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Molecular Dynamics of Methylphenylsiloxane Chains

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ABSTRACT: Molecular dynamics is used to analyze the motions of backbone and lateral groups that lead to the formation and dissociation of excimer-forming conformations in methylphenylsiloxane. Several structures are studied: two fragments of linear poly(methylphenylsiloxane) with 14 (P14) and six (P6) monomer units, the cyclic trimer (C3) in its two configurations, cis and trans, and the disiloxane (DS) as a model for a single diad. It was found that the distribution of distances between C_1 atoms in a diad of any structure and the corresponding rotational angle distribution do not show the clear distinctions between different states that are typical of RIS models. Nevertheless, excimer-forming sites can be defined as diad conformations with distances between neighbor C_1 atoms below 4.2 Å, which correspond to ample ranges of the rotational angles (0−110° in DS), to angles between phenyl rings of about 15° with a certain staggering of the aromatic groups, and to angles between Si−C_1 bonds in neighbor rings below 45°. This conformation of the excimer-forming site is very different from the one observed in hydrocarbon analogous polymers. Large differences can also be observed in the set of movements necessary to form excimer sites in both types of polymers. In DS, P14, and P6, the two bonds of a diad rotate in a coordinated way, keeping the sum of dihedral angles about constant. Changes of $\phi_1 + \phi_2$ from any value to 30° are accompanied by changes in the angle between phenyl rings from around 90° to 15° and by the approach of the two chromophores to a distance smaller than 4.2 Å. During this time, ϕ_1 and ϕ_2 may suffer more than 20 random changes. These complex chain motions are quite different from the simple rotation through a backbone bond where either ϕ_1 or ϕ_2 changes by 120°, which is the type of motion usually associated with the excimer formation in polystyrene-like chains. Transitions to form excimer sites are also discussed in term of time-dependent distributions of the conformational variables. The frequency of transitions between excimer sites and the other conformational states is larger for C3 and for DS than for P14 and P6, and calculated relative values of the rate constant for excimer formation are in agreement with photophysical experimental results. The distribution of transition times can also help to interpret the existence of a fraction of isolated chromophores in the polymer.

Introduction

Siloxane chains are the basis for many elastomeric materials, because of their excellent elastic properties, that they retain even at low temperatures.[1] Despite differences depending on lateral substituents, the common elastomeric characteristics of polysiloxanes can be attributed to the Si−O structure of their backbone,[2] which is very “flexible” (at least, when compared with C−C, typical of vinyl and other polymers). This flexibility is the result of several molecular characteristics. First, the torsional barriers of the Si−O bonds are low, of the order of tenths of a kilocalorie, compared with several kilocalories in the case of C−C bonds.[2] Because of this low torsional barriers, the rotational states are not sharply defined, and the conformational surface is very shallow in PDMS[2] and also in some other dialkyl polysiloxane chains.[3−7] Second, the steric restraints between lateral groups, which in a C−C backbone limit chain motion, are here greatly alleviated:[2] on one hand, because the lateral groups are more distant from the backbone (the bonds Si−C are longer than C−C) and, on the other hand, because these lateral groups are also more distant from each other (the bond Si−O is longer than C−C, and the bond angle Si−O−Si is wider than tetrahedral).[2]

At the usual distances separating lateral groups, the interactions between them are attractive rather than repulsive.[2] This attraction is especially important when the substituent is a phenyl group.[8,9] Thus, in poly(methylphenylsiloxane) (PMPS), the attraction between consecutive phenyl groups is the dominant interaction for the conformational properties of the chain.[8,9] Because the attraction between phenyl rings is stronger than the other interactions, the conformational surface of PMPS chain is not as shallow as that of PDMS. Thus, the PMPS surface presents a well, rather profound (3 kcal), which corresponds to the conformational states where two consecutive phenyl rings are at a close distance.[9] But energy barriers of 3 kcal, although much higher than in PDMS, are still small when compared with the barriers in C−C chains. So, it continuous to hold with PMPS what is said about PDMS, that the rotational states are not sharply defined. Thus, the conformational energy maps for the diads of PMPS show wide ranges of rotational angles where the energy changes by less than 0.5 kcal.[9]

But the siloxane structure is soft not only with respect to torsion but also with repect to bending. Fluctuations in the Si−O−Si angle are large, so a model structure rigid with respect to bond angles suffers. Relaxing structures change the picture, because they allow states that are prohibited in the rigid structure, thanks to small distortions in bond lengths and bond angles (besides the fluctuations in torsion).[4−7,9] The softness allows also for the appearance of particular sequences

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of rotational states whose stability is determined by the coupling or interactions between the lateral groups of the sequence, more than by the stability of the backbone rotational states themselves, which in fact are ill-defined. Thus, very stable triad conformations are determined by interphenyl attraction in PMPS,[9] and tetrad and longer sequences are determined by steric couplings between the lateral alkyl chains in polydialkylsiloxanes.[6,7]

The phenyl substitution of PMPS has the additional interest that the lateral group is a chromophore, which allows for the study of the polymer with the resources of photophysics.[10,11] Especially extensive has been the study of the fluorescence emission from PMPS.[12−23] Since the chromophores are directly attached to the backbone, the state and motion of the phenyl groups (as detected by the fluorescence) should be a direct consequence of the conformational states and dynamics of the backbone. The formation of excimers by pairs of phenyl rings depends on the conformation of the chain: either on the equilibrium distribution of conformational states or on the dynamic of transitions between these states, depending on whether the lifetime of the excited chromophore is shorter or longer than the average time required for a transition between conformational states.

For an excimer between two chromophores to be formed, the backbone bonds have to rotate such that they place the two phenyl rings at a short distance in the sandwich-like conformation which is typical of excimers. Because of the wider Si−O−Si angle, the planes of two consecutive phenyl rings are not perfectly parallel when they form this sandwich-like conformation in the PMPS chain.[12] Also, the two consecutive phenyl rings have some rotational freedom in this sandwich-like conformation of PMPS.[24] Both things are contrary to what happens in a C−C backbone, such as polystyrene, where the planes of consecutive phenyl rings are parallel and severely restricted to rotation.

The modeling of the polymer chain by means of a relaxing (instead of fixed) structure should be especially needed for the analysis of excimer-forming conformations. In these conformations the distances between phenyl rings are shortest, and small displacements from fixed bond lengths, fixed bond angles, and defined rotational isomers should contribute to their relative stability. We shall adopt here such a relaxing structure in order to analyze the excimer-forming conformations of PMPS. The kinetics of the process by which the chain falls into one of these excimer-forming conformations is one of our aims here, also, since it may be helpful for the interpretation of experimental rate constants from photophysics. To this end, we use molecular dynamics simulation (MD) and obtain the frequency of transitions between conformational states. This calculation is not so straightforward here as it is in C−C chains, because the conformational states of the siloxanes are not sharply defined and, therefore, no clear jumps between them serve to define transitions. Previous results on the distribution of rotational angles for the backbone bonds in PMPS have shown that all values of the rotational angle have a significant probability.[25] Although the distribution function has maxima close to the traditional states t, g^+, and g^-, the valleys in between are at a considerable height.[25] This poses a difficulty for the definition of transitions between states, as we shall see when analyzing the results of the MD trajectories.

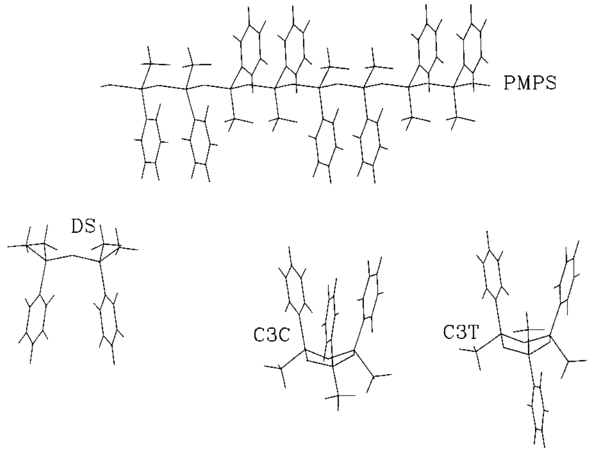

Figure 1. The molecules studied.

The kinetics of excimer formation between two consecutive chromophores (diad) is usually analyzed considering a one bond rotation of the backbone from a nonexcimer conformation to an excimer-forming one. However, in PMPS the two backbone bonds of the diad rotate in a coordinated fashion, such that the lateral groups are not displaced from each other at the same rate as the individual bonds rotate.[25] So, the time needed for a bond rotation is roughly 1 order of magnitude shorter than the time needed for the approach of two phenyls to an excimer-forming conformation.[25] This poses another difficulty for the analysis of the transitions in the simulation.

In the present work we analyze in detail, with the help of MD, which are the backbone and lateral group motions that lead to the formation and dissociation of excimer-forming conformations. We shall try to answer several questions. First, which molecular parameters are needed to define such formation and dissociation? Is the scalar distance between the centers of mass of the two phenyl groups enough, or is it necessary to define also the angle between the planes of the two rings? Which are the special combinations of the two backbone rotational angles in a diad that lead to such formation and dissociation? Do other combinations of rotational angles in longer sequences, triad, tetrad, etc., contribute significantly to excimer-forming conformations not included in the diads? Second, we try to estimate with MD the kinetic parameters that are obtained from experiment. The experimental time-resolved monomer and excimer decays of these polymer systems have shown that the main contribution to excimer formation is kinetic, due to a conformational transition monomer → excimer, but that there is also a sizable contribution from monomers that cannot suffer such conformational transition in the lifetime of the chromophore (isolated monomers) and that there is also a static contribution, due to the direct excitation of pairs of monomers that are coupled in the ground state (preformed dimers). Is it possible to recognize these contributions in the MD trajectories and obtain estimates for the kinetic parameters? This aim leads the work to be described in the sequel.

Methods

Molecules. The molecules studied (Figure 1) are all methylphenyl-substituted siloxanes, but they belong to three different classes: (a) linear fragments of the PMPS chain; (b) the cyclic trimer; (c) the disiloxane. Two linear fragments are studied, one with 14 monomer units (P14) and the other with six monomer units (P6). Both are end-capped with −OH groups, and their tacticity is 100% heterotactic triads, namely, alternation of meso (*m*) and racemo (*r*) diads. This overall tacticity resembles that of most real polymers, in which the proportion of *m*/*r* diads is nearly 50/50% and the relation of iso/hetero/syndio triads nears 25/50/25%.[10] So, the tacticity chosen here, albeit regular, is the one more akin to that of polymers being studied experimentally. The tricycle is modeled here in its two stereochemical configurations: cis (C3c) and trans (C3t). The cis isomer has all three phenyl groups on the same side of the cycle plane, while the trans isomer has two phenyl groups on the same side and the third phenyl group on the opposite side of the cycle plane. The disiloxane is 1,1′,2,2′-tetramethyl-1,2-diphenyldisiloxane (DS). It is used here as a nonpolymeric model.

Molecular Dynamics. The MD calculations have been performed with the module *Discover 3* from Molecular Simulations Inc.[26] The force field and dielectric constant have been the same described before when reporting conformational energy maps.[9] Temperature for MD has been 300 K. Because of the flexibility of the siloxane chain, enough transitions occur at 300 K without the need to go to higher T. The molecular structure is first optimized until minimum energy (with a criterion of 0.001 for maximum derivative). This minimized structure is heated gradually until the working temperature is attained. Then long thermalization takes place: first by direct velocity scaling, for 1 ns, and then with the Nosé method, for another 1 ns. After this thermalization, the trajectory in which data are collected starts. The same Nosé method is used, with an integration time step of 0.25 fs. The frequency of data collection and the time length of the trajectory vary, depending on the size of the molecule and the property being analyzed. The extreme cases are as follows. For bond rotations a finer frequency is required, and this can reach down to 5 fs (in order to test that the results being obtained are not sensitive to the frequency). For equilibrium distribution of distances a longer trajectory is needed, and this can reach up to 2.5 ns, but then the frequency is coarser. The minimum number of frames analyzed in each case goes from 5001 for the largest molecule, P14, to 20 000 for the smallest one, DS. But P14 consists of 13 diads, so each one of the 5001 frames of P14 contains six samples representing *m* and *r* diads.

The DS molecule has been used to check that the MD procedure described above gives true statistical probabilities at T. To this end, we have compared the occurrence of conformational states in the MD trajectory with the probabilities calculated at T from the energies obtained by minimization. The conformational energies are obtained by scanning the two backbone bonds of DS, ϕ_1, ϕ_2, at 5° intervals, with averaging over rotations of the lateral groups at each fixed ϕ_1, ϕ_2 pair. As example, the region of the conformational map $-150^\circ > \phi_1 > 30^\circ$, $-30^\circ < \phi_2 < 150^\circ$ (one-quarter of total map) (trans is 0°) has a Boltzmann probability, calculated from the conformational energies, equal to 0.56, at 300 K. The fraction of total frames within this same region in a MD trajectory (300 K) is also 0.56.

Results

The sandwich-like conformation of two phenyl chromophores is met when the two rings overlap in a parallel arrangement, at a close distance. For two consecutive phenyl rings this requires that the intervening Si−O, O−Si bonds adopt special values of their rotational angles. We shall discuss later the rotational angles and the parallelism between rings and start, first, with the distance between the two phenyl groups.

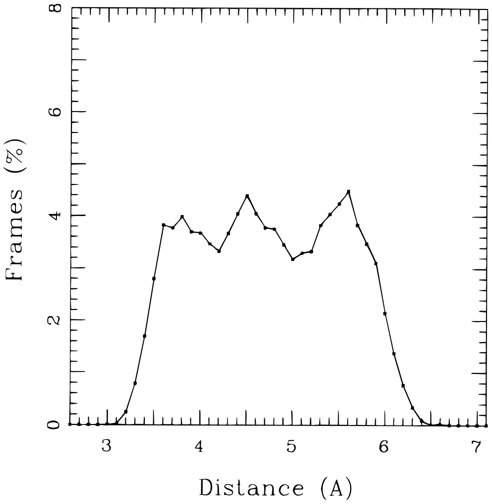

Figure 2. Distribution of distance between phenyl rings, *d*, in disiloxane (DS).

Distance Distribution. To characterize the approach of two consecutive phenyl rings, we use the distance *d*, defined as the distance between the phenyl ring C atoms that are directly bonded to Si. In a chain molecule there is a distance *d* for each pair of monomer units. In Figure 2 it is shown the distribution of distances for disiloxane (DS). The distribution is very flat, there is no clear distinction between differentiated states, and almost any separation between phenyls (within the range allowed by the geometry of the molecule) is equally likely. So, there is an arbitrariness in defining the range of *d* values that should represent the excimer-forming state. We shall see later how we can resolve this ambiguity, but for the moment, let us proceed taking $d < 4.2$ Å as the upper bound to define excimer-forming states. In minimization, the shortest distance found is 3.6 Å. Here, at 300 K, the distribution starts at 3.2 Å, or 0.4 Å shorter than the minimum value at 0 K. At $T > 0$, excimer-forming conformations should cover a range of distances above and below 3.6 Å, due to fluctuations, and this range should be wider above the minimum than below it. Thus, cutting at 4.2 Å, or 0.6 Å above the minimum, seems reasonable to define excimer-forming states. With this definition, 29.6% of all frames are excimer-forming states in DS.

In Figure 3 we show the distribution of distances for the linear polymer (P14). This chain has 13 *d* values (13 diads), of which we have chosen 10 central ones (5 *m* and 5 *r*) for averaging. There are some differences between the *m* and *r* distributions. The percentage of excimer-forming states ($d < 4.2$ Å) is larger for *r* than for *m* diads. The difference can be justified in terms of steric effects between the methyl groups. In an excimer-forming conformation the two phenyls are in front of each other (four bond interaction: Ph···Ph). The other groups facing each other (in this conformation) are Me···Me, in the *m* diad, and Me···O, in the *r* diad; hence a higher steric retraint in the *m* case.

Comparing Figures 2 and 3, one sees that the distribution for the linear polymer differs notably from the

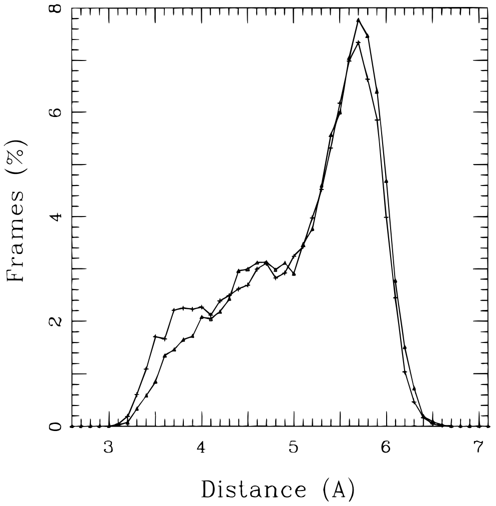

Figure 3. Distribution of distances between consecutive phenyl rings, *d*, for the diads *meso* (△) and *racemo* (+) in the linear polymer (P14). Mean values over five *m* and five *r* diads (the central ones, excluding terminals).

distribution for the dimer (DS). The difference has no consequence, however, on the fraction of time a given chromophore spends in an excimer-forming state. Using the criterion $d < 4.2$ Å, we find that the average diad (average over all 13 diads in P14) has 15.2% of its frames in an excimer-forming conformation. But each phenyl group belongs to two diads, so it spends 15.2% of the time in an excimer-forming conformation with the neighbor on one side and another 15.2% with the neighbor on the other side—overall 30.4%, practically as in DS. The appearance of the diad distribution is different because, in the case of the polymer, each phenyl group has two other neighbors to choose, while in the dimer it has only one.

The percentage of excimer-forming states could be counted on a per chromophore basis. In such a scale, the dimer has 29.6/2 = 14.8% (DS) and the linear polymer has 15.2 × 13/14 = 14.1% (P14). Over this value, there can be an additional enhancement of the polymer with respect to the dimer, if there are excimer-forming conformations in sequences longer than the diad, namely, if two phenyl rings at the ends of a triad, a tetrad, and so on couple together in a sandwich-like conformation. The distribution of distances for triads, tetrads, etc. (not shown) have very low values for $d <$ 4.2 Å. Under such upper bound for *d*, an average triad (average over the 12 triads in P14) gives excimer-forming states only in 2.7% of total frames, whereas tetrads and higher sequences have insignificant contributions. So, counting on a per chromophore basis, triads add another 2.7 × 12/14 = 2.3% of excimer-forming states to the linear polymer (P14).

Let us consider now the cyclic trimer. In the cis isomer (C3c), any phenyl group has the other two as neighbors to give an excimer-forming state. But, in the trans isomer (C3t), one of the phenyl groups is on the opposite side of the cycle and never gives an excimer-forming state, so the other two phenyls can give such state only with each other. With the condition $d < 4.2$ Å, the percentage of total frames giving excimer-forming states is 27.7% for the diad of the trans isomer and 23.1% for the average diad of the cis isomer. The cyclic trimer experimentally studied is $^1/_4$ cis and $^3/_4$ trans. So, the weighted average, per diad, or per chromophore, is 12.7% (C3). The proportion in C3 is lower because of the phenyl which never gives an excimer-forming conformation.

Table 1. Distribution Function for the Backbone Rotational Angles in the Polymer Chain (P14) (Average over All 26 Rotational Angles)

rotational angle, ϕ (deg)	distribution function	rotational angle, ϕ (deg)	distribution function
−180	0.0198	0	0.0432
−120	0.0325	60	0.0233
−60	0.0272	120	0.0212

The distance distribution of DS (Figure 2) is rather uniform, and no clearly separated states can be discerned. However, one can see three faint peaks, which could be attributed to the presence of three states (with respect to interphenyl distances). Although such three states overlap extensively, one can crudely choose their limits at 4.2 and 5.1 Å, which correspond to distinct features in the distribution of both the dimer and the polymer (Figures 2 and 3). At approximately these values of 4.2 and 5.1 Å the distribution of DS has minima (marking the border between two peaks), and the distribution of P14 has inflection points (marking the border between two shoulders or shoulder and peak).

Rotational Angles. This division into three states according to distance represents a selection or filtering of rotational states of the chain.

The rotational angle distribution is a rather smooth function, which nowhere vanishes, so that a nonzero baseline remains between the peaks.[25] As an illustration of this baseline, we give, in Table 1, the distribution at regular intervals of the rotational angle. The difference between the maximum peak and the lowest valley (0.043 − 0.020 = 0.023) is of the same magnitude as the valley itself.

The state of $d < 4.2$ Å has this baseline filtered out, so that only peaks departing from zero remain, and the state $d > 5.1$ Å filters out any peaks and has only a constant baseline. This can be seen in Figure 4 for the two rotational angles of DS. But, even after having filtered the constant baseline, the peaks that remain are still very broad, giving similar probabilities to ample ranges of rotational angles, rather than defining narrow rotational isomeric states.

Angle between Phenyl Rings. This filtering of states according to distance also affects the parallelism between the planes of the two phenyl rings. We define the angle formed between these two planes as φ. In the excimer-forming states the rings should be parallel ($\varphi = 0°$). The distribution of φ for the range of distances $d < 4.2$ Å in fact presents sharp maxima close to $\varphi = 0°$, but they occur at $\varphi = \pm 15°$, that is, slightly displaced from perfect parallelism, which can justify the lower stability of excimers in these siloxanes.

By specifying the condition $d < 4.2$ Å, we get significant values of the φ distribution only in a restricted range of ±30° around these maxima and negligible values when the planes are in positions close to perpendicular ($\varphi = 90 \pm 30°$). Thus, when the phenyl rings approach each other from the point of view of distance, they do it adapting the angle between planes to the close to parallel position. On the contrary, by specifying the condition $d > 5.1$ Å, the distribution has its maximum at the perpendicular position ($\varphi = 90°$). Therefore, *d* is enough criterion to define excimer-forming states.

Angle between Si−Ph Bonds. A similar conclusion can be reached if we consider the orientation between the phenyl rings by defining the vectors that join each

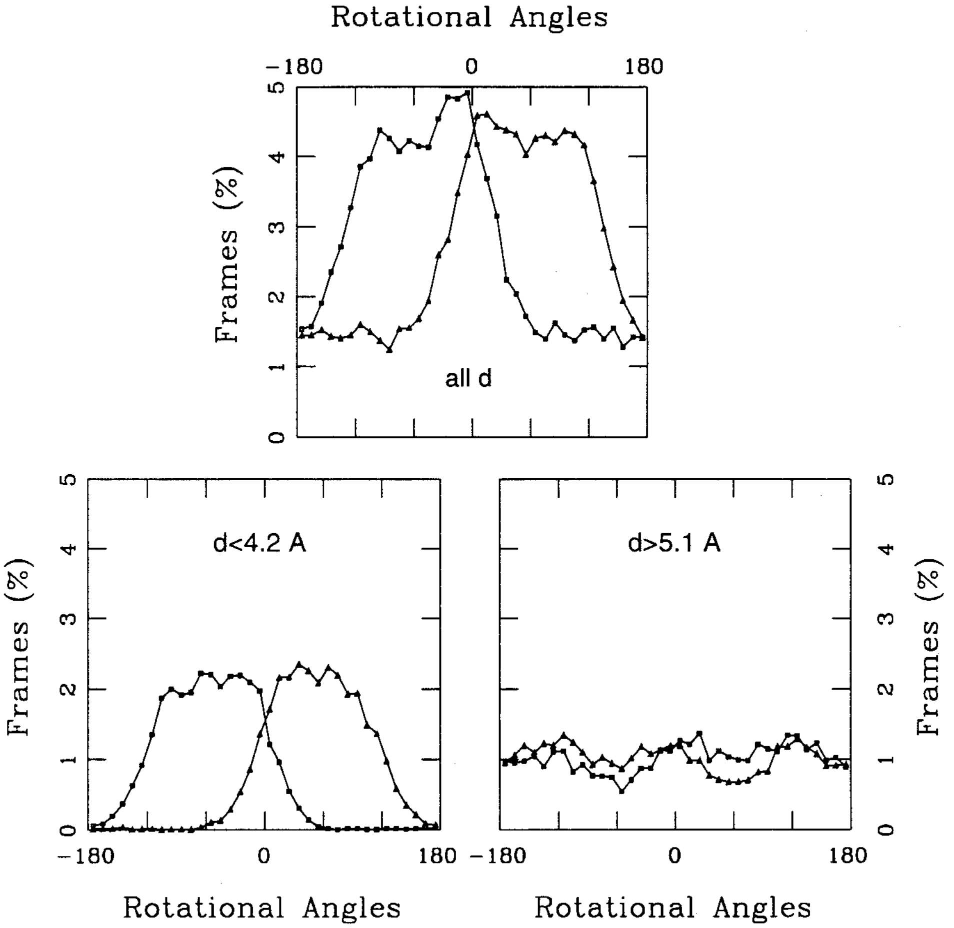

Figure 4. Distribution of rotational angles, ϕ_1, ϕ_2, for bonds Si−O and O−Si, in the dimer (DS), selected according to ranges of the interphenyl distance, *d*.

ring (its C atom) to the backbone (Si). We call ψ the angle formed by two such vectors of consecutive units. The time evolution of ψ is entirely parallel to that of *d* along the trajectory. There is a certain equivalence between the dividing limits of scalar distance $d < 4.2$ Å, $d > 5.1$ Å and the limits $\psi < 45°$, $\psi > 90°$ for the range of angles between vectors.

This equivalence can be more strikingly seen by dividing the distance distribution into blocks corresponding to separate ranges of the angle between vectors. In Figure 5 are shown these partial distance distributions of DS that result when ψ is separated in the ranges $\psi < 45°$, $45° < \psi < 90°$, $\psi > 90°$. We can see that each range of ψ corresponds to one of the three peaks in the distribution of *d*. So, separating states according to scalar distance is very much the same as separating states according to angle between vectors.

There is practically no overlap between the distribution for $\psi < 45°$ and the distribution for $\psi > 90°$. So, these two angle ranges correspond to clearly separated states according to distance. The distribution for the intermediate range $45° < \psi < 90°$ overlaps with the other two, and the points where it crosses with them are precisely $d = 4.2$ Å and $d = 5.1$ Å. Thus, the probability of distances $d < 4.2$ Å is always higher in the distribution for $\psi < 45°$, and the probability of distances $d > 5.1$ Å is always higher in the distribution for $\psi > 90°$. Despite the overlap, the three partial distributions represent distinct states, and therefore, it seems justified to simplify things using only the criterion based on *d* to classify the states that are excimer-forming ones.

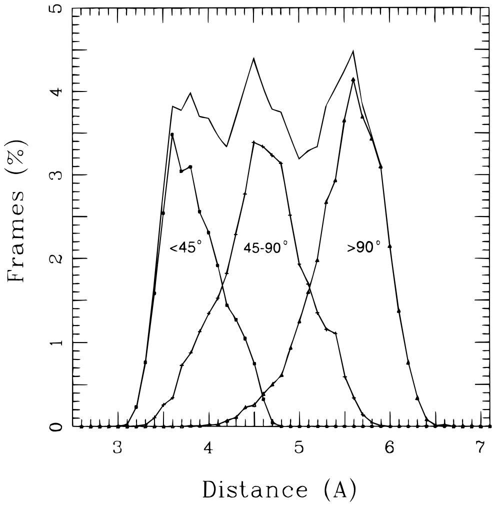

Figure 5. Distribution of interphenyl distances, *d*, for selected values of the angle between Si−Ph vectors, ψ, in the dimer (DS). Curves are for all ψ; $\psi < 45°$; $45° < \psi < 90°$; and $\psi > 90°$.

Coordinated Backbone Rotations. The time evolution of the backbone rotational angles shows that the two bonds of a diad (Si−O, O−Si) rotate in a coordinated way. For most of the time, when one bond rotates in one sense, the other bond rotates, equivalently, but in the opposite sense.[25] In this coordinated motion, the two phenyls attached to the Si atoms suffer almost no displacement with respect to each other.[25] That is, ϕ_1 and ϕ_2 change values during this rotation/counterrota-

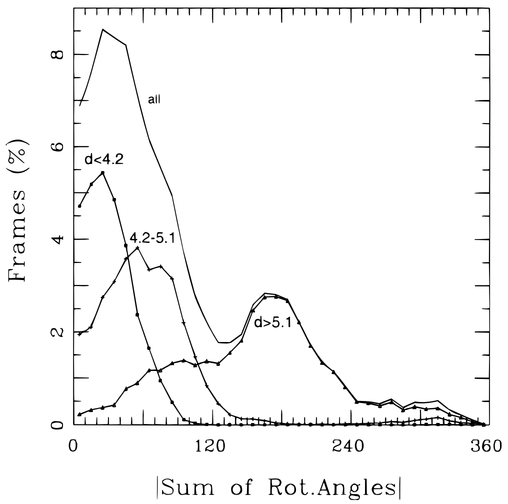

Figure 6. Distribution of the sum of dihedral angles, $|\phi_1 + \phi_2|$, for the backbone bonds Si–O, O–Si in the dimer (DS), for selected values of the interphenyl distance, d: $d < 4.2$ Å; $4.2 < d < 5.1$ Å; $d > 5.1$ Å.

tion, but d stays constant. Since ϕ_1 and ϕ_2 change values in opposite senses, their sum stays constant, the same as d. So, $\phi_1 + \phi_2$ and d should be correlated.

In fact, the time evolution of the sum of dihedral angles, $\phi_1 + \phi_2$, and of the interphenyl distance, d, are entirely similar. Each individual ϕ_i varies with time faster,[25] but their sum, $\phi_1 + \phi_2$, and the distance, d, vary more slowly, because of the coordination between the rotations of the two bonds in the diad.

In Figure 6 is shown the distribution of $|\phi_1 + \phi_2|$ for DS. We see that the partial distributions corresponding to the states $d < 4.2$ Å and $d > 5.1$ Å have their maxima at $|\phi_1 + \phi_2| = 25°$ and 175°, respectively. The perfectly eclipsed conformation of the two phenyl rings would correspond to $|\phi_1 + \phi_2| = 0°$, so the value 25° indicates a certain staggering in the excimer-forming states (again a possible source of the relatively lower stability of PMPS excimers). This sum of dihedral angles, $|\phi_1 + \phi_2| = 25°$, can be achieved by different combinations of the individual ϕ_1, ϕ_2. In Figure 7 are shown three examples of conformations having $|\phi_1 + \phi_2| = 30°$ with different values of ϕ_1, ϕ_2. We can see that each of the individual angles rotates up to 90° while the interphenyl distance remains within the region of excimer-forming states ($d < 4.2$ Å). (Here, the individual angle values shown are for the rotational angles defined with respect to the phenyl lateral groups, and taking trans as 180°, because this definition gives a clearer picture of the conformational map.)

The conformational map of a diad represents ϕ_1 as abscissa and ϕ_2 as ordinate. The conformations that have the same value of $|\phi_1 + \phi_2|$ lie, in such a map, along a line that is parallel to the diagonal (see Figure 7). So, the coordinated rotations of the backbone give large displacements in abscissa and ordinate, but keeping nearly parallel to the diagonal, and the distance, d, changes more slowly than the individual ϕ_i's.

The transition from a nonexcimeric state to an excimer-forming one requires a displacement toward the diagonal, namely, some deviation from the strictly parallel line. An example of such transition from a nonexcimer state to an excimer-forming one is shown in Figure 8, for the middle diad in the polymer chain (P6). The interphenyl distance starts at 5.68 Å and ends at 3.32 Å, during this piece of trajectory. Simultaneously, $|\phi_1 + \phi_2|$ starts at 91° and ends at 24°, but the individual angles change much more: ϕ_1 by 179° (from −121° to 58°) and ϕ_2 by 245° (from −150° to −180° and then from 180° to −35°). It is conceivable that the approach and separation of phenyl rings could occur along lines that cross the conformational map perpendicular to the diagonal and not always parallel to it, but this perpendicular route is not seen in the trajectories.

When the interphenyl distance changes, the points of the trajectory suffer obviously a certain displacement

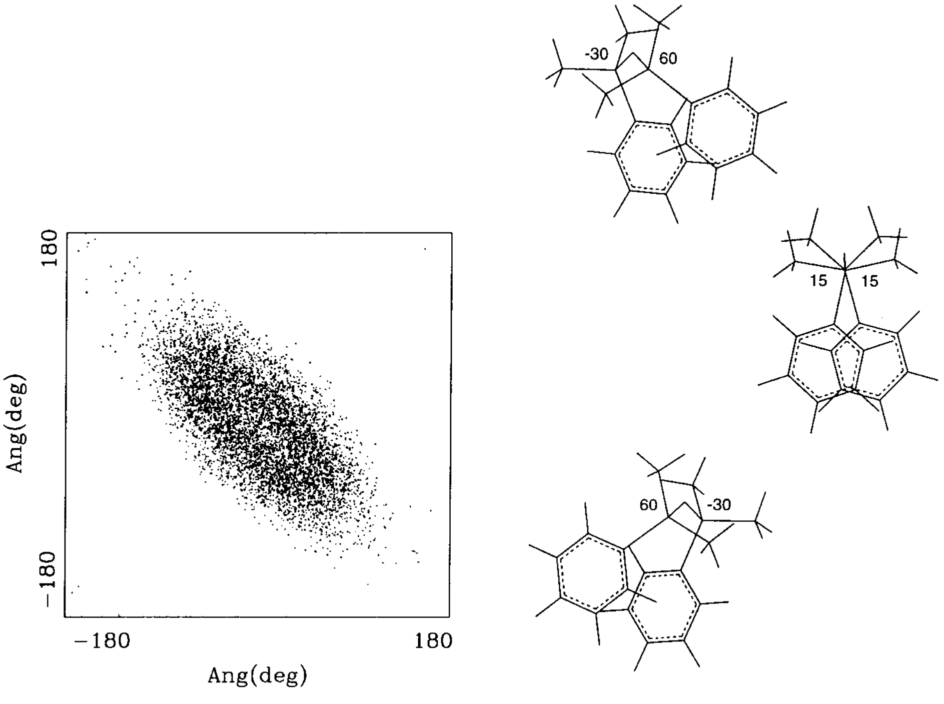

Figure 7. Three conformations having the same sum of dihedral angles, $|\phi_1 + \phi_2| = 30°$, and conformational map, ϕ_2 vs ϕ_1, showing the points of the MD trajectory which give $d < 4.2$ Å, for the dimer (DS). (ϕ is defined with respect to the phenyl groups and taking 180° as trans.)

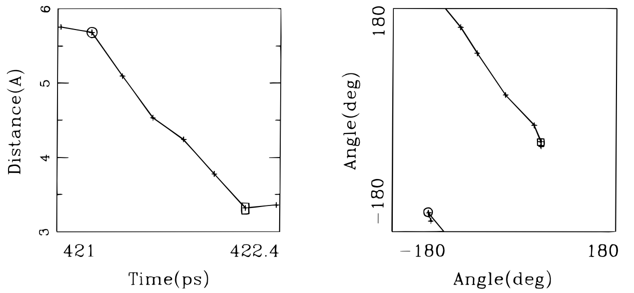

Figure 8. One of the transitions to an excimer-forming conformation suffered by the middle diad in the linear polymer (P6). Interphenyl distance, *d*, as a function of time and conformational map for the two backbone dihedrals, ϕ_2 vs ϕ_1.

in the direction perpendicular to the diagonal. Thus, in the transition of Figure 8, the end point is closer to the diagonal than it is the starting point. But this displacement toward the diagonal does not occur by direct crossing of the map in a perpendicular direction (which would be the shortest path in order to reduce the interphenyl distance). Instead, it occurs by gradual sliding toward the diagonal along a line that is mostly parallel to it. It happens in this way because of the coordination in the motions between the two backbone bonds of the diad.

Time-Dependent Distributions. We can follow the time evolution of the distribution of states. This can be helpful in defining transitions between excimer-forming states and nonexcimer states. At a certain instant, a given backbone bond is in a rotational state, $\phi(0)$, and a given diad is in an interphenyl distance state, $d(0)$. After a certain time interval, t, these values have changed to $\phi(t)$ and $d(t)$, respectively. As starting time we can take any frame along the trajectory. So, considering all frames, we count how many times the backbone bond has rotated by the amount $\phi(t) - \phi(0)$ from any starting value $\phi(0)$ or how many times a diad has moved phenyl groups by the amount $d(t) - d(0)$ from any starting value $d(0)$. In this way, we get the distribution of $\phi(t) - \phi(0)$ or $d(t) - d(0)$ after an interval t has elapsed from any point in the trajectory. We do this for different values of t. The distribution obtained is time-dependent. For very short times, it is almost a delta function, because nearly all bonds or diads are still in their starting values. As time advances, the distribution flattens progressively with t, because bonds rotate and phenyl groups change distance increasingly from their starting positions. At sufficiently long times, the distribution finally stays constant. This happens when the bonds or diads have enough time to reach equilibrium from the starting point.

In Figure 9 we give an example of time-dependent distribution for the rotational angle of a middle bond in the polymer backbone (P14). The distribution is given at four different values of the time interval: $t = 0.1$, 1, 10, 100 ps. Note that there is a point where the four curves meet or a point where the rotation is equally frequent or probable at all time intervals. Such a situation is like a spectroscopic isosbestic. Isosbestics denote interconversion between two different states. Here, it should be between two different rotational states. This point of constant probability occurs at $\phi(t) - \phi(0) = \pm 60°$. This is reasonable, because the states of higher probability in the equilibrium distribution of rotational angles are separated by 120° (Table 1).[25] Thus, a jump of 120° between these states would give an isoprobable point at the middle of the range (60°).

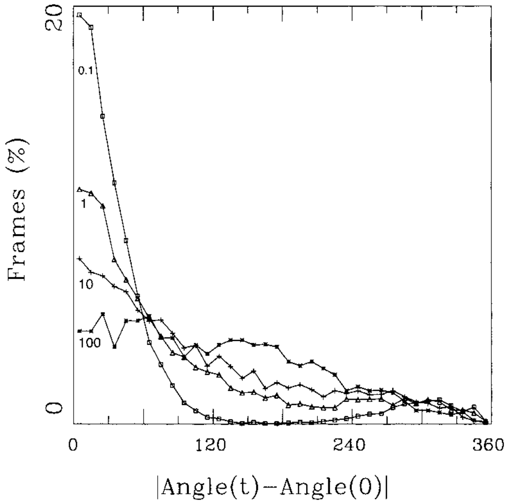

Figure 9. Time-dependent distribution of $|\phi(t) - \phi(0)|$, for the rotational angle of a middle backbone bond in the polymer chain (P14), after different time intervals: $t = 0.1$, 1, 10, 100 ps.

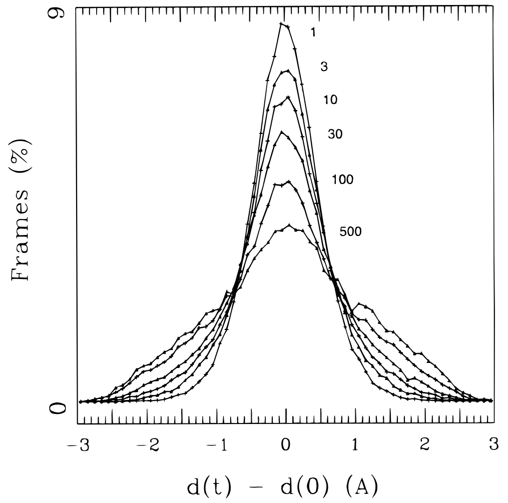

Figure 10. Time-dependent distribution of $d(t) - d(0)$, for the interphenyl distance of an average diad in the polymer chain (P14) (average over the 10 middle diads), after different time intervals: $t = 1$, 3, 10, 30, 100, 500 ps.

In Figure 10 we show the time-dependent distribution for the interphenyl distance, $d(t) - d(0)$, of an average diad in the polymer chain (P14) (average over the 10 middle diads). The curves correspond to six different time intervals: $t = 1$, 3, 10, 30, 100, 500 ps. Note that here, also, we find points of constant probability, where the curves corresponding to different times meet. Again, an interconversion between two different states is taking place, but now the two states are defined by the interphenyl distance. The value of d at which this isoprobable point occurs is $d(t) - d(0) = \pm 0.75$ Å. Thus, the two d states that are interconverting differ by 1.5 Å. So, when speaking about transitions between d states, one should be considering jumps of the order 1.5 Å.

However, the states in d are not clearly resolved; there is a lot of overlap. This led us before to define the excimer-forming states by an upper bound in d and the nonexcimer states by a lower bound in d. The difference between these two limits (4.2 and 5.1 Å) was 0.9 Å, to which there should correspond a larger difference when measured between the cores of the ranges bounded by

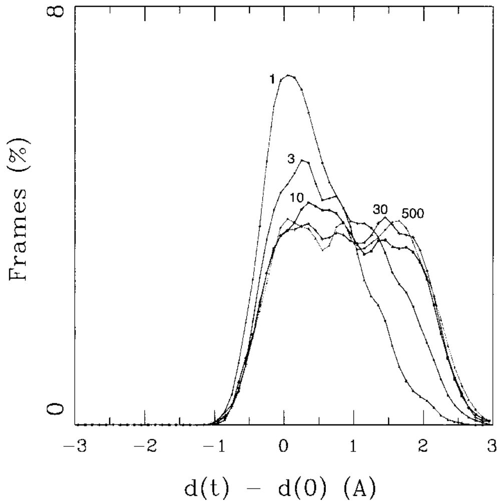

Figure 11. Partial time-dependent distribution (smoothed) of $d(t) - d(0)$, corresponding to the range $d(0) < 4.2$ Å; for the interphenyl distance of the dimer (DS), after different time intervals: $t = 1, 3, 10, 30, 500$ ps.

the limits. Where the cores are exactly located is not possible to say because of the overlap, but we could guess by looking at the maxima or shoulders in the equilibrium distribution (Figures 2 and 3). There is a state of short distances at 3.8−3.9 Å (from the maximum in DS or the shoulder in P14) and a state of long distances at 5.6−5.8 Å (from the maxima in DS or P14). The difference between both is about 1.8−1.9 Å, similar to the value now found. It is clear that the difference between the limits that bound states should be larger than 0.75 Å, the distance for interconversion, and that the centers of the states should differ by about 1.5 Å.

There is a third state in between these two limits. It corresponds to the conformations in the middle of the transition between the excimer-forming state and the nonexcimer state. Each diad spends a considerable fraction of time in these intermediate conformations, and in many cases, it leaves an excimer-forming or a nonexcimer state to this intermediate one but returns to the same state of departure instead of crossing to the opposite one. In these cases we cannot speak of a transition excimer-forming state ↔ nonexcimer state. For this reason, we are paying attention only to the extreme states, because we assume that a true transition occurs only when the diad passes from one of these to the other. If it enters into the intermediate state but returns to the starting one, we take that just as a fluctuation, not as a conformational jump.

Up to now we have analyzed the overall time-dependent distribution. This includes all values of d as starting states, $d(0)$. A deeper insight could be gained by looking at the different d states separately, that is, by dividing all the initial states, $d(0)$, into three blocks, corresponding to the three states $d(0) < 4.2$ Å, $4.2 < d(0) < 5.1$ Å, $d(0) > 5.1$ Å, and following the time evolution of each block separately. In this way we get the partial time-dependent distribution for each d state. In Figure 11 is shown the partial time-dependent distribution function (smoothed), which starts from the excimer-forming states: $d(0) < 4.2$ Å, in the dimer (DS). These starting excimer-forming states dissociate as time advances, the sharp peak broadens, and the distribution displaces to longer distances, until it gives a broadened version of the equilibrium distribution of Figure 2. When the starting states are nonexcimer, $d(0) > 5.1$ Å, the starting peak also broadens, but now evolving toward excimer-forming states, and the distribution displaces toward shorter distances, until, at the end, it also gives a brodened version of the equilibrium form of Figure 2.

Table 2. Frequency of Transitions to Excimer-Forming States (As Measured by Interphenyl Distance Approach, *d*) and Frequency of Transitions between Backbone Rotational States (*ϕ*)

	DS	P14	P6	C3
interphenyl distance, d	107 ns^{-1}	41 ns^{-1}	43 ns^{-1}	98 ns^{-1} (cis); 122 ns^{-1} (trans)
backbone rotation, ϕ	0.6 ps^{-1}			

In these partial distribution functions of the dimer (DS) the equilibrium form is reached after 20−30 ps. The same analysis, when performed on the diads of the linear polymer (P14), yields a much slower relaxation toward equilibrium. Not until 100−200 ps can the distributions be considered constant with time in the polymer. So, the mechanism of formation and dissociation of the excimer-forming conformations is much the same in the dimer and in the polymer, with equal states and distances, but the relaxation toward equilibrium is slower in the polymer.

Frequency of Transitions. This different relaxation of polymer and dimer could be detected directly by counting the number of transitions between states that occur, per unit time, in each system. For the reasons given above, we count as transition nonexcimer state → excimer-forming state every time d enters the range $d < 4.2$ Å coming from the range $d > 5.1$ Å. In the piece of trajectory between the moment d leaves $d > 5.1$ Å and the moment it reaches $d < 4.2$ Å there can be other crossings of any of these two limits, but they are considered fluctuations, not real transitions, and thus are not counted. So, the intermediate range, $4.2 < d < 5.1$ Å, is just a buffer, and only when the trajectory has crossed both limits is the transition completed.

The results for the number of such transitions in the linear polymers, the cyclic trimer, and the dimer are shown in Table 2. They are given as transitions experienced by one diad, per nanosecond. In the case of the dimer there is only one diad, but in the case of the polymers, each chromophore of the chain experiences these numbers of transitions with each one of its two neighbors. So, the difference with the dimer is not so large when counted per chromophore. But, even considered on a per chromophore basis, it still results that the number of transitions is larger in the dimer than in the polymer.

The values for the polymer in Table 2 are averaged over the middle diads (m and r). But if we average separately the *meso* and *racemo* diads in P14, we find that the frequency is larger in the m case. When we analyzed the equilibrium distance distribution (above), we realized that the m diads have a lower percentage of excimer-forming states. This was attributed to steric effects, due to repulsion between Me groups. This same repulsion between Me groups seems to act as a trigger of the transitions to and from the excimer-forming conformation, giving the higher frequency of the m diads.

The interphenyl distance is the parameter most representative for the analysis of excimer-forming conformations and of the transitions to/from them. This distance is the result of the coordinated rotation of two bonds, such that the sum of the rotational angles of

Table 3. Distribution of Times for a Transition Nonexcimer State → Excimer-Forming State[a]

	t_{max}	t_{avg}	t_{end}
DS	1.5−2	4.7	40
C3c	1.5−2	4.9	36
C3t	1.5−2	4.0	22
P6	1.5−2	11.6	110
P14	1.5−2	12.2	200

[a] t_{max} = maximum of the distribution, or most probable time. t_{avg} = mean time, or average of the distribution. t_{end} = end time, or time at which the distribution goes to zero. All values in ps.

these two bonds has the same time variation as the distance. But the bonds rotate fast, and the rotational angles vary much faster than their sum. We can represent this bond rotation by counting the number of transitions between rotational states that take place in unit time. As we know (above), the rotational states are separated by 120°. We take as starting positions the angle values −60°, 60°, and 180° and count a transition whenever the angle has changed to another of these three values. The result for the rotation of a bond, in DS, is given in Table 2.

We can see that the frequency of transitions between rotational states is 1 order of magnitude higher than the frequency of transitions between distance states. In other words, many backbone bond rotations take place in a single distance approach. It is the simultaneous rotation of the two bonds that is represented by the frequency of Table 2, because both rotations are coordinated in the diad.

The frequency of bond rotation in Table 2 is a mean value, averaged over the two backbone bonds in the molecule and over the three possible jumps between the states −60°, 60°, and 180°. If we avoid this averaging, then we find that the faster rotations are 60° ↔ 180°, in ϕ_1, and −60° ↔ 180°, in ϕ_2. The molecule has two conformations that are excimer-forming ones: (180°, 180°) and (60°, −60°). Therefore, the rotations are faster when they occur between rotational states that give excimer-forming conformations.

Distribution of Transition Times. We have counted the transitions nonexcimer state → excimer-forming state that occur per unit time. That is an overall value. But, how is the distribution of times for these transitions? This question is of interest for the photophysics, because the transitions, to be effective, have to occur within the lifetime of the chromophore. We shall characterize the distribution of times by three parameters: t_{max}, t_{avg}, and t_{end}. The maximum of the distribution, or most probable time, is t_{max}. The mean time for the transition, or average of the distribution, is t_{avg}. And the time at which the distribution goes to zero, namely, the time after which the diad has certainly undergone the transition, is t_{end}.

The results obtained are contained in Table 3. The most probable time, t_{max}, is short, 1.5−2 ps, and it is the same for all the molecules, dimer, linear polymer, cyclic trimer. So, t_{max} is peculiar to the structure at the one diad level. The mean time for the transition, t_{avg}, is larger and depends on the size of the molecule. For the smaller molecules, dimer and cyclic trimer, it is 4−5 ps, while for the linear polymers it is 11−12 ps, the lower of these two values being for the shorter chain, so that a chain length dependence can be inferred. Finally, the time at which the distribution ends, t_{end}, is much larger and follows the same molecular size dependence as the mean time. Not until about 200 ps can one be sure that the transition has taken place in the longer chain (P14), while this value is only about 40 ps in the dimer and even shorter in the cyclic trimer. So, for a given lifetime in the range 40−200 ps, the probability of transition would be one for dimer and trimer, but smaller than one for the polymer, which means that, in such a lifetime, all the diads of dimer and trimer molecules have undergone the transition, while in the polymer some diads still remain without having experienced the transition. This end time of the distribution is very much dependent on chain length (110 ps for P6, 200 ps for P14), so one can envisage the situation where the lifetime be situated above t_{end} for short chains and below t_{end} for longer ones, such that the photophysical behavior be different in low and high molecular weight samples.

The values shown in Table 3 for the cyclic trimer and the linear polymer are mean values—in the case of the linear polymer, averaged over six (P14) or three (P6) middle diads, and in the case of the cis isomer of the cyclic trimer (C3c), averaged over its three diads. The trans isomer has only one diad that gives excimer-forming states; so the value given is for this diad. The other two diads in this same isomer have one phenyl ring in the trans position, which gives zero excimer-forming states at any time. Thus, the value of t_{avg} and t_{end} for these diads would be ∞ in Table 3.

Discussion

The time-resolved fluorescence spectra of the siloxane systems studied here provide experimental quantities that can be related to our MD simulations. First, it is the kinetic rate constant for the excimer formation, k_a, which measures the rate at which the excimers are formed by a kinetic mechanism. In the traditional view, this mechanism is a bond rotation that brings together the two chromophores of the excimer. Our present MD simulations show that the approach of two chromophores involves the rotation of two bonds in a coordinated fashion and that the frequency of approach is much slower than the frequency of each bond rotation. Second, it is the fraction of monomers that are isolated or unable to form excimer in the lifetime of the chromophore. The origin of such isolation in the polymer could be understood in terms of the very long transition times (tail of the distribution) which are calculated by MD.

Experimentally, it has been found that the dimer (DS) has no isolated monomers,[11,21] the polymers give a fraction of isolated monomers in the range 2−10%, the value increasing with molecular weight of the sample,[11,21] and the cyclic trimer (C3) gives about 23% isolated monomers[11,23] (data at 20 °C). A hint as to why the linear polymers have a sizable amount of isolated monomers but the small dimer has none comes from the distribution of transition times calculated in MD (Table 3). This distribution dies away much more slowly in the polymer than in the dimer (t_{end} is 3−5 times longer for P6, P14 than it is for DS). So, after all phenyl rings have undergone a transition to an excimer-forming state in DS, there still remain some phenyl rings in P6, P14 that have not yet undergone the transition and remain as isolated monomers. The explanation for the high value of isolated monomers in the cyclic trimer comes from the chromophore that is in the opposite side of the cycle in the trans isomer.[11,23] The MD trajectories show that this chromophore never approaches any of the other two chromophores at distances within the range of excimer-forming states. So, it is in fact isolated, and its contribution should be equal to the proportion of the trans isomer in the experimental sample, which is 0.23.[23]

We now consider the kinetic rate constant for excimer formation, which we call k_a. The experimental values for k_a are high, denoting a fast process, in accord with the flexibility of the siloxane backbone. For the dimer (DS) it is $k_a = 8.0$ ns^{-1},[11,21] for the polymer samples somewhat higher, 13−16 ns^{-1},[11,21] and for the cyclic trimer 13.4 ns^{-1} [11,23] (data at 20 °C). We can understand these differences polymer/dimer or cycle/dimer in terms of the MD results. k_a can be estimated from MD by using the frequency of transitions to an excimer-forming state and the residence time in such a state. The frequency of transitions, f, gives the number of transitions to the excimer-forming state that occur in unit time, and the residence time fraction, r, gives the fraction of total time that is spent in such excimer-forming states. Then, the unimolecular rate constant is estimated by $k_a \sim f/r$.

For the dimer, the value of f for distance approach is 107 ns^{-1} (Table 2), and the corresponding value of r is 0.296 (see subsection Distance Distribution). For the polymers, the result of f is 41−43 ns^{-1} (Table 2), and the value of r is 0.152 (subsection Distance Distribution). But in the polymer, a given chromophore can do this process with each one of its two neighbors. So, in the polymer k_a is proportional to twice f/r. Comparing polymer and dimer we get k_a(polymer)/k_a(dimer) = 1.5−1.6, which is in fair agreement with the experimental ratio 1.6−2.0. So we can interpret correctly that the rate of excimer formation is faster in the polymer chain than in the dimer, in spite of the fact that the frequency of transitions is smaller in the polymer diad than it is in the dimer molecule. To estimate k_a for the cyclic trimer (C3), we use f(trans) = 122 ns^{-1}, f(cis) = 98 ns^{-1} (Table 2) and r(trans) = 0.277, r(cis) = 0.231 (see Distance Distribution). In the trans isomer there is only one diad giving transitions to excimer-forming states, but in the cis isomer each chromophore can form such states in two consecutive diads. Considering then the relative abundance of both isomers, we finally get k_a(cyclic trimer)/k_a(dimer) = 1.5, which compares very well with the experimental ratio 1.6.

The experimental results are for dilute solutions in methylcyclohexane, but the MD calculations do not consider the molecules of solvent explicitly. The presence of solvent would slow down the transition frequencies and will also have some screening effect on the attraction between phenyl rings, thus diminishing the residence time fraction of the excimer-forming states in the equilibrium distributions. Probably, these effects are similar in the different structures so that the relative values are good estimates concording with experiment.

However, the question remains as to how realistic are the calculations without explicit inclusion of solvent molecules. As a rough test on how the solvent may influence the results, we have run a short (500 ps) MD trajectory with one DS molecule in the presence of 25 solvent (methylcyclohexane) molecules, at 300 K. The system was constructed with the *Amorphous Cell* module,[26] under periodic boundary conditions, at the density of the pure solvent (0.763 g cm^{-3}). The results show that the frequency of transitions (5.1 → 4.2 Å) is 4−5 times slower than without solvent molecules and that the fraction of excimer-forming states (d < 4.2 Å) is about 40% lower than without solvent molecules. The factor affecting the frequency of transitions is similar to that found in other studies on the influence of solvent,[27] but the factor affecting the fraction of excimer-forming states can have a large error (although it goes in the direction expected), because the trajectory is not long enough to be statistically reliable (with such number of molecules). A much more extensive computational effort would be required.

Despite this shortcoming, many of the conclusions regarding the dynamics of the chain backbone are not altered substantially when the solvent molecules are considered explicitly. For example, the coordination between rotations of the two bonds in a diad is the same, so that the trajectories advance parallel to the diagonal of the conformational map (ϕ_2 vs ϕ_1) also, and the distribution of rotational angles remains very broad, with a baseline which is about $^1/_3$ of the peak maximum value, the same as in the abscence of solvent molecules. Nevertheless, further work is required for a more precise exploration of the solvent effects.

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