

Dynamics of conformational transitions to isomeric states favoring intramolecular excimer formation in polymeric chains. Application to dimer models of polystyrene

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The dynamic rotational isomeric states model, which has been recently proposed to investigate the dynamics of local conformational transitions in polymers, is elaborated to formulate the increase in the number of excimer-forming sites through rotational sampling. The transition rate matrix governing the rate of passage between the subsets $\{\phi\}_a$ and $\{\phi\}_b$, consisting of excimer-forming and non-excimer-forming conformations, respectively, is modified such that microstates in $\{\phi\}_b$ are nonrecurrent, in contrast to the stationary process of conformational transitions in chains in equilibrium. The theory allows for the calculation of the fraction $P'(a)$ of sites that undergo transition to excimer-forming states at least once prior to time t , as well as mean first passage time from $\{\phi\}_b$ to $\{\phi\}_a$, as a function of real chain conformational characteristics and structural properties. Application of the model to the meso and racemic dyads in polystyrene confirms the fact that conformational mobility of the chain plays a major role in intramolecular excimer formation. Comparison with experiments demonstrates that the decay of the monomer fluorescence in styrene dimers is predominantly governed by the process of conformational transitions.

I. INTRODUCTION

Intramolecular excimer formation in polymers is the object of increasing interest.¹ In general, the extent of excimer formation in a polymer in dilute solution can be influenced by the conformational characteristics of the chain and by the rate of intramolecular singlet energy migration. The subject here is those systems in which intramolecular singlet energy migration can be neglected. Excimer fluorescence in dilute solution is a useful tool for investigation of the conformational statistics and dynamics of chains in which energy migration is of negligible importance. Since intramolecular excimer formation in such systems is determined by the formation of well-defined cyclic conformations during the lifetime of the initially excited chromophore, measurements of the intensities I_M and I_D of the excited monomer and excimer emission, respectively, provide important information about the conformational characteristics of the chain, as first pointed out by Longworth and Bovey.² Experiments with polymeric chains of variable size, terminated with identical chromophores at the ends, have been used to study cyclization dynamics and equilibria.³ When the chains are sufficiently long, Jacobson-Stockmayer theory⁴ or its version⁵ modified to take into account the directional correlations of the bonds at the chain ends, can be used to interpret data. For shorter chains, complete enumeration techniques and Monte Carlo simulations using the rotational isomeric state (RIS) model⁶ are preferred over analytical models. Such approaches are successful to the extent that the observed properties are determined by the equilibrium statistics of the chain. An early application of the RIS model to estimate the fraction of excimer-forming sites in solid polymers was performed by Frank and Harrah.⁷

Recently, steady-state emission and excitation spectra have been measured in dilute solution for dimethyl terephth-

alate and polyesters with different flexible spacers between the aromatic rings.⁸ The ratio I_D/I_M was found to exhibit an odd-even dependence on the number of flexible units (1-3 units for ethylene oxide^{8(a)} or 2-6 units for methylene^{8(b)}) between the rings. This dependence is similar to the behavior predicted by the equilibrium RIS analysis of the population of conformations of the flexible spacer that are conducive to excimer formation by nearest-neighbor chromophores.

Although the behavior of the polyesters⁸ exhibits a close correspondence to that expected from an equilibrium analysis that ignores chain dynamics, several experiments with other systems show that excimer emission is often highly dependent on the mobility of the bichromophoric compound.⁹ In fact, time-resolved measurements of intramolecular excimer formation from low molar mass bichromophoric compounds dispersed at very low concentration in bulk polymers is a powerful tool to probe the mobility of polymer matrices, the motions of the fluorescent probe being coupled with those of the host matrix.¹⁰ Excimer emission is more intense in media permitting fast rotameric transitions of the probe that create new excimer-forming sites during the lifetime of the excited chromophore. Similarly, in many polymers containing photoactive centers, intramolecular excimer emission is stronger if isomeric transitions to conformations favoring excimer formation are performed quickly. For instance, the fact that the meso dyad in polystyrene (PS) (and its diastereoisomeric dimer models) presents an I_D/I_M ratio substantially greater than that of the racemic dyad^{9,11,12} is explained on the basis of the heights of the barriers that must be crossed to assume excimer-forming conformations. In the meso dyad, the excimer conformation (tt) is easily formed from the most stable ground state (tg or gt) through passage over a barrier of about 2-3 kcal/mol. The equivalent transition in the racemic dyad, which is from tt to $t\bar{g}$ (or $\bar{g}t$), requires the crossing of a much higher bar-

rier, as first pointed out by Monnerie *et al.*^{11,12} on the basis of conformational energy maps.^{13,14} This example clearly demonstrates that there can be a substantial contribution to excimer emission from sites which are not suitable for complex formation initially, but assume the required geometry before the excited chromophore is deactivated by another mechanism. A complete theoretical analysis of excimer fluorescence should then take into account the dynamic aspects of the phenomenon, in addition to equilibrium properties.

For the case of short flexible segments separating the two interacting chromophores, a dynamic model that considers real chain conformational characteristics is required. Such a model, referred to as the dynamic RIS model,¹⁵ was recently developed as an extension of the formalism first introduced by Jernigan.¹⁶ As the name indicates, the model makes use of the fundamental concepts and assumptions underlying the well established RIS model of polymer statistics. It relies essentially on the calculation of the time-dependent probabilities of transitions within the whole space of isomeric conformations available to a finite sequence of pairwise interdependent bonds. Comparison with previous theoretical work, simulation of Brownian dynamics and relaxation data from NMR experiments, supports the use of the model as a tool to investigate local motions in polymers.¹⁷⁻¹⁹

For the present study, an extension of the model to treat the dynamics of the excimer sampling process is formulated. The theory is presented in the next section. As the theory contains both the static and dynamic aspects of the process, the main emphasis will be placed on the comparison of the relative influence of equilibrium statistics and chain dynamics in governing the extent of excimer emission.

Analysis of local motions by the dynamic RIS model is described in Sec. III. According to the model, the stochastics of conformational transitions obey a continuous parameter, discrete states, stationary Markov process.²⁰ In excimer formation, however, conformations favorable for excimer emission are considered as absorbing states, i.e., the initial equilibrium distribution of conformations is perturbed such that there is gradual increase in the number of sites contributing to excimer formation.

In Sec. IV, the model is applied to the meso and racemic dyads in polystyrene, which is one of the first excimer forming polymers studied experimentally. In the accompanying paper,²¹ the dynamic RIS model will be employed to investigate excimer formation in various polyesters, in comparison to the experimental work of Mendicuti *et al.*⁸ The two distinct examples of systems analyzed in the two papers illustrate cases where either the dynamic or the static effect dominates the observed qualitative behavior.

II. DESCRIPTION OF LOCAL MOTIONS BY THE DYNAMIC RIS MODEL

Let $\{\phi\}$ represent the set of configurations available to a segment between two chromophoric groups in the chain. Let us assume N bonds in the segment are subject to orientational motion. On the premises of fixed bond lengths and bond angles, the set of the torsional angles of the bonds is the only variable that determines a given configuration.⁶ Thus

$\{\phi\}$ contains ν^N elements provided that ν rotational isomeric states are available to each bond. The elements of $\{\phi\}$ will be denoted by ϕ_i , $i = 1, \nu^N$. Each ϕ_i is characterized in turn by the specific set of torsional angles of the N bonds in motion.

The segments are subject to Brownian motion in the form of conformational transitions between isomeric states, although the equilibrium distribution of the various configurations is conserved. In the language of the stochastic theory, the motion of the segment obeys a discrete state, continuous parameter stationary process.^{20,21} The passage from one configuration to another is prescribed by the $\nu^N \times \nu^N$ transition probability (or conditional probability) matrix $C^{(N)}(t)$. The superscript (N) in $C^{(N)}(t)$ and in the following refers to the number of rotating bonds in the segment between the chromophores. The element $C_{ij}^{(N)}$ of $C^{(N)}(t)$ represents the conditional probability of occurrence of configuration ϕ_i at time t , provided that the sequence is initially in configuration ϕ_j .²² $C^{(N)}$ is evaluated from the solution of the master equation.^{15,19}

$$C^{(N)}(t) \equiv \frac{dC^{(N)}(t)}{dt} = A^{(N)}C^{(N)}(t), \quad (1)$$

where $A^{(N)}$ is the transition rate matrix, whose ij th element ($i \neq j$) is the Arrhenius-type rate constant for the transition from configuration ϕ_j to configuration ϕ_i . The elements of $A^{(N)}$ satisfy the relation

$$A_{ii}^{(N)} = -\sum_j A_{ji}^{(N)}, \quad j \neq i \quad (2)$$

which is characteristic of conservative processes.²⁰ Also, from the principle of detailed balance for systems in equilibrium, we have

$$A_{ij}^{(N)} P_j^{(N)}(0) = A_{ji}^{(N)} P_i^{(N)}(0) \quad (3)$$

or

$$C_{ij}^{(N)} P_j^{(N)}(0) = C_{ji}^{(N)} P_i^{(N)}(0), \quad (4)$$

where $P_i^{(N)}(0)$ and $P_j^{(N)}(0)$ are the equilibrium probabilities of the i th and j th configurations, respectively. They are elements of the probability vector $P^{(N)}(t)$ at $t = 0$. Thus $P^{(N)}(t)$ represents the instantaneous probabilities of the ν^N configurations. It should be noted that Eq. (1) may equivalently be written for $P^{(N)}(t)$ as

$$P^{(N)}(t) = A^{(N)}P^{(N)}(t). \quad (5)$$

The off-diagonal elements of $A^{(N)}$ have the general form^{15,16}

$$A_{ij}^{(N)} \equiv r = A_0 \exp(-E_{ij}/RT), \quad (6)$$

where E_{ij} is the activation energy for the conformational transition from ϕ_j to ϕ_i . It is determined from the height of the saddle to overcome during the transition. The front factor A_0 depends on the conformational characteristics of the chain and the surrounding medium. It is accepted to be inversely proportional to solvent viscosity.¹⁹ r is the rate constant for the transition considered. R and T are the gas constant and absolute temperature, respectively.

Equation (1) is also called the forward equation.^{20,22} It may be shown that as a consequence of the constancy in time of $A^{(N)}$, the backward equation

$$C^{(N)}(t) = C^{(N)}(t)A^{(N)} \quad (7)$$

is also valid for the same process.

The formal solution to Eq. (1) or (7) is unique and equal to

$$C^{(N)}(t) = \exp\{A^{(N)}t\} \quad (8)$$

provided that $A^{(N)}$ is finite and $A_{ij}^{(N)} \neq -\infty$. The initial condition $C^{(N)}(0) = I^{(N)}$, where $I^{(N)}$ is the identity matrix of order ν^N , is used in Eq. (8). $C^{(N)}(t)$ may equivalently be expressed in terms of the eigenvalues and eigenfunctions of $A^{(N)}$ as

$$C^{(N)}(t) = B^{(N)} \exp\{\Lambda^{(N)}t\} [B^{(N)}]^{-1}, \quad (9)$$

where $B^{(N)}$ and $\Lambda^{(N)}$ are obtained from the orthogonal transformation

$$A^{(N)} = B^{(N)} \Lambda^{(N)} [B^{(N)}]^{-1}. \quad (10)$$

Here $\Lambda^{(N)}$ is the diagonal matrix of the eigenvalues $\lambda_1, \lambda_2, \dots, \lambda_{\nu^N}$ of $A^{(N)}$, i.e.,

$$\Lambda^{(N)} = \begin{bmatrix} \lambda_1 & & & \\ & \lambda_2 & & \\ & & \ddots & \\ & & & \lambda_{\nu^N} \end{bmatrix}. \quad (11)$$

$B^{(N)}$ is the matrix whose i th column represents the eigenvector associated with λ_i , $i = 1, \nu^N$. $[B^{(N)}]^{-1}$ is the inverse of $B^{(N)}$. One of the eigenvalues, say λ_1 , is identically equal to zero and ensures convergence to equilibrium properties at long times, while all others are negative.^{19,22,23} $|\lambda_i|$ physically represents the frequency of the i th mode contributing to local orientational relaxation. Consequently, any transient property related to local orientational motion may be expressed as a sum of exponentials $\sum k_i \exp(\lambda_i t)$, where k_i depends on the intrinsic structural and conformational characteristics of the chain and on the property investigated, and is easily evaluated using $B^{(N)}$, $P^{(N)}(0)$, etc.¹⁹ For further details about the dynamic RIS model, the reader is referred to Refs. 15–19.

III. STOCHASTICS OF EXCIMER FORMATION

The set $\{\phi\}$ of all configurations available to the segment of N bonds may be divided into two subsets $\{\phi\}_a$ and $\{\phi\}_b$ such that $\{\phi\}_a$ comprises the configurations which favor excimer formation, i.e., those in which the terminal aromatic groups are allowed to assume the geometry required for excimer formation.²⁴ The remaining configurations belong to $\{\phi\}_b$. The two sets are representative of two macrostates a and b whose respective probabilities may be evaluated from

$$P^0(a) = \sum_{\phi_i \in \{\phi\}_a} P_i^{(N)}(t), \quad \phi_i \in \{\phi\}_a, \\ P^0(b) = 1 - P^0(a) = \sum_{\phi_j \in \{\phi\}_b} P_j^{(N)}(t), \quad \phi_j \in \{\phi\}_b. \quad (12)$$

In the above equations, ϕ_i and ϕ_j may be viewed as the microstates composing the macrostates a and b , respectively. For the above process where all microstates intercommunicate as described by Eqs. (2) and (3), the probability $P^{(N)}(t)$ remains unchanged and equal to $P^{(N)}(0)$, regardless of the time argument, unless the initial probability distribution

of various configurations is perturbed, i.e., different from the one dictated by equilibrium statistics. Consequently, $P^0(a)$ and $P^0(b)$ are constant for all t and determined by the equilibrium statistics of the chain. These values also represent the time averages of the two macrostates for a given segment.

Thus, according to the above description any depletion in the concentration of excimer-forming sites is counterbalanced by the creation of new favorable sites such that $P^0(a)$ is conserved. The time dependence of the transition probabilities is portrayed in Fig. 1. A general expression for the instantaneous probability of excimer-forming sites may be written as

$$P^t(a) = P(a/a)P^0(a) + P(a/b)P^0(b), \quad (13)$$

where the superscript t refers to the time different from zero. Here $P(a/b)$ denotes the transition or conditional probability of macrostate a at time t , given macrostate b at $t = 0$. Similar definitions apply for $P(a/a)$, $P(b/a)$, $P(b/b)$. Since from the principle of detailed balance

$$P(a/b)P^0(b) = P(b/a)P^0(a) \quad (14)$$

it may be easily shown from Eqs. (13) and (14) that for the process described above $P^t(a) = P^0(a)$ for all t .

If on the other hand, one is concerned with the total number of segments that passed at least once through an excimer-favoring state, this is no longer a reversible equilibrium problem. There is a gradual increase in $P^t(a)$, from the initial equilibrium value $P^0(a)$ to 1. In this case, the excimer-forming configurations are considered as absorbing states such that back transitions from $\{\phi\}_a$ to $\{\phi\}_b$ are precluded.²⁵ The configurations in $\{\phi\}_b$ are said to be nonrecurrent and the transition rate matrix for such a process should be modified such that transitions from $\{\phi\}_a$ to $\{\phi\}_b$ are prevented.²² The latter is achieved by equating suitable columns of $A^{(N)}$ (those corresponding to states in $\{\phi\}_a$ to zero, while keeping the others unchanged).²⁰ Thus the rates of conformational transitions within subset $\{\phi\}_b$ and in the direction $\{\phi\}_b \rightarrow \{\phi\}_a$ are identical to those of the stationary process.

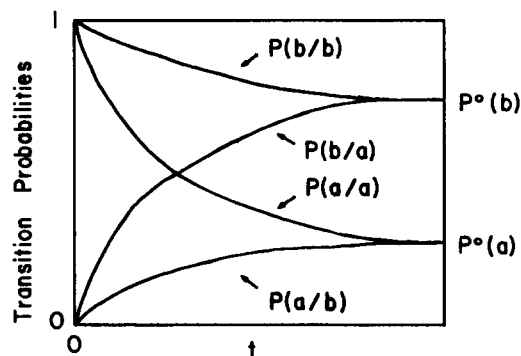


FIG. 1. Time dependence of the transition probabilities $P(a/b)$, $P(a/a)$, $P(b/a)$, and $P(b/b)$ between macrostates $\{\phi\}_a$ and $\{\phi\}_b$, for the stationary process of conformational transitions in polymeric segments in equilibrium. $P(a/b)$ and $P(b/a)$ increase from zero to the equilibrium probabilities $P^0(a)$ and $P^0(b)$ of the two macrostates, respectively. Also, $P(b/b) + P(a/b) = P(a/a) + P(b/a) = 1$, at all times.

By suitable permutation of columns, the transition rate matrix $A_n^{(N)}$ of the absorbing process may be written as

$$A_n^{(N)} = \begin{bmatrix} 0 & D \\ 0 & E \end{bmatrix}. \quad (15)$$

Here the subscript n is appended to $A_n^{(N)}$ to distinguish the rate matrix corresponding to the new nonequilibrium process from $A^{(N)}$ of the equilibrium process. The submatrices E and D refer, respectively, to conformational transitions within $\{\phi\}_b$ and those from $\{\phi\}_b$ to $\{\phi\}_a$. They are directly taken from the rate matrix $A^{(N)}$ of the equilibrium process. Their respective sizes are $N_b \times N_b$ and $N_a \times N_b$ where N_a and N_b are the number of microstates (or configurations) in $\{\phi\}_a$ and $\{\phi\}_b$, respectively. Clearly, $N_a + N_b = \nu^N$.

The transition probability matrix of the absorbing process assumes the form

$$C_n^{(N)}(t) = \begin{bmatrix} I & G(t) \\ 0 & H(t) \end{bmatrix}, \quad (16)$$

where I is the identity matrix of order N_a . It follows from the property

$$C_{ij}^{(N)}(t) = \delta_{ij} \quad (17)$$

for all absorbing states ϕ_j in the irreversible process. δ_{ij} is the Kronecker delta. $H(t)$ and $G(t)$ in Eq. (16) refer to instantaneous transition probabilities within $\{\phi\}_b$ and from $\{\phi\}_b$ to $\{\phi\}_a$, in analogy to the corresponding submatrices E and D in $A_n^{(N)}$. However, in contrast to D and E which are the same in $A^{(N)}$ and $A_n^{(N)}(t)$, the transition probabilities in $H(t)$ and $G(t)$ are quite different from their analogs in $C^{(N)}(t)$. In fact, our purpose is to evaluate the submatrix $G(t)$, in particular, which accounts for the passage from $\{\phi\}_b$ to $\{\phi\}_a$. The latter may be determined by inserting $A_n^{(N)}$ and $C_n^{(N)}(t)$ in the backward equation (7). This leads to

$$\dot{G}(t) = D + G(t)E. \quad (18)$$

Written in component form Eq. (18) yields a set of non-homogeneous first-order differential equations with constant coefficients. It is subject to the initial condition $G(0) = I$. It should be noted that D and E are known from the equilibrium process. The $N_a \times N_b$ equations may be solved for the unknown transition probabilities, i.e., the elements of $G(t)$, at a given time, by either analytical or numerical method. Clearly, at long times all elements of G , and consequently $P'(a)$, approach unity. The transition probability $P_n(a/b)$ from $\{\phi\}_b$ to $\{\phi\}_a$ in the irreversible process is

$$P_n(a/b) = \left[\sum_i \sum_j G_{ij}(t) P_j^{(N)}(0) \right] / \sum_j P_j(0), \quad (19)$$

where $G_{ij}(t)$ is the ij th element of $G(t)$. Subscripts i and j correspond to microstates in $\{\phi\}_a$ and $\{\phi\}_b$, respectively, as

$$A^{(2)} = \begin{bmatrix} -2r_1 & r_{-1} & r_{-1} & 0 \\ r_1 & -(r_2 + r_{-1}) & 0 & r_{-2} \\ r_1 & 0 & -(r_2 + r_{-1}) & r_{-2} \\ 0 & r_2 & r_2 & -2r_{-2} \end{bmatrix}. \quad (23)$$

follows from the definition of $G(t)$. By inserting Eq. (19) into Eq. (13), the time-dependent probability of excimer-forming sites becomes

$$P'(a) = P^0(a) + \sum_i \sum_j G_{ij}(t) P_j^{(N)}(0). \quad (20)$$

It should be recalled that $P'(a)$ accounts for the probability of polymeric segments that at least once have been transformed into an excimer forming state, during the time interval t . Thus, although the instantaneous probability of segments favorable to excimer emission is constant and equal to the equilibrium value $P^0(a)$ at all times, that of the segments which assume one of the microstates in $\{\phi\}_a$, prior to t is a gradually increasing function of time. The gradual increase or the accumulation of segments which at least once undergo the conformational transition to $\{\phi\}_a$, is accounted for by the second term in Eq. (20).

A representative measure of the rate of transition from $\{\phi\}_b$ to $\{\phi\}_a$ is the mean first passage time $\langle \tau \rangle$ from the first macrostate to the second. Following Oppenheim,²³ the latter is evaluated from

$$\langle \tau \rangle = \int_0^\infty t \dot{\rho}(t) dt = \int_0^\infty \rho(t) dt, \quad (21)$$

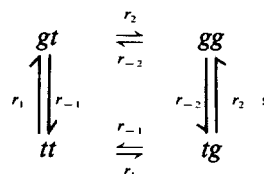
where $\rho(t)$ is defined as the probability that the random event considered has not occurred before time t . In our case this is the probability that a randomly selected segment in the ensemble has not undergone the transition to macrostate $\{\phi\}_a$, at time t , i.e., simply

$$\rho(t) \equiv P'(b) = 1 - P'(a). \quad (22)$$

By substituting Eq. (22) into Eq. (21) and carrying out the integration the first passage time is easily calculated, as will be illustrated below.

IV. APPLICATION TO POLYSTYRENE

Conformational energy maps indicate that a two-state scheme, consisting of the *trans* (t) and *gauche* (g) states for each skeletal bond, is suitable for treating the statistics of polystyrene.¹⁴ Consequently, four isomeric states tt , tg , gt , and gg are available to each dyad.²⁷ The kinetic scheme for conformational transitions is



where r_1 , r_{-1} , r_2 , and r_{-2} are the rate constants associated with the indicated transitions. The transition rate matrix corresponding to the above scheme is

Here the superscript (2) indicates that the segment between the chromophoric groups comprises two mobile bonds.

The conformational characteristics of meso dyads differ considerably from those of racemic dyads. *tt* states are those favoring excimer formation in meso dyads, as may be directly concluded from the examination of the geometrical structure of the repeating unit, whereas in racemic dyads excimer emission is expected to take place from state $t\bar{g}$ and $\bar{g}t$. Here \bar{g} refers to a state with negligibly small probability of occurrence, due to severe steric interaction between the phenyl rings and the groups or atoms adjacent to the dyad. Also the transition from the most stable ground state *tt* in racemic dyad, to the excimer forming states ($t\bar{g}$ and $\bar{g}t$) necessitates the passage over a relatively high barrier.^{13,14} Thus (i) the equilibrium population of excimer forming sites in racemic dyads is negligibly small and (ii) the conformational transitions sampling those sites are at least one order of magnitude slower than those taking place in the meso dyads. As a result, the efficiency of excimer formation in racemic dyads is far lower than that in meso dyads, as confirmed by steady-state and transient fluorescent spectra.^{9,11,28} Itagaki and collaborators²⁸ show that the excimer emission from diastereoisomeric model compounds of PS in which the excitation is mostly absorbed by chromophores in racemic dyads, is controlled by the influx of that excitation energy into neighboring meso dyads which readily assume an excimer-forming conformation. They point out that the *tt* conformer in meso dyads appears to be mainly responsible for the excimer emission in PS, in agreement with quantum mechanical calculations by Blonski *et al.*²⁹ Accordingly, we will direct our attention to the dynamics of meso dimers, in particular, where the energy migration does not contribute²⁸ to excimer emission.

A. Meso dyad

In meso dyads the *tt* state is the only absorbing one. Consequently r_1 in Eq. (23) is equated to zero in this case. The transition rate matrix associated with the irreversible process reads

$$A_n^{(2)} = \begin{bmatrix} 0 & r_{-1} & r_{-1} & 0 \\ 0 & -(r_2 + r_{-1}) & 0 & r_{-2} \\ 0 & 0 & -(r_2 + r_{-1}) & r_{-2} \\ 0 & r_2 & r_2 & -2r_{-2} \end{bmatrix} \quad (24)$$

From the comparison with Eq. (15), we have

$$D = [r_{-1} \quad r_{-1} \quad 0] \quad (25)$$

and

$$E = \begin{bmatrix} -(r_2 + r_{-1}) & 0 & r_{-2} \\ 0 & -(r_2 + r_{-1}) & r_{-2} \\ r_2 & r_2 & -2r_{-2} \end{bmatrix} \quad (26)$$

for the submatrices defining the rates of transitions from $\{\phi\}_b$ to $\{\phi\}_a$, and within $\{\phi\}_b$, respectively. The transition probabilities $G_{ij}(t)$ from microstate ϕ_j in $\{\phi\}_b$ to microstate ϕ_i in $\{\phi\}_a$ are the quantities of interest.²⁴ They obey the set of differential equations:

$$\begin{aligned} G_{12} &= r_{-1} - (r_2 + r_{-1})G_{12} + r_2G_{14}, \\ G_{13} &= r_{-1} - (r_2 + r_{-1})G_{13} + r_2G_{14}, \\ G_{14} &= r_{-2}G_{12} + r_{-2}G_{13} - 2r_{-2}G_{14} \end{aligned} \quad (27)$$

as follows from Eq. 18. It should be recalled that subscripts 1, 2, 3, and 4 appended to G (and P^i , E , D below) refer to states *tt*, *tg*, *gt*, and *gg*, respectively. The set of Eq. (27) is solved by the method of Laplace transforms. The solution is

$$G_{1i} = 1 + B_i \exp(\lambda_1 t) + C_i \exp(\lambda_2 t), \quad i = 2,3,4, \quad (28)$$

where

$$\begin{aligned} \lambda_{1,2} &= -(r_{-1}/2 + r_2/2 + r_{-2}) \\ &\quad \pm [(r_{-1}/2 + r_2/2 + r_{-2})^2 - 2r_{-1}r_{-2}]^{1/2}, \end{aligned} \quad (29)$$

$$B_2 = B_3 = \frac{r_{-1}(\lambda_1 + 2r_{-2})}{\lambda_1(\lambda_1 - \lambda_2)}, \quad (30)$$

$$B_4 = \frac{2r_{-1}r_{-2}}{\lambda_1(\lambda_1 - \lambda_2)}, \quad (31)$$

$$C_i = -1 - B_i, \quad i = 2,3,4. \quad (32)$$

Inserting the above results into Eq. (20), the probability of *tt* states which favor excimer emission increases with time according to

$$\begin{aligned} P^i(a) &= 1 + \sum_{i=2}^4 P_i^{(2)}(0) B_i \exp(\lambda_1 t) \\ &\quad + \sum_{i=2}^4 P_i^{(2)}(0) C_i \exp(\lambda_2 t), \end{aligned} \quad (33)$$

where the initial probabilities $P_i^{(2)}(0)$ may be taken as identical to equilibrium probabilities. As may be seen from Eq. (33), two orientational modes with relaxation frequencies $|\lambda_1|$ and $|\lambda_2|$ contribute to the dynamic process of excimer formation. They are interrelated as

$$\lambda_1 \lambda_2 = 2r_{-1}r_{-2} \quad (34)$$

as follows from Eq. (29). In the limit as t goes to infinity, the exponential terms in Eq. (33) vanish (as both λ_i 's are negative), i.e., $P^\infty(a) = 1$. In the other limit of $t = 0$, using Eq. (32), we obtain

$$P^i(a) = 1 - \sum_{i=2}^4 P_i^{(2)}(0) = P_1^{(2)}(0),$$

as expected. Thus $P^i(a)$ increases from the equilibrium probability of *tt* states at $t = 0$, to unity at long times, according to Eq. (33). The mean first passage time from $\{\phi\}_b$ to $\{\phi\}_a$ is

$$\langle \tau \rangle_m = - \sum_{i=2}^4 \left(\frac{B_i}{\lambda_1} + \frac{C_i}{\lambda_2} \right) P_i^{(2)}(0) \quad (35)$$

as may be deduced from Eqs. (21), (22), and (33). The subscript m appended to $\langle \tau \rangle$ refers to the meso dyad.

B. Racemic dyads

The excimer forming states $t\bar{g}$ and $\bar{g}t$ in racemic dyads are highly improbable from the energetic point of view as mentioned above. Their occurrence is usually neglected in statistical treatments of PS chains.¹⁴ The most stable ground states are the *tt* and *gg* states in racemic dyads. There is no suitable path involving one saddle for the passage from the

state gg to $t\bar{g}$ (or $\bar{g}t$) as may be seen from conformational energy maps. Thus the creation of excimer-favoring sites in racemic dyads results almost entirely from the conformational transitions of tt dyads, which account for about 90% of the equilibrium population of various conformations. The above notation may be adopted if r_1 now denotes the rate of passage from tt to $t\bar{g}$ or $\bar{g}t$ states and the states $t\bar{g}$ and $\bar{g}t$ are now identified with subscripts 2 and 3. Following the above steps, D and E reduce to

$$D = \begin{bmatrix} D_{21} \\ D_{31} \end{bmatrix} = \begin{bmatrix} r_1 \\ r_1 \end{bmatrix} \quad (36)$$

and

$$E = [E_{11}] = [-2r_1] \quad (37)$$

which leads, as expected, to

$$\dot{G}_{i1} = r_1 - 2r_1 G_{i1}, \quad i = 2,3 \quad (38)$$

and

$$G_{i1} = 1/2[1 - \exp(\lambda_1 t)], \quad i = 2,3 \quad (39)$$

with

$$\lambda_1 = -2r_1. \quad (40)$$

Clearly, the fraction of segments that undergo, at least once, transitions to $t\bar{g}$ or $\bar{g}t$ states before time t becomes

$$P'(a) = 1 - \exp(\lambda_1 t) \quad (41)$$

using the approximation $P_1^{(2)}(0) \approx 1$. The mean first passage time $\langle \tau \rangle_r$ from $\{\phi\}_b$ to $\{\phi\}_a$ for the racemic dyad equals

$$\langle \tau \rangle_r = -P_1^{(2)}(0)/\lambda_1. \quad (42)$$

C. Calculations

Data for energy minima and heights of the saddles between isomeric states are estimated from the available conformational energy maps for the meso dyads in polystyrene.^{13,14} The values used in calculations are listed in Table I. A barrier height of 2.5 kcal/mol is assigned to the transition $t\bar{g}/\bar{g}t \rightarrow tt$ in the meso dyad. This value directly follows from conformational energy maps computed with the 6-12 energy function truncated at $\sigma = 5 \text{ \AA}$ for all atom pairs.¹⁴ Those semiempirical maps were found³⁰ to be representative of conformational characteristics of PS chains including sol-

vent effects. As to the racemic dyad, the barrier height for the transition of interest, i.e., $tt \rightarrow t\bar{g}/\bar{g}t$ is taken as 4.6 kcal/mol. Although this value is lower than the one predicted by semiempirical force-field calculations, Arrhenius plots of the ratio I_D/I_M against T^{-1} in several temperature-dependent excimer fluorescence experiments with PS or its model compounds^{11,12,31,32} indicate apparent activation energies of about 2.5 and 4.6 kcal/mol, for the meso and racemic dyads, respectively. Those activation energies are attributed to the heights of the rotational barriers to assume excimer-forming states, and are adopted in the present work.

The values at the energy minima are used to calculate the equilibrium probabilities $P_i^{(2)}(0)$ ($i = 1,4$) of the conformational isomeric states. The latter may also be evaluated from the eigenvector associated with the zero eigenvalue of the equilibrium process, as pointed out earlier.^{18,19} As to the barrier heights, they are substituted as E_{ij} into Eq. (6) to calculate r_i ($i = \pm 1, \pm 2$) corresponding to different conformational transitions. The value $A_0 = 0.9 \times 10^{11}/\text{s}$ is adopted for the front factor in Eq. (6), from the comparison (see sequel) with previous work.⁹ For a comparative study of the dynamics of the excimer sampling process in the meso and racemic dyads of PS, under the same environmental conditions (solvent, temperature, etc.), the choice of the absolute value of A_0 is immaterial. It should be recalled that the latter depends on the solvent nature as it is inversely proportional to solvent viscosity, and that the eigenvalues $|\lambda_i|$ or the frequencies of the various relaxational modes contributing to local orientational motions are linearly proportional to A_0 .^{18,19} As a result, the same qualitative and quantitative predictions are preserved regardless of the time scale, which varies linearly with solvent viscosity.

Calculations are performed for $T = 300$ and 350 K . The increase in the probability of segments that at least once assume a configuration favorable for excimer formation is calculated from Eqs. (33) and (41) for the meso and racemic dyads, respectively. The frequencies $-\lambda_1$ and $-\lambda_2$ in the two cases are found from Eqs. (29) and (40), respectively. The resulting probability curves are drawn in Fig. 2. The

TABLE I. Conformational and activation energies.

State	Conformational energies (kcal/mol)	
	Meso	Racemic
(1) tt	1.6	0
(2) $t\bar{g}$	0.7	2.8
(3) $\bar{g}t$	0.7	2.8
(4) gg	3.3	1.5
Activation energies in r_i ($i = \pm 1, \pm 2$) ^a		
i	Transition (kcal/mol)	Meso
1	$tt \rightarrow t\bar{g}$	1.6
-1	$\bar{g}t \rightarrow tt$	2.5
2	$t\bar{g} \rightarrow gg$	4.3
-2	$gg \rightarrow t\bar{g}$	1.7

^aStates $t\bar{g}$ and $\bar{g}t$ are equivalent.

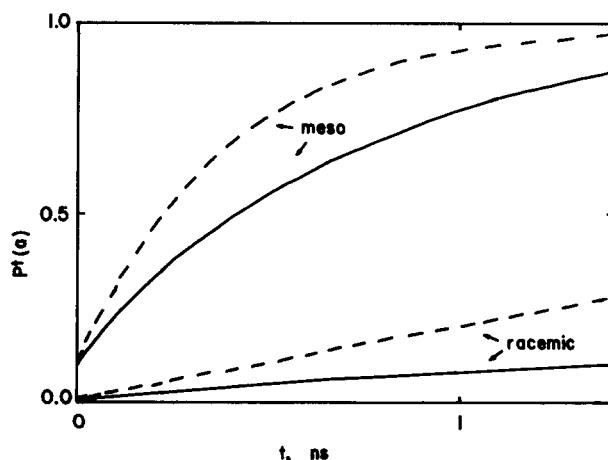


FIG. 2. Increase in the fraction or probability $P'(a)$ of excimer-forming sites by the rotational sampling of conformational transitions for the meso and racemic dyads in PS, at 300 K (solid curves) and 350 K (dashed curves). Data in Table I with $A_0 = 0.9 \times 10^{11}/\text{s}$ is employed in dynamic RIS calculations.

most striking feature from the examination of Fig. 2 is the considerably faster increase of $P'(a)$ in meso dyads compared to that of racemic dyads. This is a direct consequence of the relative frequencies of excimer sampling process in the two isomers. Although their ratio diminishes at higher temperature (350 K), the significant departure between the $P'(a)$ curves corresponding to the meso and racemic dyads is still persistent. The mean first passage times are calculated from Eqs. (35) and (42) for the meso and racemic dyads, respectively. Their respective values are 6.7×10^{-10} and 1.13×10^{-8} s, at 300 K, using the above front factor, i.e., the process of creation of sites favorable to excimer emission is ~ 17 times slower in the racemic dyad at room temperature, compared to meso dyads, as follows from the ratio $\langle \tau \rangle_r / \langle \tau \rangle_m \approx 17$.

V. CONCLUSION AND DISCUSSION

In the present work, the dynamics of the process of conformational transitions to states favoring excimer formation has been theoretically investigated. The previously introduced dynamic RIS model is used to treat the irreversible process of accumulation of sites which are suitable for the formation of the complex. The transition rate matrix governing the rate of passages between conformational isomers is modified such that a new stochastic process where the excimer forming states are absorbing states, is constructed.

The theory allows for the quantitative determination of the time dependent increase in the number or probability $P'(a)$ of sites belonging to $\{\phi\}_a$, i.e., the subset of conformations with the required geometry for excimer formation, within the whole configurational space $\{\phi\}$. The mean first passage time from the complementary subset $\{\phi\}_b$ (i.e., $\{\phi\}_b = \{\phi\} - \{\phi\}_a$) to $\{\phi\}_a$ is evaluated from the time dependence of $P'(a)$.

Inasmuch as real structural properties and conformational characteristics are included in the model, the theory should account for the observed differences in the behavior of different polymeric systems provided that the influence of conformational characteristics of the chain is not significantly complicated by the simultaneous effect of energy migration. As an illustration, the formulation developed in the present study has been applied to the meso and racemic dyads in polystyrene. The calculations show that the meso dyad exhibits a considerably faster increase in the number of conformations favoring excimer formation, compared to the racemic dyad. The mean first passage times for the two isomers are calculated to be in the ratio of $\langle \tau \rangle_r / \langle \tau \rangle_m \approx 17$. Measurements with 2,4-diphenylpentanes yield a ratio of ~ 22 for the rates of excimer formation in racemic and meso dyads.¹¹

It should be recalled that the theory limits dynamic interdependence between bonds to only first neighbors along the chain. Long-range interactions are neglected as commonly done in the treatment of equilibrium statistics. Thus the contribution to excimer formation from the coupling of chromophoric groups which are separated by more than a repeating unit, is neglected, assuming the interaction between first neighbors to be the major factor controlling the observed spectra.

As to the front factor A_0 in Eq. (6), a representative value for the specific polymeric system may be estimated from previous experimental studies, as recently carried out for polyoxyethylene solutions.¹⁹ In the dynamic RIS model, A_0 and consequently the rates of conformational transitions are assumed¹⁹ to be linearly proportional to the reciprocal viscosity. Recent excimer fluorescence studies³³ with polystyrene in cosolvent mixtures indicate a linear dependence of excimer to monomer intensity ratio I_D/I_M , on the inverse of solvent viscosity η^{-1} , which supports the validity of the above assumption. The same study by Masegosa *et al.*³³ draws attention to the fact that in isotactic PS the predominant mechanism for excimer formation is the rotation of skeletal bonds during the lifetime of one chromophore in the excited state, in agreement with previous studies. If in the present study we adopt a value of $A_0 = 0.9 \times 10^{11}$ /s, the time constant $|1/\lambda_1|$ associated with the process of excimer formation becomes equal to 0.72 and 12 ns in the meso and racemic dyads, respectively. These time constants play the major role in governing the dynamics of the excimer sampling process. It should be noted that the second relaxational mode with time constant $|1/\lambda_2|$, in the present work, is representative of the transitions of those segments which are initially in *gg* states, to states conducive to excimer emission. In meso dyads, they are faster by about one order of magnitude compared to the dominant mechanism (with time constant $|1/\lambda_1|$), due to the lower barrier to surmount. However, their *a priori* probability of occurrence is very low such that their influence on the predicted $P'(a)$ curves is negligible.

The contribution from the meso dyads is the major factor dominating the decay of the monomer fluorescence in PS or its model compounds. The experimental decay of monomer fluorescence for PS or its model compounds is satisfactorily approximated by a dual exponential of the form

$$I_M(t) = A_1 \exp(\lambda_1 t) + A_2 \exp(\lambda_2 t), \quad (43)$$

where the coefficients A_1 and A_2 sum up to unity thus normalizing $I_M(t)$ in the interval $0 < t < \infty$, and $\lambda_i = 1/\tau_i$ where τ_i is the best fitting time constant. The decay in monomer fluorescence is mainly due to the decrease in the number of excited single chromophores by forming excimers. If the excimer formation in meso dyads is predominantly governed by the process of conformational transitions, this decay curve is expected to obey a similar functional form as the rise in the number of excimer-forming sites. For an understanding of the extent of the role of conformational transitions in prescribing the decay curves, A_i and λ_i which are found^{9,28,34} to yield the best fit with experiments are compared with the exponential terms in Eq. (33). Table II gives a comparison of the terms $A_i \exp(\lambda_i t)$ ($i = 1, 2$) in Eq. (43) and the two exponential terms in Eq. (33). The A_1 and A_2 values in the present work in Table II, are evaluated from

$$-\sum_{i=2}^4 P_i^{(2)}(0)B_i \quad \text{and} \quad -\sum_{i=2}^4 P_i^{(2)}(0)C_i,$$

respectively, as follows from Eq. (33). It is interesting to note that the first term $A_1 \exp(\lambda_1 t)$ which mainly dominates $I_M(t)$ is well accounted for by the present model. This result confirms that local chain dynamics play an important role in the excimer fluorescence of isotactic PS. The second term in

TABLE II. Decay parameters of monomer fluorescence in PS and its model compounds.

Ref.	$-1/\lambda_1$ (ns)	A_1	$-1/\lambda_2$ (ns)	A_2
9 and 28	0.5–0.7	0.70	4–6	0.30
34	0.88	0.997	15	0.003
Present work ^a	0.72	0.901	0.1	0.002

^a A_1 and A_2 sum up to $1 - P^0(a)$ in the present treatment, as follows from Eqs. (32) and (33). Upon normalization they equate to 0.998 and 0.002, respectively.

Eq. (43) is of secondary importance in determining $I_M(t)$, as apparent from the coefficients A_i , $i = 1, 2$. Itagaki *et al.* correlate their value (~ 6 ns) to the time required for the transition $gg \rightarrow gt$ or tg in meso dyads at room temperature. This value does not however agree with the present analysis, where a much faster passage time (~ 0.1 ns) is predicted for the same transition, and is explained on the basis of the corresponding lower barrier to overcome. As to $-1/\lambda_2$ from the work of Soutar *et al.*,³⁴ this is attributed²⁸ to the overlapping of the excimer fluorescence. Thus, if attention is confined to the first term which plays a major role in $I_M(t)$, satisfactory correlation between the values estimated from the conformational stochastics of the chain and those resulting from experiments is obtained. It should be noted that the single exponential time constant $|1/\lambda_1| \approx 12$ ns calculated for racemic dyads by using the same front factor A_0 and the apparent activation energy 4.6 kcal/mol, agrees with the value (11 ns) reported by Itagaki *et al.*^{9,28} and de Schryver *et al.*¹¹ The present analysis suggests the adoption of $A_0 \approx 10^{11}$ /s for future investigation of the dynamics of dilute polystyrene solutions.

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²⁶Same indices as those associated with the corresponding elements of $A_n^{(N)}(t)$ and/or $C_n^{(N)}(t)$ are adopted for the elements of G , H , D , and E , to avoid confusion, i.e., the subscripts are representative of a given microstate and not the serial order within submatrices. For example, $G_{\text{meso}} = [G_{12}G_{13}G_{14}]$.

²⁷The state g corresponds to a positive or negative dihedral angle, depending on the enantiomeric state of the bond. Following the convention used in Ref. 14, bonds in d and l states undergo right- and left-handed rotations, respectively.

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