Conformational Analysis of Cyclic Poly(methylphenylsiloxane). Excimer-Forming Sites and Side-Group Rotation

Arturo Horta*

Departamento de Química Física, Facultad de Ciencias, Universidad a Distancia (UNED), 28040 Madrid, Spain

Inés F. Piérola, Ana Rubio, and Juan J. Freire

Departamento de Química Física, Facultad de Ciencias Químicas, Universidad Complutense, 28040 Madrid, Spain

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ABSTRACT: A Monte Carlo simulation method (MC) that uses the rotational isomeric state model (RIS), modified to consider fluctuating rotational angles and excluded volume interactions, is applied to cyclic poly(methylphenylsiloxane) (c-PMPS) with 50% meso diads, to determine the percentage of conformers that are excimer-forming sites (EFS) in the average equilibrium conformation. Calculations were performed as a function of temperature (5–60 °C) and of the number of backbone bonds (N) in the range 8–60. The EFS population of cycles with $N < 20$ shows the opposite trend to that of linear PMPS; it increases with N. For large cycles with $N > 20$, EFS level off to the same value as for the homologous linear PMPS (about 61%). For the cyclic tetramer ($N = 8$), the MC result depends on the ring-closure distance considered and is slightly larger than the result obtained by direct calculations on all 16 conformations allowed by the geometrical restrictions imposed by ring closure (43%). Several mechanisms for excimer dissociation have also been considered. For large cycles, excimer dissociation through rotation of a backbone bond requires 4.8 kcal/mol for racemic diads, and it is not allowed for meso diads. For the smallest cycle considered here ($N = 8$), such rotational excimer dissociation is not possible, but 15% excimers may dissociate through the interconversion of two isoenergetic conformations. The conformational energy map of two neighboring phenyl rings has been calculated. The results show that these side groups may freely rotate around the Si–phenyl bond by as much as 60° with respect to the parallel sandwichlike conformation and that such motions require only the excimer binding enthalpy (3.2 kcal/mol) to dissociate the excimer. In consequence, this last mechanism may compete with others to give excimer dissociation.

Introduction

Linear and cyclic homologous siloxanes show marked differences in some of their physical properties.[1] Some differences have also been observed in the photphysical behavior of cyclic[2,3] and linear[4–7] phenylsiloxanes, which we intend to explain in this work, making use of their respective conformational distributions.

Conformational analysis based on the Monte Carlo method has been broadly used to explain excimer fluorescence of dichromophoric molecules,[8] and recently, it has also been applied to polymers.[9–11] The conformational analysis determines the proportion of conformers that are excimer-forming sites (EFS) in the ground-state average equilibrium conformation. In phenylsiloxanes, EFS are conformers with a parallel sandwichlike disposition of neighbor phenyl rings, and this corresponds[9,12] to meso diads in conformation tt or $\bar{g}\bar{g}$ and to racemic diads in $\bar{g}$t or t$\bar{g}$ conformation. The population of EFS is related to the excimer-to-monomer intensity ratio (I_E/I_M) in systems in which dynamical processes (like rotations or segmental diffusion) do not contribute significantly to excimer formation or dissociation.[13,14] It is also related to energy migration since EFS behave like traps for the exciton; a larger proportion of EFS means a shorter distance for energy migration.[12]

The conformational energy together with torsional barriers (1.6 kcal/mol for siloxanes[15]) and the excimer binding enthalpy (3.2 kcal/mol for phenylsiloxanes) relates to the difficulty to reach an excimer-forming site or to dissociate an excimer through rotations involving single backbone bonds. This information is very important for understanding the temperature dependence of excimer emission[5,6] or complex fluorescence decays.[7]

Here we extend to cyclic poly(methylphenylsiloxane) (c-PMPS) the conformational analysis previously made[9] for linear PMPS (l-PMPS) with a modified Monte Carlo simulation method, and we compare it with direct calculations performed on all possible conformations of the cyclic tetramer (c-TMPS). Conformational energy maps are also drawn for pairs of neighbor phenyl rings in order to analyze the mechanisms of excimer dissociation, a photophysical process typical of phenylsiloxanes.

Methods and Theoretical Calculations

Monte Carlo Simulation. The procedure followed is a slightly modified version of the general calculation scheme described in ref 9. It allows the analysis of linear polymers having asymmetric chains (it was applied to isotactic and syndiotactic PMPS and to PMPS of intermediate tacticity). Here, it is adapted to the study of cyclic chains having the same characteristics. Specifically, the results are obtained for PMPS cycles generated with 50% meso diads, in order to compare with the experimental data available for samples of such tacticity and also to compare with the theoretical results obtained before for linear PMPS chains.

Basically, the calculation procedure has not been changed. Once a given stereochemical sequence with a random distribution of meso and racemic diads is obtained, the conditional probabilities for each rotational angle are calculated by using eq 1 and 2 of ref 9 (considering independent Gaussian fluctuations in the rotational angles, $\delta\varphi = 15°$). Then the chain conformation is generated by selecting the conformational angles according to these probabilities. Finally, the position coordinates of the $N + 1$ segments are calculated with respect to a fixed reference frame.

The reference frame chosen has the O atom at the origin, the first bond, O–Si, along the positive z axis, and the second bond, Si–O, on the positive x part of the xz plane. The calculation of coordinates for each sequence allows consideration of the excluded volume by rejecting sequences in which the distance between

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Chart I

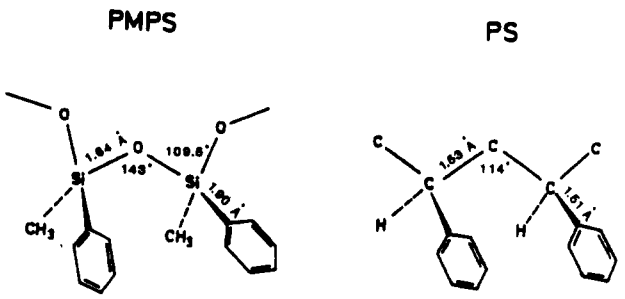
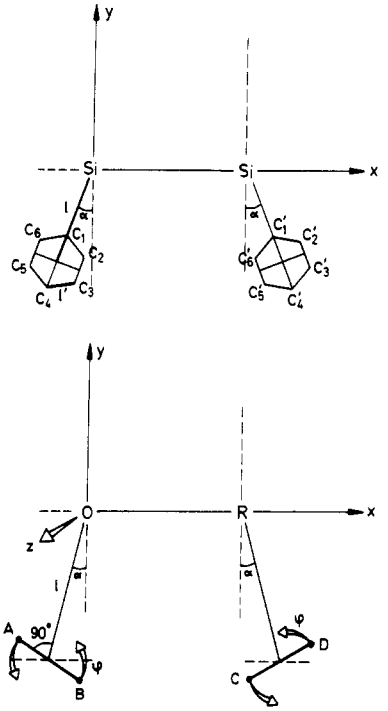


Chart II



any pair of segments separated by five or more bonds is smaller than a given value, chosen as R_0 = 3 Å, the same as for linear chains.

Once it is verified that the generated chains obey the conditions of the model, they are then analyzed to find which ones can be considered as cycles. The distance between the first and the last segment of the sequence (ring closure distance R_{Ring}) is obtained, and only those conformations in which such a distance is equal or lower to a given value, taken as representative of intramolecular cyclization, are accepted as cycles. The calculations have been performed with values R_{Ring} = 4 and 5 Å, in consonance with the interval chosen by Beevers and Semlyen.[16]

Molecular Parameters. In order to describe the cyclic chains of PMPS, we have adopted the molecular parameters of Mark and Ko.[17]

EFS Population and Conformational Energy. The calculation of EFS has been done in the same way as described for the case of linear PMPS. The energy of one diad (m or r) in any conformational state is independent of whether the chain is open or closed. So, its values for c-PMPS are the same as given in Table II of ref 9.

Energy Map for Two Neighboring Phenyl Rings. In order to clarify the possible role of certain geometric arrangements of neighboring phenyl rings on excimer dissociation, we have performed calculations of phenyl–phenyl interactions in a diad, for the case of PMPS, and also for PS, for the sake of comparison (see Chart I).

For PMPS, the value of angle α, as defined in Chart II, is obtained first. Since the backbone bond angles are different, the planes of the phenyl substituents are nonparallel to each other and α is not zero. The geometrical data necessary are indicated in Chart I. Analogously, an angle α can also be defined for PS using the C_α atoms of the backbone in place of the Si atoms of PMPS.

Table I
Parameters of Equation 1[a]

i	a_i	b_i	c_i	d_i	e_i
1	0	−1	0	0	0
2	0	−1	1	−1	1
3	0	−1	1	−1	1
4	0	−1	0	0	0
5	0	−1	−1	1	−1
6	0	−1	−1	1	−1
1′	$\bar{O}\bar{R}$	1	0	0	0
2′	$\bar{O}\bar{R}$	1	1	1	1
3′	$\bar{O}\bar{R}$	1	1	1	1
4′	$\bar{O}\bar{R}$	1	0	0	0
5′	$\bar{O}\bar{R}$	1	−1	−1	−1
6′	$\bar{O}\bar{R}$	1	−1	−1	−1

[a] $\bar{O}\bar{R}$ = 3.16 Å (see text).

The calculation procedure of α consists of obtaining the positions of the O and Si atoms (or the C_α, C_β atoms for PS) and of the C_1 and $C_{1'}$ atoms joining the phenyl rings to the backbone, for the conformational sequence in which the atoms C_1 and $C_{1'}$ and the two Si atoms of the diad are coplanar. In order to obtain the position of these atoms, use has been made of simple geometric considerations based on Chart II and of a computation subroutine developed for the calculation of coordinates in a sequence of bonds according to given values of bond lengths, bond angles, and torsional angles. The sequence of bonds to which this subroutine is applied here is the one formed by the four consecutive bonds joining atoms C_1 and $C_{1'}$. The value thus calculated for the angle α is α_{PMPS} = 9.97°. For PS, it is α_{PS} = 3.54°, considerably lower than that of PMPS, which makes it reasonable that in other calculations[18] α_{PS} is approximated to zero, corresponding to tetrahedral bonding of the aliphatic carbon atoms.

To study the interaction energy between the two phenyls, we first need to calculate the position coordinates of all their atoms (Chart II) as a function of α, of the distance between consecutive Si atoms, $\bar{O}\bar{R}$ = 3.16 Å, of the distance between the phenyl geometric center and the Si atom to which it is bonded, l, and of the bond length C_{ar}–C_{ar}, l'. This is done according to appropriate geometrical considerations in Chart II, which, for the sake of brevity, we have summarized in the following parametric formulas:

$$x_i = a_i + b_i l \sin\alpha + (3^{1/2}/2)c_i l' \cos\alpha \cos\varphi$$

$$y_i = -l \cos\alpha + (3^{1/2}/2)d_i l' \sin\alpha \cos\varphi$$

$$z_i = (3^{1/2}/2)e_i l' \sin\varphi \qquad (1)$$

(See Table I for parameter values.)

Once these coordinates are known for the given values $\varphi = \phi_1$ of one phenyl and $\varphi = \phi_2$ of the othe phenyl, with $0 < \varphi < 360°$, the conformational energy of the pair of phenyls is computed as

$$E = \sum \epsilon_{ij} \qquad (2)$$

where ϵ_{ij} is the interaction energy between two aromatic carbon atoms, i and j, separated by a distance, r_{ij}, dependent on the angle φ. The ϵ_{ij}'s are obtained by[17]

$$\epsilon_{ij} = A_{ij} r_{ij}^{-12} - B_{ij} r_{ij}^{-6} \qquad (3)$$

with $A_{ij} = 9.794 \times 10^5$, B_{ij} = 556.7, and r_{ij} in Å, which yield ϵ_{ij} in kcal/mol.

Results and Discussion

Monte Carlo Simulation. The Monte Carlo results are shown in Table II for two atactic PMPS chains representative of small (N = 8) and large cycles (N = 60). The conformational distributions of c-PMPS and l-PMPS

Table II
Relative (or Normalized) Population (f_i) of the Most Frequent Conformers of Atactic c-PMPS of $N = 8$ and 60 Backbone Bonds and Conformational Energies (E_i in kcal/mol) for $N = 60$[a]

	f_i ($N = 8$)				
conf	$R_{Ring} = 4$ Å	$R_{Ring} = 5$ Å	conf	f_i ($N = 60$)	E_i
m(tt)	0.25 ± 0.03	0.229 ± 0.003	*m(tt)*	0.44 ± 0.3	−0.87
r(tḡ)	0.18 ± 0.05	0.20 ± 0.03	r(tt)	0.1 ± 0.2	0.00
m(ḡḡ)	0.13 ± 0.01	0.012 ± 0.002	*r(ḡt)*	0.09 ± 0.1	0.07
r(ḡḡ)	0.08 ± 0.02	0.10 ± 0.02	*r(tḡ)*	0.09 ± 0.05	0.07
m(gg)	0.08 ± 0.02	0.025 ± 0.008	r(tg)	0.09 ± 0.1	0.07
m(tg)	0.06 ± 0.02	0.051 ± 0.009	r(gt)	0.09 ± 0.1	0.07
r(tg)	0.04 ± 0.03	0.05 ± 0.01	m(gt)	0.02 ± 0.1	0.96
r(gg)	0.04 ± 0.03	0.10 ± 0.01	m(tg)	0.02 ± 0.01	0.96
r(tt)	0.03 ± 0.03	0.036 ± 0.005	m(tḡ)	0.02 ± 0.04	0.96
m(ḡḡ)	0.02 ± 0.01	0.037 ± 0.007	m(ḡt)	0.02 ± 0.01	0.96
r(ḡt)	0.01 ± 0.01	0.033 ± 0.007	r(gg)	0.01 ± 0.1	1.09

[a] Calculated at 25 °C with the Monte Carlo simulation method. Conformers corresponding to EFS are italic, and those whose contribution is less than 1% have been omitted. R_{ring} is the distance allowed for ring closure.

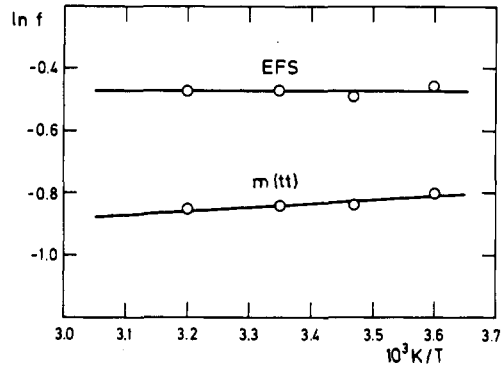


Figure 1. Temperature dependence of m(tt) conformers and total excimer-forming site population for an atactic c-PMPS with $N = 40$ and $R_{Ring} = 4$ Å.

both with $N > 40$ are practically the same (see ref 9 and Table II). The most remarkable features of such average conformations of $N > 40$ are as follows.

(i) The first feature is the presence of a large contribution of ḡ conformers that are sterically prohibited for similar hydrocarbon polymers[12,18] due to the different bond distances.[18]

(ii) The second feature is the large stability of conformers that are EFS and their consequently large contribution to the total population: 60.3% for l-PMPS[9] and 62% for c-PMPS. This was previously[9] explained by the attractive interaction of neighboring phenyl rings in siloxanes. In hydrocarbon polymers, such as polystyrene, that interaction is repulsive and the EFS population is comparatively very low:[11,12] 2.6%. This difference is a mere consequence of the different separation between adjacent phenyl rings in the two polymers.

(iii) The third feature is the low activation energy for rotational sampling of EFS due to the very small differences of conformational energy between the different conformers (see Table II) and the low torsional barriers typical of siloxanes: 1.6 kcal/mol.[15] In this way, the activation energy for the formation of excimers in large c-PMPS is 1.7 kcal/mol for racemic diads and 1.6 kcal/mol for meso diads.

c-PMPS with $N > 40$ is also very similar to l-PMPS in the temperature dependence of its EFS population. Figure 1 shows that m(tt) conformers, the largest contribution to EFS, decrease slightly upon increasing temperature, but the total EFS population remains practically constant, within the uncertainty of our results.

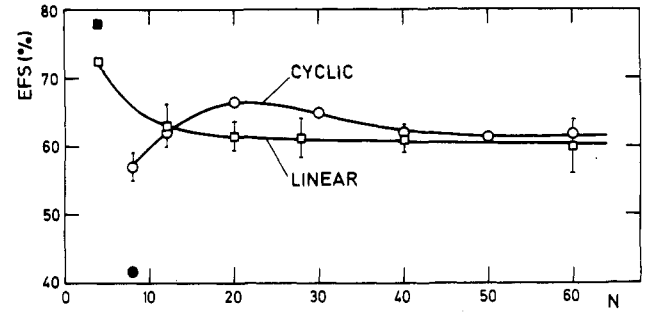


Figure 2. Excimer-forming site population for atactic cyclic ($R_{Ring} = 4$ Å) and linear (from ref 9) PMPS as a function of the number of backbone chain bonds (N), at 25 °C. Filled points correspond to the dimer with end groups (■) and to the direct calculation performed on all the RIS conformations of the cyclic tetramer (●).

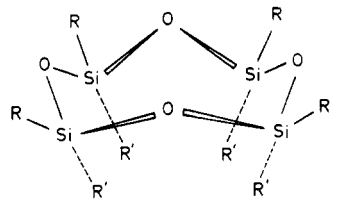
The largest difference between c-PMPS and l-PMPS is the molecular weight dependence of the conformational distribution and, in particular, of the EFS population (Figure 2). For $N > 40$, the EFS population levels off at about the same value (approximately 61%), but for low N values, EFS shows the opposite trend in cycles and linear chains. In l-PMPS, EFS decrease (increasing N) because the contribution of r(tḡ) and r(ḡt) decreases and the contribution of meso diads does not change much. In c-PMPS, EFS increase because the contribution of m(tt) increases, whereas the overall contribution of racemic diads does not change much. In accordance with these results, the tacticity must play an important role in the molecular weight dependence of the PMPS photophysical properties and also in the different behavior of cycles and linear chains.

On the other hand, for $N > 12$, the conformational distributions are the same (within the precision of our calculation) for $R_{Ring} = 4$ or 5 Å, but for $N < 12$, a small difference can be observed (see Table II for c-TMPS). Upon decreasing R_{Ring}, gauche conformers increase in racemic diads and decrease markedly in meso diads. This suggests that for real cycles, with $R_{Ring} = 0$, the conformational distribution may be very different. Since for $R_{Ring} = 4$ or 5 Å, 2×10^5 chains must be generated in each sample to get at least 10^2 cycles, the computing time would be prohibitive for smaller values of R_{Ring}. Fortunately, for small cycles, the total number of possible conformations is not too high and a direct calculation of EFS can be performed.

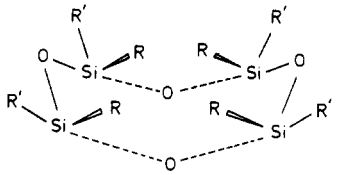
Cyclotetramethylphenylsiloxane. We consider now the tetramer, $N = 8$. A shorter ring with $N = 6$ exists, but the structure of this trimer is expected to differ somewhat from the rest of the rings. The dimethyl trimer is an essentially planar molecule with bond angles distorted with respect to those corresponding to $N \geq 8$ due to the ring closure of such a few number of bonds.[19] The dimethyl cyclic tetramer has been found to be a highly flexible molecule.[20] With eight bonds, there is a certain conformational freedom. But the closure condition severely limits the number of bonds whose conformational states can be chosen arbitrarily. Only two rotational angles are independent, the remaining six angles being determined by ring closure.

With such a small number of variable torsional angles, it is relatively easy to enumerate all the possible conformations of c-TMPS, adopting also for this molecule the usual rotational isomeric state model with states t, g, and ḡ.[21] In the case of the tetramer, the ring cannot form if any single bond is in a trans state.[20] Therefore, the conformational isomeric states allowed for c-TMPS are just g and ḡ.

Chart III



(A)



(B)

The EFS in r diads are tḡ and ḡt.[9] Since the t state is forbidden by ring closure, none of the EFS conformations, tḡ or ḡt, are present in the cyclic tetramer. Hence, the r diads do not contribute EFS to c-TMPS. The tacticity of the c-TMPS's studied has been determined as 50% r.[24] Since the 50% r fraction contributes no EFS, the proportion of EFS in c-TMPS has to be necessarily ≤ 50%. In m diads, the EFS are tt and ḡḡ.[9] Only the ḡḡ conformation is possible, because of the lack of t states in the ring. Thus, the EFS in c-TMPS are just those of the m(ḡḡ) conformation. Let us see what participation these m(ḡḡ) states make to the total 50% m diads.

With g and ḡ as allowed conformational states, there are only two types of structures that the cyclic tetrasiloxanes can have.[25] Let us call these structures A and B. Chart III shows these two structures for the isomer mmmm. Their geometry is as follows. If we define a plane containing the four Si atoms, then in structure A all four oxygen atoms lie on the same side of this plane, and in structure B, the oxygen atoms alternate sides (one O on one side and its neighboring O's on the opposite side of the Si plane).[26] In each structure, two overall conformations are possible. Let us see which ones.

We have to consider the different stereoisomers. Four stereoisomers of c-TMPS can be isolated: mmmm, rrrr, mrmr, and mmrr. Their relative abundance, under different conditions of cyclization equilibrium, has been found to be very close to the ideal values for the random cyclization of atactic chains.[27] These are[27] mmmm, 0.125; rrrr, 0.125; mrmr, 0.25; and mmrr, 0.5. The overall conformations of these isomers are shown on Table III.

In these conformations, there are several types of interactions between groups or atoms. The interactions between the substituent groups methyl (Me) and phenyl (Ph) are the most important ones here. These can be Ph–Ph, Ph–Me, and Me–Me. The number of these types of interactions present in each conformation is shown on Table III. The rest of the interactions between groups or atoms are equal in all conformations shown, so it is enough to consider these three pairs (Ph–Ph, Ph–Me, Me–Me) in order to compare the relative stability or probability of each conformation. This probability has been calculated as the Boltzmann factor (normalized for each isomer) of the energy obtained by adding the energies of these Ph–Ph, Ph–Me, Me–Me interactions. The result is shown on Table III.

Every time a pair of phenyl groups interact, an excimer-forming site is formed. Therefore, the number of EFS present in a given conformation (Table III) is equal to the number of Ph–Ph interactions taking place in it. Since this Ph–Ph interaction has the highest attractive energy, the conformations having more numerous EFS are the most probable ones (for each isomer).

The number of EFS in each isomer is obtained by adding the contribution from its conformations, each weighted by its relative probability, and the total number of EFS in the c-TMPS sample, by summing the contributions from the different isomers, each weighted by its abundance in the sample. The result is that 43% of the diads in c-TMPS are EFS (Figure 2). That makes the difference between the dependences of EFS on N for linear chains and cycles even larger than previously described.

Thus, the proportion of EFS in the short cycle $N = 8$ is 19% lower than it is in the long cycle $N \geq 12$. Due to this smaller proportion of EFS, the fluorescence ratio I_E/I_M is expected to be lower in c-TMPS than in the long cycles. This prediction is in accordance with what is experimentally found for these cycles,[3] but such concordance must be considered with caution, because the fluorescence ratio is determined not only by the conformational equilibrium population but also by the rotational sampling of EFS during the excited-state lifetime.[13]

Another point of interest in the photophysical behavior of the cyclic methylphenylsiloxanes is that these cycles show excimer dissociation, the same as the linear polymer does.[3] In the case of the long cycles, this is not unexpected, since the long cycles have enough conformational flexibility to allow for a mechanism of coupled single-bond rotation, the same as in the linear chain. But in the case of the short cycles, the situation is not so clear, because rotation about a single bond is not possible without, at the same time, rotating the other bonds of the short cycle. Thus, a change in the overall conformation is required. Let us see if this is likely to occur.

With $N = 8$, we have only four overall conformations for each isomer (Table III). Excimer dissociation implies passage from a conformation with an EFS to another conformation in which this EFS is not present. In the mmmm isomer, this conformational change is very unlikely, because of the large stability of the conformation having four EFS. Also, in the mmrr isomer, the conformation with two EFS is very stable. But in the mrmr isomer, all four conformations are equally likely. Change from one to another expends no conformational energy and is therefore very easy. In this change, excimer dissociation takes place. (The number of EFS is kept constant (one excimer-forming site), but the excimer-forming site existing in a given diad disappears while a new excimer-forming site is formed in a different diad.) Thus, the overall change in conformation of this isomer could explain the existence of excimer dissociation. However, the contribution of this dissociable mrmr isomer to the total EFS is just 15%, the remaining 85% of EFS being mostly nondissociable. This proportion seems not enough to explain the experimental spectra, where excimer dissociation is dominant, just as in the long cycles or linear polymer.[3] We shall see that the other mechanism can also occur.

Lateral Group Rotation. Other mechanisms of excimer dissociation, different from coupled single bond rotation of the backbone, can be envisaged. In the siloxanes, bond inversion is a possibility.[28] Another possibility is lateral group rotation. In the excimer, two neighboring phenyl groups are parallel in a sandwich-type disposition. Rotation around the Si–Ph bond can destroy this parallel geometry and dissociate the excimer. This mechanism of excimer dissociation by lateral group rotation has the advantageous feature that it could operate similarly in all molecules, be it short cycles, long cycles,

Table III
Excimer-Forming Sites of All the Possible RIS Conformations of the Four Stereoisomers of the PMPS Cyclic Tetramer ($N = 8$)

isomer	structure	conformation	no. of interacting groups: Ph–Ph	Ph–Me	Me–Me	no. of EFS	probability[a]
mmmm	A	m(gg̃)m(gg̃)m(gg̃)m(gg̃)	4			4	0.998
		m(gg)m(gg)m(gg)m(gg)			4		0.000
	B	m(gg̃)m(gg)m(gg̃)m(gg)	2		2	2	0.001
		m(gg)m(gg̃)m(gg)m(gg̃)	2		2	2	0.001
mmrr	A	m(gg̃)m(gg̃)r(gg̃)r(gg)	2	2		2	0.935
		m(gg)m(gg)r(gg)r(gg̃)		2	2		0.001
	B	m(gg̃)m(gg)r(gg̃)r(gg̃)	1	2	1	1	0.032
		m(gg)m(gg̃)r(gg)r(gg)	1	2	1	1	0.032
mrmr	A	m(gg̃)r(gg̃)m(gg)r(gg)	1	2	1	1	0.25
		m(gg)r(gg)m(gg̃)r(gg̃)	1	2	1	1	0.25
	B	m(gg̃)r(gg)m(gg)r(gg̃)	1	2	1	1	0.25
		m(gg)r(gg̃)m(gg̃)r(gg)	1	2	1	1	0.25
rrrr	A, B					0	

[a] Calculated at 25 °C with the following energies of interaction (kcal/mol):[17] Ph–Ph, −2.5; Ph–Me, −0.9; Me–Me, −0.5.

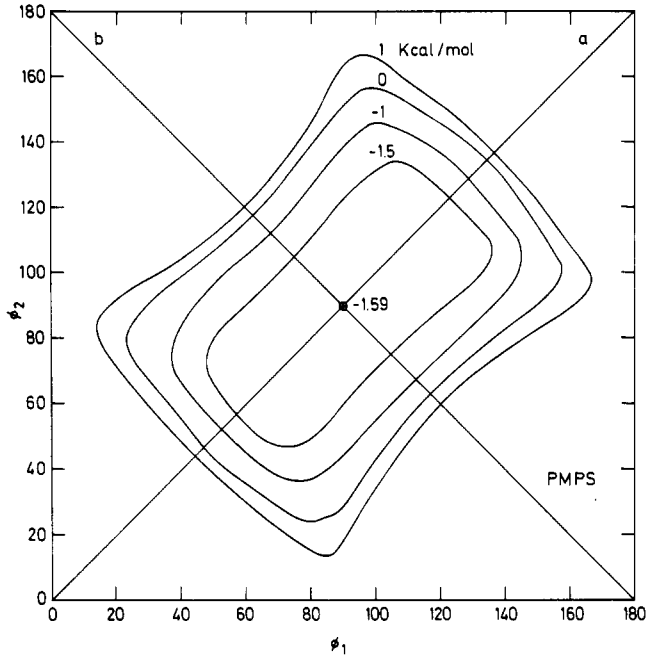


Figure 3. Conformational energy map for a PMPS diad undergoing rotation of the two lateral phenyl rings around their corresponding Si–Ph bonds.

or the linear polymer, and explain the similarity in dissociation found experimentally for all these molecules.[3]

In view of this possibility, we have explored the conformational energy map for a pair of neighboring phenyl rings of a diad in methylphenylsiloxane.

The map of conformational energy is shown on Figure 3. ϕ_1 and ϕ_2 are the torsional angles for rotation around bond Si–Ph of each phenyl group in the diad. They are defined such that the parallel sandwichlike disposition of the two phenyl groups occurs for $\phi_1, \phi_2 = 90°$. This is the minimum of conformational energy. The two diagonals of the energy map are not equivalent, because they correspond to different relative rotations of the phenyl groups. Diagonal a corresponds to the rotation of both groups in the same sense, thus keeping them always parallel (see Chart IV), while diagonal b corresponds to rotations of the groups in opposite senses (Chart IV), which makes them impinge on each other at smaller displacements from the minimum. Hence, the energy increases faster along diagonal b than along diagonal a.

We can see in Figure 3 that the rotation of lateral phenyl groups is very unrestricted. There is a wide range of

Chart IV

torsional angles over which the rotation of phenyl groups is practically isoenergetic. Thus, from $\phi_1, \phi_2 \simeq 60°$ to $\phi_1, \phi_2 \simeq 120°$ the variation in conformational energy is less than 0.1 kcal/mol. Even for the conformation in which the energy is maximum ($\phi_1, \phi_2 = 0, 180°$), the value is not excessively high, only 3.4 kcal/mol above the minimum corresponding to the parallel sandwichlike arrangement ($\phi_1, \phi_2 = 90°$). Therefore, complete flipping of the phenyl rings is a relatively probable event.

This high freedom to lateral phenyl group rotation in the siloxane chain is in contrast with what happens in hydrocarbon chains, such as polystyrene (PS). In PS the rotation of phenyl lateral groups cannot occur without conflicting with serious steric hindrances. The conformational energy map for a PS diad, calculated following the same procedure as described for the siloxane diad (see Chart II), is shown on Figure 4. We can see the dramatic difference between the PMPS and PS diads. In PS, rotation of the lateral phenyl group is severely limited. The minimum of the conformational energy is very sharp in the case of PS and very shallow in the case of PMPS. For a simpler comparison, we show in Figure 5 the section of the conformational energy surfaces at $\phi_1 = 90°$.

According to these results, when a PS diad is in an EFS conformation (minimum), it is extremely unlikely that it leaves such a conformation by lateral group rotation. Hence, lateral group rotation is not a mechanism for excimer dissociation in the case of PS. However, in PMPS the minimum of energy does not correspond to a unique conformation. The EFS ($\phi_1, \phi_2 = 90°$) is within a wide range of conformations that are equally likely. There is a large entropy associated with the energy minimum in PMPS. The phenyl groups can oscillate freely over a wide range around the minimum. Also, the barrier of 3.4 kcal/mol is not very high, so that complete or 180° rotation of the phenyl groups can take place.

Consequently, the phenyl groups can approach and depart from the perfect sandwichlike EFS conformation by lateral group oscillation in PMPS, and only the excimer binding enthalpy may be needed to dissociate the excimer in the excited state.

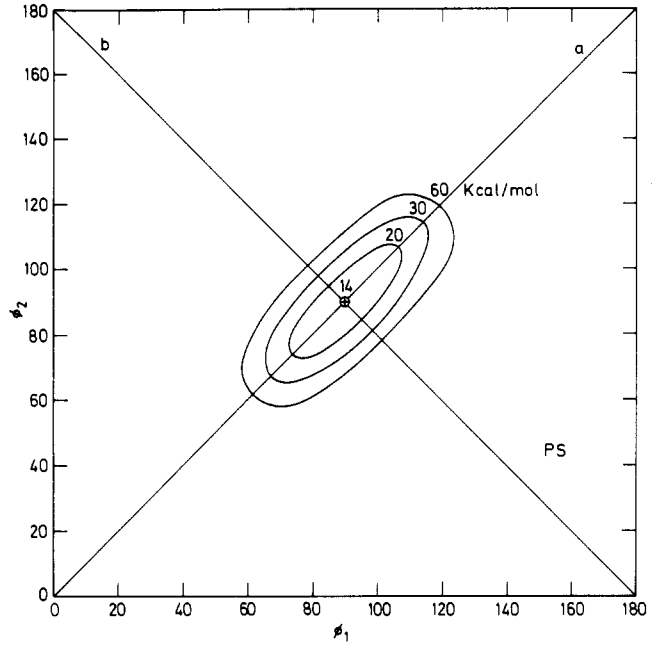


Figure 4. Conformational energy map for a PS diad undergoing rotation of the two lateral phenyl rings around their corresponding C–Ph bonds.

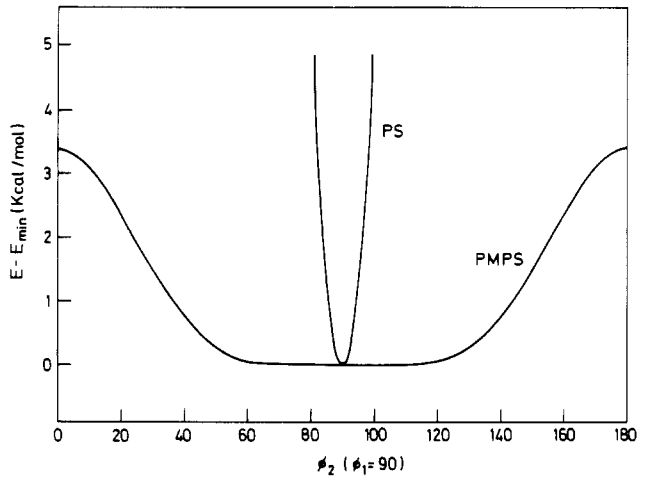


Figure 5. Conformational energy of PMPS and PS diads as a function of the torsional angle of one of the phenyl rings when the other is fixed at $\phi_1 = 90°$.

We conclude then that lateral group rotation is a mechanism for excimer dissociation which can compete with backbone rotation in the siloxanes. The mobility of the lateral phenyl grups in siloxanes should be important in discussing not only the mechanism of excimer dissociation but also the mechanism of excimer formation in this type of molecule.[7]

Added Remarks. Finally, we should mention that, after completion of this work, we have become aware of a very recent reformulation of the conformational analysis of poly(dimethylsiloxane) based on an analysis of molecular dynamic trajectories.[29] This re-formulation leads to new sets of statistical weights that give a greater importance to the gauche placements and alleviate the restrictions on second-order interactions. The new model is consistent with previous calculations, and experimental results for the mean square end-to-end distance, mean dipole moment, and its temperature dependence significantly improve the previous theoretical predictions of equilibrium cyclization constants for small rings. It is reasonable to assume that the model employed here for PMPS chains also admits important modifications so that the conformational description of the smallest rings can be specially affected. However, we believe that the main conclusions of the present work will not qualitatively change with the introduction of more realistic parameters, though a more sophisticated conformational analysis for PMPS is clearly needed and the use of molecular dynamics techniques would be particularly pertinent.

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References and Notes

(1) Semlyen, J. A. *Cyclic Polymers*; Elsevier: London 1986.
(2) Wu, S. K.; Jiang, Y. C.; Rabek, J. F. *Polym. Bull.* **1980**, *3*, 319.
(3) Semlyen, J. A.; Horta, A.; Piérola, I. F. To be published.
(4) Salom, C.; Horta, A.; Hernández-Fuentes, I.; Piérola, I. F. *Macromolecules* **1987**, *20*, 696.
(5) Salom, C.; Gómez-Antón, M. R.; Horta, A.; Hernández-Fuentes, I.; Piérola, I. F. *Macromolecules* **1987**, *20*, 1627.
(6) Salom, C.; Hernández-Fuentes, I.; Piérola, I. F.; Horta, A. *Macromolecules* **1989**, *22*, 1874.
(7) Maçanita, A.; Horta, A.; Piérola, I. F. *Macromolecules* **1991**, *24*, 1293.
(8) (a) Ito, S.; Yamamoto, M.; Nishijima, Y. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 363. (b) Gorin, S.; Monnerie, L. *J. Chim. Phys.* **1970**, *67*, 869. (c) Stegen, G. E.; Boyd, R. H. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1978**, *19*, 595. (d) Moritani, T.; Fujiwara, Y. *J. Chem. Phys.* **1973**, *59*, 1175.
(9) Rubio, A.; Freire, J. J.; Piérola, I. F.; Horta, A. *Macromolecules* **1989**, *22*, 4014.
(10) Blonski, S.; Sienicki, K. *Macromolecules* **1986**, *19*, 2936.
(11) Gelles, R.; Frank, C. W. *Macromolecules* **1982**, *15*, 741.
(12) (a) Semerak, S. N.; Frank, C. W. *Adv. Polym. Sci.* **1983**, *54*, 31. (b) Winnik, M. A. *Photochemical Tools in Polymer Science*; NATO ASI Series; D. Reidel: Dordrecht, 1986.
(13) Masegosa, R. M.; Hernández-Fuentes, I.; Piérola, I. F.; Horta, A. *Polymer* **1987**, *28*, 231.
(14) Renamayor, C. S.; Gómez-Antón, M. R.; Piérola, I. F. *J. Appl. Polym. Sci. Symp. Ser.* **1990**, *45*, 317.
(15) (a) Scott, D. W.; Messerly, J. F.; Todd, S. S.; Guthrie, G. B.; Hossenlopp, I. A.; Moore, R. T.; Osborn, A.; Berg, W. T.; McCollough, J. P. *J. Phys. Chem.* **1961**, *65*, 1320. (b) Almenningen, A.; Bastiansen, O.; Ewing, V.; Hedberg, K.; Trattenberg, M. *Acta Chem. Scand.* **1963**, *17*, 2455.
(16) Beevers, M. S.; Semlyen, J. A. *Polymer* **1972**, *13*, 385.
(17) Mark, J. E.; Ko, J. H. *J. Polym. Sci. Polym. Phys. Ed.* **1975**, *13*, 2221.
(18) Yoon, D. Y.; Sundararajan, P. R.; Flory, P. J. *Macromolecules* **1975**, *8*, 776.
(19) Oberhammer, H.; Zeil, W.; Fogarasi, G. *J. Mol. Struct.* **1973**, *18*, 309.
(20) Timofeeva, T. V.; Dubchak, I. L.; Dashevsky, V. G.; Struchkov, Y. T. *Polyhedron* **1984**, *3*, 1109.
(21) This is an oversimplification[22] but is common practice in the field[22] and will be used here also for the sake of comparison with other studies.[23]
(22) Grigoras, S.; Lane, T. H. *J. Comput. Chem.* **1987**, *8*, 84.
(23) Flory, P. J. *Statistical Mechanics of Chain Molecules*; Wiley: New York, 1990.
(24) Llorente, M. A.; Piérola, I. F.; Saiz, E. *Macromolecules* **1985**, *18*, 2663.
(25) Carmichael, J. B.; Kinsinger, J. B. *Can. J. Chem.* **1964**, *42*, 1996.
(26) Other structures could be considered if the rotational angles were allowed conformations outside the g and ḡ states.[22]
(27) Wright, P. V.; Beevers, M. S. Reference 1, Chapter 3.
(28) Debolt, L. C.; Mark, J. E. *J. Polym. Sci., Polym. Phys. Ed.* **1988**, *26*, 989.
(29) (a) Bahar, I.; Zúñiga, I.; Dodge, R.; Mattice, W. L. Personal communication of manuscripts to be published.

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