Adaptation of Macrocyclization Equilibrium Theory to the Formation of Intramolecular Excimers in End-Labeled Linear Chains

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ABSTRACT: K_e, the intramolecular excimer equilibrium constant under conditions where the dynamics of rotational isomeric transitions is suppressed, is examined on the basis of the theory of macrocyclization proposed by Flory, Suter, and Mutter in 1976. The conformational averages of the required moments and polynomials are calculated using their exact matrix generation method. The calculations can rationalize the appearance of a maximum near $m = 15$ in the I_E/I_M values that have been reported for pyrene–$(CH_2)_m$–pyrene. In order to achieve this agreement, it is imperative that the theoretical analysis incorporate the probability of a proper angular correlation of the two pyrene ring systems when the separation of their centers is 0.35 nm.

Introduction

Interaction of a chromophore in a singlet electronic excited state with another chromophore in its electronic ground state can lead to the formation of a stable complex called an excimer. This complex, which is stable only in the presence of electronic excitation, requires extensive overlap of π-electrons that is achieved when the chromophores are in a sandwichlike arrangement with a separation of 300–400 pm.[1] The conformations conducive to the intramolecular formation of an excimer by nearest neighbor aromatic groups can be identified with the aid of a rotational isomeric state analysis of the flexible portion of the chain between the two rings.[2] The local conformation is of the greatest importance when the number of bonds in the flexible spacer is small. The influence of the local conformations is clearly evident in the dependence of the fluorescence on the number of methylene units in alkanes end-labeled with pyrene.[3]

Polymers with the repeating sequence A–B_m, where A is a chromophore that can form an excimer, B is a flexible spacer, and m ranges over small integers, may also exhibit a complicated dependence of the fluorescence on m.[4] Dependence of the population of the excimer on m was calculated using rotational isomeric theory and a direct enumeration procedure,[4-6] which identifies the conformations that can form an excimer. Direct enumeration calculates the relative orientation of the aromatic rings in A–B_m –A for all conformations defined by a rotational isomeric state model of B_m, and those conformations that satisfy the criteria for excimer formation are determined. This procedure has been shown to be effective for chains in which A has a very short fluorescence lifetime.[6] Under these conditions, the relative intensity of fluorescence from the excimer and monomer is determined by the equilibrium distribution of rotational isomers and is insensitive to the dynamics of conformational transitions from one rotational isomer to another. The dynamics of these transitions may become important for chromophores with longer fluorescence lifetimes.[7,8]

The present work shifts attention to the analysis of the formation of excimers in A–B_m–A when the number of bonds about which rotation may occur is so large that direct enumeration becomes cumbersome but is still too small to permit neglect of the influence of the local conformation. Here we adapt the theory of macrocyclization for analysis of the dependence on m of the formation of an intramolecular excimer in an end-labeled polymer. An example of this type of system is the α,ω-dipyrenylalkanes, pyr–$(CH_2)_n$–pyr, n = 2–16 and 22, in which Zachariasse et al.[3] found that the ratio of the intensity of excimer to monomer fluorescence, I_E/I_M, is a sensitive function of n. When attention is confined to their samples for which $n \geq 10$, the smallest value of I_E/I_M is obtained when $n = 10$, the largest value is obtained when $n = 13$, and the value when $n = 22$ is only slightly smaller than the value when $n = 13$. This behavior is different from a prediction based on the probability for an end-to-end vector of zero, $W(0)$, in a freely jointed chain. That simple model for the chain statistics predicts $W(0)$ is proportional to $n^{-3/2}$. As will be shown below, the appearance of the maximum near $n = 13$ can be rationalized by inclusion in the analysis of the requirement that the two pyrene units must have the proper angular orientation, as well as the proper separation.

Method

Flory, Suter, and Mutter[9-11] developed a theoretical treatment of macrocyclization to calculate concentrations of cyclic species in ring–chain equilibrates. They successfully applied this theory to the rationalization of the macrocylization equilibrium constants in poly(dimethylsiloxane) and poly(6-aminocaproamide). In their treatment, the cyclization theory of Jacobson and Stockmayer[12] is elaborated so as to take account of correlations between the directions of terminal bonds in the chain conformations in which the end-to-end distance, r, approaches zero. The system treated by the theory of Flory, Suter, and Mutter is described with the aid of Figure 1. The ring is formed from n chain atoms joined by $n - 1$ bonds. The atoms of the segment are numbered 0 to $n - 1$, as in Figure 1, and the bonds are indexed 1 to $n - 1$. Formation of a ring involves establishment of bond n, shown as a dashed line in Figure 1, between atoms 0 and $n - 1$, thereby producing coalescence of virtual atom n with atom 0. Virtual bond $n + 1$, shown dotted in Figure 1, must also be parallel to bond 1. The latter requirement forces the proper angle between bonds n and 1.

Figure 2 is a simple modification of Figure 1 so that it depicts intramolecular formation of an excimer by a flexible polymer with benzene rings at the ends. Atoms 1 and n are virtual atoms located at the centers of the benzene rings. Bonds 2 and n are virtual bonds that con-

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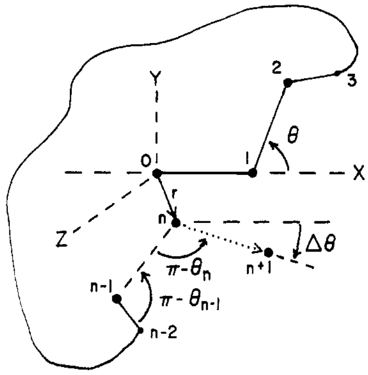

Figure 1. Acyclic segment of n atoms, indexed 0 through $n - 1$, in a conformation approaching the requirements for cyclization. (Redrawn from Flory, Suter, and Mutter.[9])

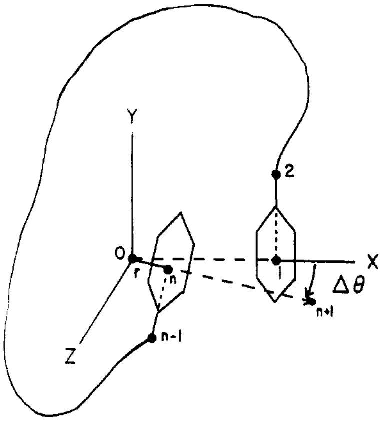

Figure 2. Polymer segment with benzene rings at the ends, in a conformation approaching the requirements for formation of an excimer.

nect the center of a benzene ring to the carbon atom in the flexible spacer that is bonded to that ring. Virtual bonds 1 and $n + 1$, both of length ~350 pm, are normal to the planes of the benzene rings. The ideal excimer has a vector of zero length from virtual atom 0 to virtual atom n and a value of zero for $\Delta\theta$, thereby producing coincidence of virtual bonds 1 and $n + 1$. In order to exhaust all possible excimers, three additional figures should be drawn, because virtual bonds 1 and $n + 1$ may extend in either direction from an aromatic ring. For a flexible chain with a rotation potential that is symmetric about $z = 0$, as is the case for $(CH_2)_m$, the excimers described by these four pictures are of equal probability. Hence the population of excimers for end-labeled chains with a symmetric rotation potential can be deduced from the analysis of Figure 2 alone.

The conformation of the segment is specified by rotations $\varphi_2, \varphi_3, ..., \varphi_n$ about $n - 1$ internal bonds. According to the scheme represented in Figure 2, formation of an excimer is contingent upon fulfillment of three conditions: (1) Atom n must be situated within a volume element $\delta\mathbf{r}$; i.e., the vector, $\mathbf{r}_n$, from atom 0 to atom n, must vanish with a volume element $\delta\mathbf{r}$. (2) The direction of bond vector 1 must yield an acceptable bond angle $\pi-\theta_n$ of $\pi/2$ at atom n (or 0), within tolerable limits. This condition further requires that γ, defined by $\gamma = \cos\Delta\theta$, where $\Delta\theta$ is the angle between virtual bond $n + 1$ and virtual bond 1, must fall within the range $1 - \delta\gamma$ to 1. (3) The conformation specified by torsional angles $\varphi_2, \varphi_3, ..., \varphi_n$, weighted according to its probability of occurrence, must be acceptable. The potential difficulties arising from neglect of the rotation about the new bond 1 depend on the symmetry of the aromatic ring system. If the ring system can be described by an ellipse with axial ratio a/b, there is no difficulty when a/b = 1, but a problem may exist if a/b is much different from one. Ring systems that belong to plane point group 1 are likely to present greater problems than those that belong to plane point group 2, 2*m* or 2*mm*, which in turn are more difficult than those that belong to 6 or 6*mm*.

By the adaptation of the treatment of the macrocyclization equilibrium constant, denoted by K_m by Flory, Suter, and Mutter,[9-11] to this situation, we are led to the following equation for the excimer equilibrium constant, denoted by K_e, in the limit of very high viscosity (or very short fluorescence lifetime), such that the influence of the dynamics of conformational transitions from one rotational isomer to another is suppressed.

$$K_e = \sum(\sigma_{cn}L)^{-1}\, 2\Gamma_0(1)\, W_n(0)\, \Phi_{01} \qquad (1)$$

Here, $W_n(0)$ is the probability density of end-to-end vectors in the region $\mathbf{r} = 0$, σ_{cn} is the symmetry number of the ring formed by 0 to n atoms, and L is Avogadro's number. The summation is over the four pictures, one of which is shown by Figure 2, where virtual bonds 1 and $n + 1$ extend in either direction from the plane of a ring. In the present case, where the rotational potential for the bonds is symmetric, all four terms in the sum are identical, and K_e is $4(\sigma_{cn}L)^{-1}\, 2\Gamma_0(1)\, W_n(0)\, \Phi_{01}$.

The factor $\Gamma_0(\gamma)$ is the probability distribution of γ when $\mathbf{r} = 0$. Then $\Gamma_0(1)$ is the probability that $\Delta\theta = 0$ for chains with $\mathbf{r} = 0$. If the directions of virtual bonds 1 and $n + 1$ are correlated when $\mathbf{r} = 0$ within $\mathbf{dr}$, then the probability density of γ is not uniform over the interval $-1 \leq \gamma \leq 1$. Φ_{01} is the probability distribution of torsional angles, where $\mathbf{r} = 0$ and $\gamma = 1$. This torsional factor is ignored on the grounds that its effect probably is small, as the benzene rings belong to plane point group 6*mm*, and its inclusion would complicate the analysis. Pyrene, from plane point group 2*mm*, would have a/b somewhat different from 1 if it were represented by an ellipse. Nevertheless, we will adopt the approximation where Φ_{01} is unity when these conditions are fulfilled, yielding

$$K_e = \sum(\sigma_{cn}L)^{-1}\, 2\Gamma_0(1)\, W_n(0) \qquad (2)$$

The probability density was expressed in terms of a scalar Hermite expansion.

$$W_n(0) = (3/2\pi\langle r^2\rangle)^{3/2}\,(1 + 15g_4 + ...) \qquad (3)$$

Truncation of the series at g_4 was found to give the best agreement with other approximations,[10] where g_4 is given by

$$g_4 = -(1/8)(1 - 3\langle r^4\rangle/5\langle r^2\rangle^2)(...) \qquad (4)$$

Following Flory et al.,[9] we expand the direction correlation distribution $\Gamma_{\mathbf{r}}(\gamma)$ in the Legendre polynomials $P_k(\gamma)$

$$\Gamma_{\mathbf{r}}(\gamma) = \sum A_{k,\mathbf{r}} P_k(\gamma)$$
$$2\Gamma_{\mathbf{r}}(\gamma) = \sum(2k + 1)\langle P_k\rangle_{\mathbf{r}} P_k(\gamma) \qquad (5)$$

For the geometry required for formation of an excimer, $\Delta\theta = 0$, $\gamma = 1$, and $P_k(\gamma) = 1$, where $\langle P_k\rangle_{\mathbf{r}}$ are the average of polynomials over the configurations having the specific value of $\mathbf{r}$. Averaged polynomials are $\langle P_0\rangle_{\mathbf{r}} = 1$, $\langle P_1\rangle_{\mathbf{r}} = \langle\gamma\rangle_{\mathbf{r}}$, $\langle P_2\rangle_{\mathbf{r}} = 1/3(3\langle\gamma^2\rangle_{\mathbf{r}} - 1)$, $\langle P_3\rangle_{\mathbf{r}} = 1/4(10\langle\gamma^3\rangle_{\mathbf{r}} - 6\,\langle\gamma\rangle_{\mathbf{r}})$, etc. Equation 5 then becomes[9]

$$2\Gamma_0(1) = \sum(2k + 1)\langle P_k\rangle_{\mathbf{r}=0} \qquad (6)$$

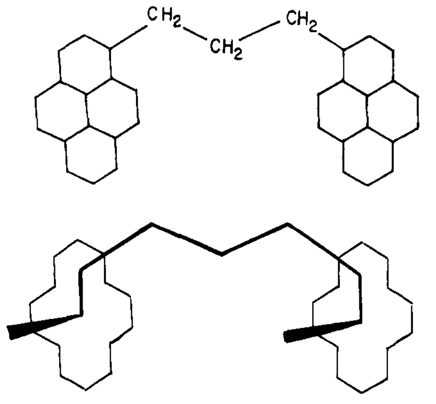

Figure 3. Pyr–$(CH_2)_3$–pyr chain (top) and its representation by eight virtual bonds (bottom). The first and last virtual bonds are normal to the plane of the pyrene ring systems.

Table I
Geometry Used in the Calculation (See Figure 3)

bond	bond length, pm	bonds	angle, deg
1	353	1, 2	90
2	209	2, 3	120
3	287	3, 4	112
4	153	4, 5	112
5	153	5, 6	112
6	287	6, 7	120
7	209	7, 8	90

$$\langle P_k \rangle_{r=0} = \{H(0)\}^{-1} [f_{k;0} - (3/2)f_{k;2} + (9/8)f_{k;4} - (9/16)f_{k;6} + ...] \quad (7)$$

where[9] $f_{k;0} = \langle P_k \rangle$, $f_{k;2} = \langle P_k r^2 \rangle / \langle r^2 \rangle - \langle P_k \rangle$, $f_{k;4} = \langle P_k r^4 \rangle / \langle r^2 \rangle^2 - 10\langle P_k r^2 \rangle / 3\langle r^2 \rangle + 5/3\langle P_k \rangle$, etc., and $H(0) = 1 + 15g_4 + ...$ Then

$$\langle P_k \rangle_{r=0} = \{H(0)\}^{-1} \{6.56\langle P_k \rangle - 11.81\langle P_k r^2 \rangle / \langle r^2 \rangle + 5.06\langle P_k r^4 \rangle / \langle r^2 \rangle^2 - 0.56\langle P_k r^6 \rangle / \langle r^2 \rangle^3\} \quad (8)$$

$\langle\,\rangle$ denotes the average without restriction on r. The quantities $\langle P_k r^{2p} \rangle$, where $p = 0, 1, 2, ...$, are evaluated from the moments, $\langle \gamma^s r^{2p} \rangle$, where $s = k, k - 2$, etc.[10]

Computation

The probability densities, $W_n(0)$, required for eq 2, were obtained by using rotational isomeric state theory to describe the conformations of the polymethylene spacers. In our approach, $W_n(0)$ was expressed in terms of a scalar Hermite expansion. g_4 was calculated from eq 4 with the moments computed by matrix methods. The angular correlation factors, $2\Gamma_0(1)$, needed for eq 2, were expressed in terms of moments. The moments $\langle \gamma^s r^{2p} \rangle$ are computed by the exact matrix multiplication methods.[2] The generator matrices have been described by Suter, Mutter, and Flory.[10]

Figure 3 depicts a pyr–$(CH_2)_3$–pyr chain. Bond lengths and bond angles are given in Table I. The first-order interaction, $\sigma = 0.43$, and the second-order interaction, $\omega = 0.034$, are those appropriate for an unperturbed polyethylene chain at 300 K.[13] For the bond pair next to each ring, ω was taken to be zero due to the much greater bulk of pyrene than of CH_2. The bond lengths and bond angles are taken from earlier work on polyethylene.[13] Dihedral angles for g^+ and g^- were centered 120° from the dihedral angle for t.

Results

The excimer equilibrium constants, K_e, were evaluated for pyr–$(CH_2)_m$–pyr according to eq 2. The scalar Hermite series approximation, truncated at g_4, was used for $W_n(0)$. The angle correlation factors $2\Gamma_0(1)$ were calculated according to eq 6. Results of these calculations are shown by the curves in Figures 4 and 5. Both the Gaussian approximation and the correction to the Gaussian approximation with g_4 predict that K_e experiences a monotonic decrease as m increases from 5 to 41.

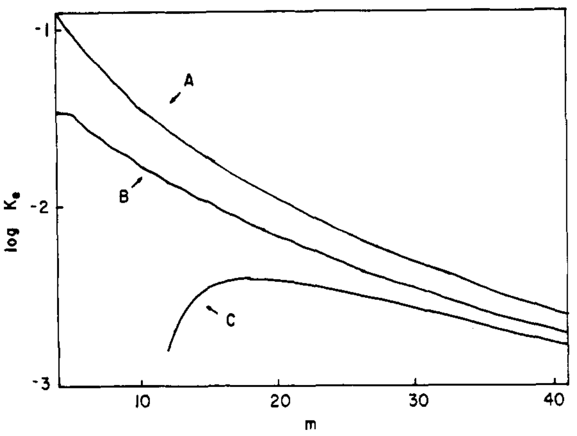

Figure 4. Values of K_e for pyr–$(CH_2)_m$–pyr as a function of m. (A) Gaussian approximation, (B) K_e calculated according to eq 3 from $W_n(0)$ as given by the scalar Hermite series expansion truncated at g_4, directional correlations between chain ends being neglected, (C) K_e obtained according to eq 2 with the incorporation of both g_4 and $2\Gamma_0(1)$.

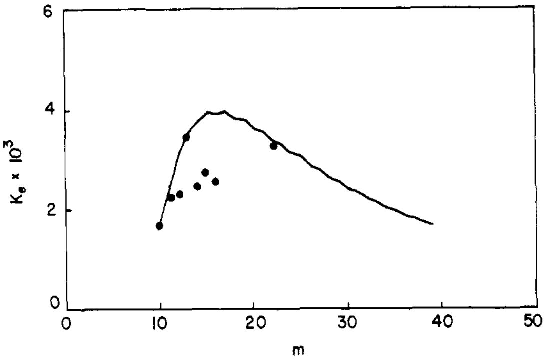

Figure 5. Values of K_e for pyr–$(CH_2)_m$–pyr, as functions of the number of methylene spacers (m). The solid line is curve C from Figure 4, and the points are I_E/I_M for pyr–$(CH_2)_m$–pyr, as reported by Zachariasse et al.[3] and scaled so that the experimental I_E/I_M and calculated K_E are coincident for $m = 13$.

Incorporation of the influence of the angular correlation, via $\Gamma_0(1)$, produces a qualitatively different behavior. Now, K_e passes through a maximum when $m = 15$. The drastic decrease in K_e at smaller m arises because the conformations that satisfy the requirement $r = 0$ tend to have an angle different from 0° for the normals to the two ring systems.

The theoretical curve in Figure 5 that includes the angular correlation is in agreement with the experimental result by Zachariasse and Kuhnle,[3] in the sense that it explains why the measured values of I_E/I_m do not experience a monotonous decrease with m but instead pass through a maximum when m is 13. The comparison of theory and experiment is shown in Figure 5. In view of the behavior of the three theoretical curves in Figure 4, it is clear that any attempt at a theoretical description of excimer emission at intermediate m should include a consideration of $\Delta\theta$ as well as r. Presumably many more terms would have to be included in the evaluation of $W_n(0)$ by eq 3 and 4 and $2c_0(1)$ by eq 6, in order to reproduce the finer details of the dependence of I_E/I_M on m. Alternatively, the assignment $\Phi_{01} = 1$, adopted throughout this treatment, may not be entirely appropriate for an aromatic ring system from plane point group 2*mm*.

The rapid increase of computer memory and computer time upon an increase in *n*, and inclusion of more terms in the series, complicates the investigation of the applicability of eq 2 for much larger numerical values of *n* (because of the large number of matrices in each serial expression) and very small values of *n* (because of the large number of terms required for convergence of the series in eq 4 and 6). However, the extrapolation of this equation would predict that K_e is proportional to $n^{-5/2}$ at large *n*, which is the result of Stockmayer and Jacobson,[12] and therefore the matrix methodology is not needed at large *n*. Conversely, at small *n* the problem can be solved by generation and examination of every conformation of the chain. The methodology described here is useful in the transition region between the domains treatable by discrete enumeration and simple analytical expressions.

One factor that is not included in the present analysis is the rate at which nonexcimer-forming rotational isomers are converted to excimer-forming rotational isomers through the process by which a dihedral angle passes over a conformational energy barrier.[14] The successful rationalization of the I_E/I_M for pyr-$(CH_2)_m$-pyr without explicit inclusion of the dynamics may arise when the dependence of the rate constant for first passage from the nonexcimer to the excimer ensemble is dominated by equilibrium quantities.[8] This situation has been shown to exist in A-B_m-A where B is CH_2 and A is C_6H_5COO.[8]

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Registry No. Pyr(CH_2)pyr, 124400-27-7.

Morphology of Highly Textured High-Density Polyethylene

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ABSTRACT: High-density polyethylene (HDPE) specimens were subjected to high orientation producing deformations below the melting point by using either a rolling mill or a channel die. After appropriate annealing protocols, the crystallographic and morphological textures were examined by using wide-angle X-ray diffraction pole figures, two-dimensional small-angle X-ray scattering and transmission electron microscopy. Although the two deformation patterns resulted in very similar crystallographic textures, the details of the morphological arrangements of crystalline lamellae were different. Quantitative considerations of the 2-D SAXS patterns led to the conclusion that lamellae that are inclined to the macroscopic orientation direction reflect a shear process within the individual lamellae rather than a rigid rotation inside the surrounding amorphous material.

1. Introduction

Modification of semicrystalline polymers from a spherulitic structure to a single crystal-like structure can be effectively achieved by rolling[1] or by channel-die compression.[2] The microstructural arrangements of such oriented semicrystalline polymers are characteried by determining the orientation of crystallographic planes and by the morphology of lamellar stacks. The spatial distribution of the crystallographic planes (pole density) can be precisely measured by wide-angle X-ray diffraction (WAXD). The lamellar structure and its orientation, on the other hand, can be analyzed by 2-D small-angle X-ray scattering (SAXS). Although 2-D SAXS has been used extensively in the past to reveal the lamellar morphology or so-called long period of oriented polymers, the interpretation of the 2-D SAXS patterns has been controversial.[3-5]

The difficulties in interpretation are partially due to the fact that there is no unique lamellar structure, especially in an oriented polymer, but are also due to the inherent characteristics of the scattering method itself (since it is impossible to determine the electron density function $\rho(r)$ of scattering matter directly from the X-ray data). To overcome this problem, transmissin electron microscopy (TEM) can be used as a complementary method to SAXS. TEM has proven to be very effective in revealing the local lamellar structure, especially of polyethylene (PE) for which an effective staining technique has been developed by Kanig[6] to delineate the inter-

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