimer conformation. Since only

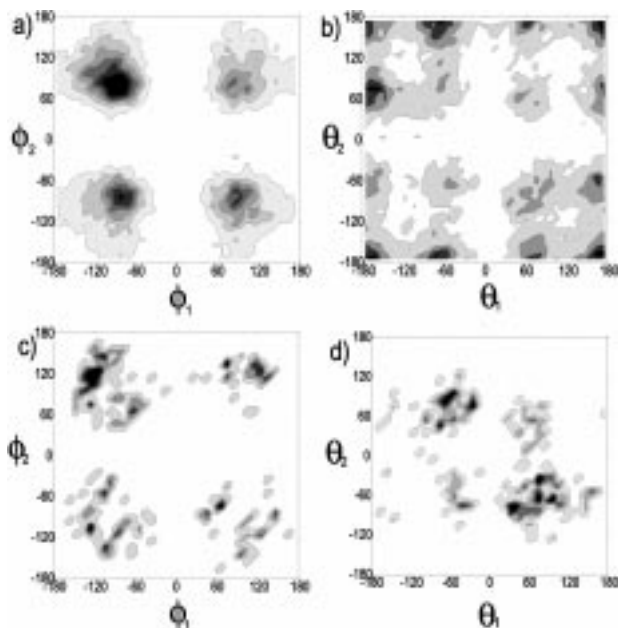


Figure 3. Correlation between angles $\theta_1-\theta_2$ and $\phi_1-\phi_2$ for Py3MPy in a vacuum at 1000 K: all conformations (top) and excimer conformations (bottom).

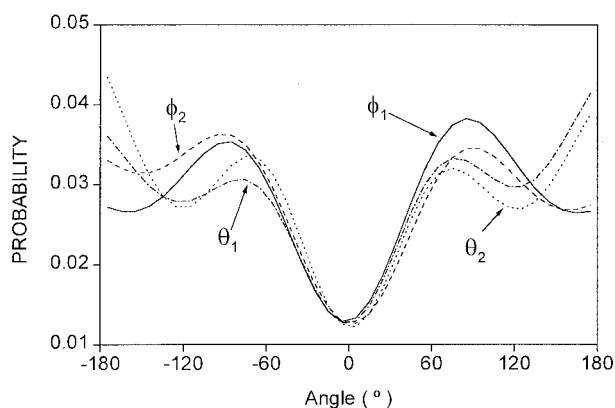


Figure 4. Probability of the torsion angles of Py3MPy adsorbed into the LDPE matrix at 333 K: ϕ_1 (—), ϕ_2 (- - -), θ_1 (- · - ·) and θ_2 (· · · ·).

these values of torsion angles ($\theta_1-\theta_2$) give rise to excimer-like conformations, it is assumed that the probability of its occurrence is proportional to the amount of excimer present.

Py3MPy in the LDPE Matrix

Rotational Angles of Py3MPy

Figure 4 shows the probability of occurrence for each conformation of Py3MPy inside the LDPE matrix as a function of the four torsion angles at ca. 333 K. Similarly to calculations for isolated Py3MPy, the highest probabilities are obtained for the two states with torsion angles ϕ_1 and ϕ_2 of ca. $c^\pm = \pm 90^\circ$. However, the torsion angle distributions are broader than in the case of the isolated Py3MPy. This fact is attributed to the interactions between the polyethylene chain segments and Py3MPy, that induce the occurrence of disturbed states. Similar behavior was obtained for the torsion angles θ_1 and θ_2 . Similar calculations were performed at 238 K, 300 K, 375 K, 390 K and 423 K. The most probable torsion angles were similar to those obtained at 333 K.

Correlation between the Angles $\theta_1-\theta_2$ and $\phi_1-\phi_2$

Figure 5 shows the probability maps for all the conformers of Py3MPy adsorbed into de LDPE matrix at 333 K (Figure 5a and 5b); in Figure 5c and 5d only excimer-forming conformations are presented. Broader distributions were obtained for the probability of conformers, g^+g^- and g^-g^+ than in the isolated case. As stated previously, intermolecular interactions with polymer segments are responsible for the occurrence of excimers in distorted conformations.

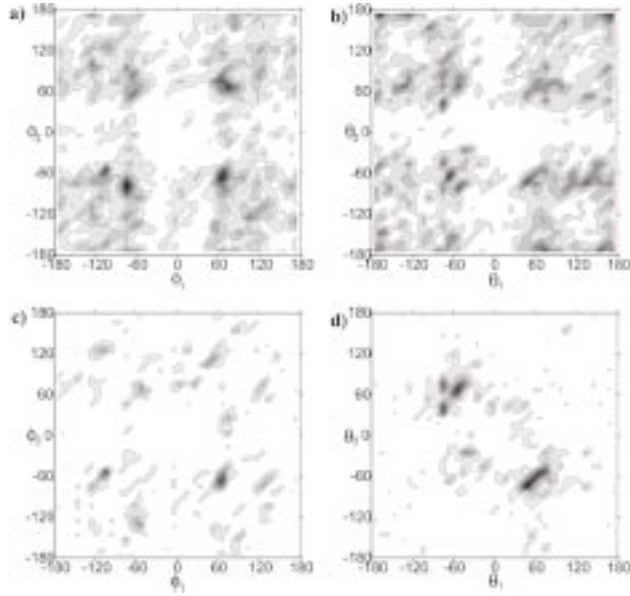


Figure 5. Correlation between angles $\theta_1-\theta_2$ and $\phi_1-\phi_2$ for Py3MPy adsorbed into the LDPE matrix at 333 K: all conformations (top) and excimer conformations (bottom).

Temperature Dependence for Sandwich-Complex Formation

In the high-temperature limit, it can be assumed that excimer formation is an equilibrium process. An equilibrium constant can be defined as:

$$K = \frac{P_E}{P_{no\ E}} = \frac{P_E}{1 - P_E} \quad (2)$$

where P_E is the probability of excimer formation. The value of free energy for the sandwich complex can be obtained from the temperature dependence on this constant.

$$\Delta G = RT \cdot \ln\left(\frac{P_E}{1 - P_E}\right) \quad (3)$$

Combining Equation (2) and (3) enthalpy and entropy changes can be computed.

$$\ln\left(\frac{P_E}{1 - P_E}\right) = \frac{\Delta H_{f,E}}{RT} + \frac{\Delta S_{f,e}}{R} \quad (4)$$

The temperature dependence on the probability occurrence of excimer conformers in vacuum (isolated form), was calculated over the temperature range ca. 600–1100 K. This temperature range was chosen to prevent the molecule trapping into some metastable state, without enough thermal energy to display conformational transitions within the simulation time. Figure 6 depicts the dependence of $\ln[P_E(1-P_E)^{-1}]$ on reciprocal temperature for the isolated molecule. The enthalpy, ΔH , and entropy, ΔS , for the excimer-formation process were determined

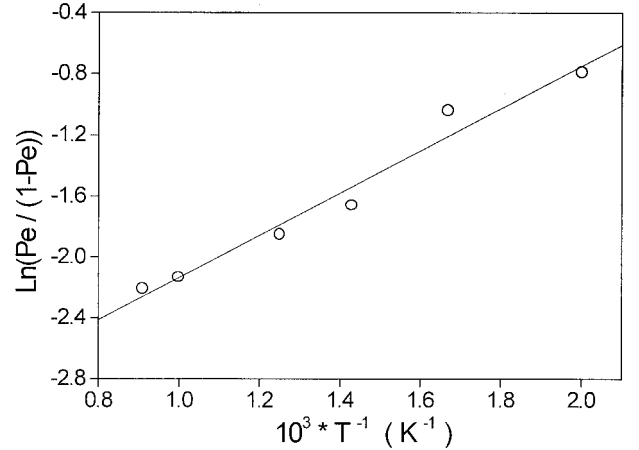


Figure 6. Variation of $\ln[P_E/(1-P_E)]$ vs. T^{-1} for Py3MPy in a vacuum.

Table 2. ΔH and ΔS for excimer formation obtained in a vacuum and in the LDPE matrix.

System	Temperature range	$\frac{\Delta H_{f,E}}{\text{kcal} \cdot \text{mol}^{-1}}$	$\frac{\Delta S_{f,E}}{\text{cal} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}}$
In vacuum	600 < T < 1100	-2.7 ± 0.2	-7.0 ± 0.3
In LDPE	T < 375	–	–
	T > 375	-0.7 ± 0.2	-5.2 ± 0.6

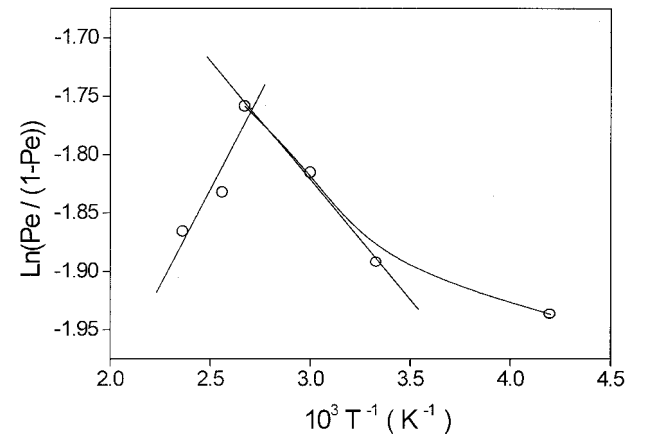


Figure 7. Variation of $\ln[P_E/(1-P_E)]$ vs. T^{-1} for Py3MPy adsorbed into the LDPE matrix.

from the slopes and the intercept of this curve (Table 2). These calculations show that the Py3MPy excimer-formation process is dependent on temperature, and it is always controlled by the enthalpy when the molecule is in the isolated form. Py3MPy is more stable when it is in excimer conformation than when it is in a more extended one.

The corresponding plot for Py3MPy adsorbed into LDPE is presented in Figure 7. A different behavior is obtained in this case. At 375 K, a maximum is observed for $\ln[P_E(1-P_E)^{-1}]$. Above 375 K, excimer formation is controlled by the thermodynamics of the process as

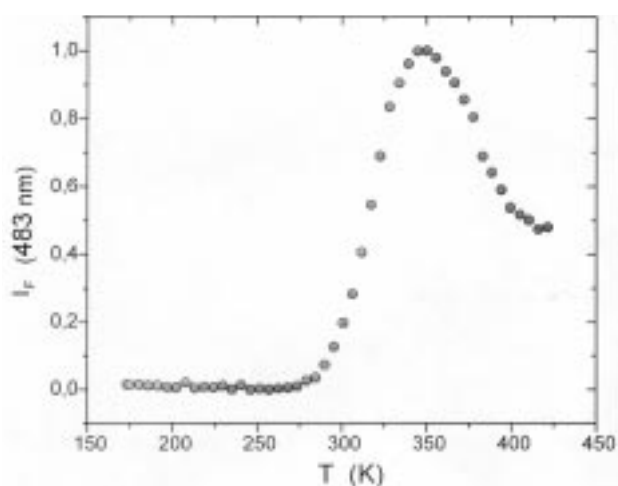


Figure 8. Excimer fluorescence intensity of Py3MPy in the LDPE matrix (adapted from ref.^[3]).

reflected by the negative sign of the slope. Below 375 K, an Arrhenius-like behavior is obtained, reflecting the influence of the matrix. The matrix may interact with Py3MPy imposing the most suitable conformations that may give rise to excimer.

In a previous experimental work using fluorescence spectroscopy,^[3] we obtained similar temperature dependence for the excimer emission of Py3MPy adsorbed into LDPE (Figure 8). The excimer emission was undetectable for temperatures below 280 K and it grew up to a maximum at ca. 375 K, which is almost coincident with the α -relaxation and with the LDPE melting process.^[3] A correlation between excimer-forming probability and polymer relaxation processes was qualitatively explained on the basis of some simple excimer-formation kinetic scheme under the low- and high-temperature limit approximations.^[25,27] Using this kinetic scheme, we considered in that paper:

1. The formation of sandwich complexes of Py3MPy inside the LDPE matrix was a diffusion-controlled

process described at the lower temperature limit, ca. <375 K. The increase of the polymer-free volume produced by the polymer β -relaxation process was considered the most important effect allowing the Py3MPy to adopt the suitable conformation for excimer formation.

2. Excimer formation at temperatures above 375 K is thermodynamically controlled (similarly to calculations made here under vacuum conditions). In this temperature range the available free volume is larger than that necessary for excimer formation and, thus, the process is intrinsically dependent on the conformational characteristics of the Py3MPy molecule.

The agreement between the theoretical temperature value calculated for the maximum probability of excimer formation, and the experimental temperature determined for the maximum fluorescence intensity for Py3MPy adsorbed into LDPE,^[3] suggests that the polymer relaxation controls the molecular conformations of Py3MPy. To prove item (1), it is necessary to calculate the volume requirements for excimer formation and to correlate it with the free-volume change of the system in the temperature range 238–375 K. Such calculation needs a deeper definition of what an excimer is from a geometrical point of view, and this is done in the next section.

Overlapping between Six-Membered Rings of Pyrene Groups

As stated previously, an excimer is formed when the pyrenyl moieties of the same molecule overlap to some extent. To obtain a deeper insight about the mechanism of excimer formation, the distribution of probability among the different possible conformers that may give rise to an excimer has been studied. All these conformers, whose overall probability of occurrence has been already presented, were distributed according to the different number of aromatic rings that overlap in the sandwich

Table 3. Overlap probability of one, two, three and four six-membered rings of pyrene groups.

		Temperature					
		600	700	800	900	1000	1100
In vacuum	1	0.147	0.129	0.065	0.057	0.048	0.042
	2	0.066	0.053	0.039	0.035	0.023	0.024
	3	0.073	0.055	0.039	0.032	0.025	0.023
	4	0.026	0.025	0.017	0.011	0.010	0.010
		Temperature					
		238	300	333	375	390	423
In LDPE matrix	1	0.038	0.041	0.042	0.049	0.047	0.050
	2	0.021	0.021	0.017	0.023	0.021	0.017
	3	0.036	0.036	0.041	0.038	0.037	0.037
	4	0.029	0.032	0.039	0.036	0.032	0.030

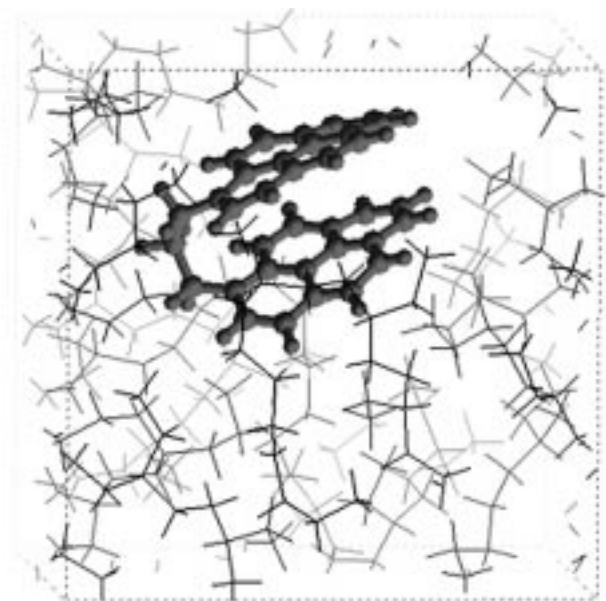


Figure 9. Illustration of an excimer conformation of Py3MPy adsorbed into the LDPE matrix.

Table 4. Radius of gyration average for non-excimer conformation and for the overlap between one, two, three and four six-membered rings of pyrene groups.

Number of overlapping rings	$\frac{\langle s \rangle}{\text{Å}}$
0	4.79 ± 0.08
1	3.94 ± 0.07
2	3.82 ± 0.08
3	3.77 ± 0.06
4	3.69 ± 0.09

complex. Thus, in a given population of excimer-forming conformers, it is possible to calculate the probability of occurrence of conformers with 1, 2, 3 or 4 rings overlapping. Results are presented in Table 3 for both isolated and inserted Py3MPy molecules. As an example of overlapping geometry, Figure 9 shows a Py3MPy conformation with four overlapped aromatic rings inside the LDPE matrix.

The calculated values in the vacuum case decrease continuously with temperature for all overlapping possibilities. This behavior is attributed to an increase of spacer mobility in the Py3MPy molecule when the temperature increases. However, the behavior for Py3MPy in the LDPE matrix is completely different. The excimer-forming probability for each overlapped complex shows a different trend with temperature. For excimers formed by the overlap of only one aromatic ring, the probability increases continuously; but for three and four overlapped rings, the probability shows a maximum at around 333 K. Since the experimental observations refer to the overall probability, it can be concluded that the experimentally observed maximum at ca. 375 K results from a combined

effect of the four complexes. This is an important difference with respect to vacuum calculations. In addition, it can be observed that in the studied temperature range, excimers formed by overlap of the four aromatic rings constitute a minimum contribution to the overall excimer probability in the isolated case, whereas in the inserted case, this contribution is clearly significant.

In Table 4, calculations of the radius of gyration of the different conformers as a function of the number of overlapped rings are presented. These calculations are averaged for all temperatures. It can be observed that the maximum value of $\langle s \rangle$, $4.8 \pm 0.1 \text{ Å}$, corresponds to a non-forming excimer conformer with no rings overlapping. The other conformations give a similar value around $3.8 \pm 0.1 \text{ Å}$. These results clearly show that excimer-forming conformers need less volume than non-excimer ones. Therefore, it seems that free volume is not the driving force for excimer formation.

Conclusions

MD and RIS/MC calculations applied to the study of the intramolecular excimer formation of isolated Py3MPy and Py3MPy adsorbed into a LDPE matrix, are capable of predicting the effect of temperature on experimentally observed behavior. The more stable conformations of Py3MPy with excimer structure were obtained for the torsion angle pairs of c^-c^+ and c^+c^+ , for angles $\phi_1\phi_2$, and g^+g^- and g^-g^+ , for angles θ_1 and θ_2 . Thus, it is expected that if some property of the system (polymer matrix/probe) increases the probability of these angles occurring, an increase in excimer probability will be induced. The enthalpic contribution obtained in a vacuum is negative for the entire temperature range, but in the LDPE matrix two different behaviors are predicted, in agreement with experimental data. For temperatures below 375 K, the process is reversed and the probability for the excimer formation increases with T . At temperatures above 375 K, well above the polymer β -relaxation, the restrictions imposed by the matrix are not very important, allowing the Py3MPy to adopt conformations suitable for excimer formation. In this temperature range, the process is only dependent on the intrinsic conformational characteristics of the Py3MPy molecule. In the low temperature range, it is revealed that free volume is not the driving force for the excimer formation process. As a matter of speculation, it is proposed that the intermolecular interaction balance could be the origin of this behavior in the low temperature range.

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