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Kinetic and Thermodynamic Aspects of Excimer Formation in 2,4-Diphenylpentanes as Polystyrene Models

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ABSTRACT: Excimer formation in diastereoisomers of 2,4-diphenylpentane, base units of polystyrene, was investigated by using stationary and nonstationary techniques in isooctane. The rate constants of excimer formation of the meso and racemic isomers were compared and related to the conformational distribution within each configuration.

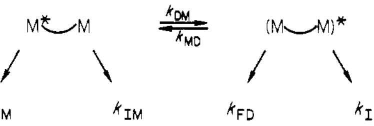
The formation of intermolecular excited-state complexes, first observed with organic molecules by Förster,[1] was extended by Hirayama[2] to 1,3-diphenylpropane. The formation of such complexes in di- and polychromophoric molecules has been and is an area of intensive research which has been recently reviewed.[3]

Although the role of configurational and conformational aspects upon intramolecular excimer formation has been pointed out,[4] polystyrene has been recently[5] analyzed using a kinetic scheme which is the monomolecular analogue of the classical intermolecular one. The role of the conformational distribution within different configurations has been discussed in the analysis of emission spectra of model systems[6] and polymers of different tacticity.[7] The difference in time-correlated properties of *meso*- and *rac*-1,1′-bis(2-naphthyldiethyl) ether was recently reported.[8]

In the present contribution kinetic and thermodynamic aspects obtained by stationary and nonstationary fluorescence methods are compared with information obtained by NMR, IR, and acoustic measurements and correlated with conformational energy maps obtained by force field calculations.[9]

Although the absorption spectra of *rac*-2,4-diphenylpentane (**1**) and *meso*-2,4-diphenylpentane (**2**) differ only slightly in their vibrational progression of the L_B band, a substantial difference in the emission characteristics is observed upon excitation at 261 nm in isooctane at room temperature.[6b] The relative importance of the excimer band is in **2** much larger than in **1**.

The temperature dependence of the quantum yields of **1** and **2** is reported in Figure 1 between 180 and 360 K. The important decrease of the "monomer" component of the emission upon increasing the temperature is partly related to the photophysical properties of the model chromophore cumene (**3**) (Figure 2). Using time-correlated single-photon analysis, we measured the time dependence of the fluorescence intensity of **1** at 282 nm ("monomer" region) and at 335 nm (excimer region) in the temperature domain between 190 and 354 K in isooctane. The emission at 282 nm can be analyzed between 300 and 354 K as a sum of two exponentials. Below 306 K this emission is characterized by a single-exponential decay. The emission at 335 nm could be analyzed as a difference of two exponentials between 234 and 324 K. Above this temperature the grow in of the emission is within the resolution of the apparatus. The respective decay parameters are presented in Figure 2. The values of λ_1 and λ_2 obtained in the monomer and the excimer regions are identical within experimental error in the accessible temperature domain. Therefore, one can, within the following scheme, obtain the rate constants of the respective processes as a function of temperature (Figure 3):



where k_{DM} is the rate constant of excimer formation, k_{MD} is the rate constant of excimer dissociation, $k_D = k_{ID} + k_{FD}$, k_{FD} is the rate constant of excimer emission, k_{ID} is the rate constant of excimer radiationless decay, k_{FM} is the rate constant of fluorescence of cumene, and k_{IM} is the rate constant of radiationless decay of cumene. In Table I the important characteristics of the system are given for **1**.

Table I
Characteristic Parameters of 1 in Isooctane

k_{DM} [a]	9×10^7 s^{-1}
k_{FM}	5.5×10^6 s^{-1}
k_{FD}	6.5×10^5 s^{-1}
E_{DM}	4.5 kcal mol^{-1}
E_{MD}	9 kcal mol^{-1}
ΔH	−4.5 kcal mol^{-1}
ΔS	−11 ± 2 cal mol^{-1} K^{-1}

[a] At 20 °C.

The difference in the activation energies $E_{DM} - E_D$ obtained from time-correlated single-photon counting equals 4 kcal mol^{-1} and is, within experimental error, identical with the value obtained on the basis of stationary measurements using the equation

$$\frac{\phi_{FD}}{\phi_{FM}} = \frac{k_{FM}}{k_{FD}} \frac{k_{DM}}{k_{MD} + k_D} \tag{1}$$

A plot of ln (ϕ_{FD}/ϕ_{FM}) as a function of $1/T$ yields in the temperature region where $k_{MD} \ll k_D$ a value of 3.7 kcal mol^{-1} for $E_{DM} - E_D$.

The rate constant of excimer formation at room temperature is 30 times smaller than the one reported for atactic polystyrene[10] determined by quenching experiments. This is due to the fact that the isotactic sequences of the atactic polystyrene will contribute more to the excimer formation than the syndiotactic ones (vide infra).

The enthalpy of formation of the intramolecular complex is 2 kcal mol^{-1} smaller than the values obtained for toluene[11] but the entropy change is substantially less negative. This can be related not only to the fact that the two chromophores are linked but also to the conforma-

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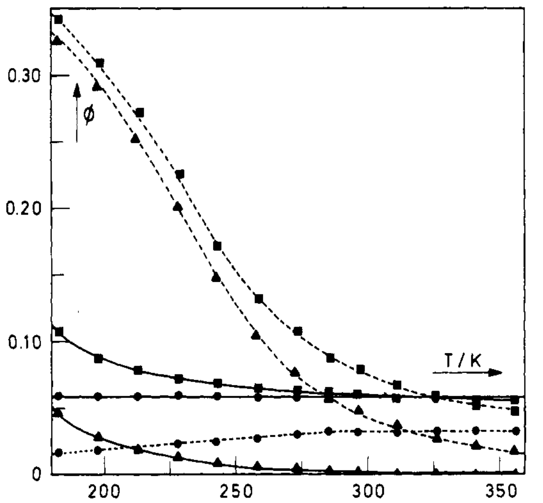

Figure 1. Quantum yields of fluorescence of 1 and 2 in isooctane as a function of temperature: (- - -) 1, (—) (2), (■) total quantum yield, (▲) monomer quantum yield, (●) excimer quantum yield.

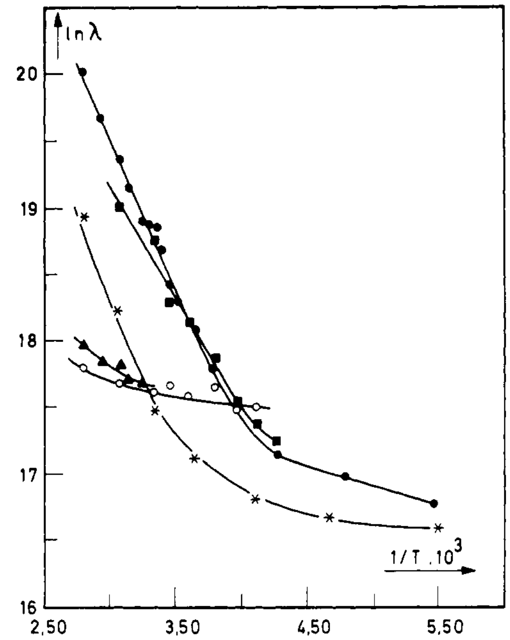

Figure 2. Logarithm of the decay parameters of 1 and 3 in isooctane as a function of $1/T$: (▲) λ_1 at 282 nm; (●) λ_2 at 282 nm; (○) λ_1 at 330 nm; (■) λ_2 at 330 nm; (*) λ of 3.

tional equivalence of T$\bar{G}$ and $\bar{G}$T in the excimer conformation (Figure 4). The dependence of the intensity of emission as a function of time of compound 2 in the 282-nm region could be analyzed only between 178 and 225 K. Above this temperature the spectral overlap and the relative importance of the excimer over the monomer emission precludes further analysis. In the 335-nm spectral region the emission could be analyzed as a difference of two exponentials between 178 and 200 K. The component of the decay describing the grow in of the excimer emission corresponds to the decay parameter measured at 282 nm in that temperature range. Above 200 K the excimer emission is analyzed as a single exponential. The decay describing the decrease of excimer intensity shows very little temperature dependence between 200 and 350 K and that within this temperature domain the dissociation of the excimer to the monomer is negligible. The characteristic parameters of 2 obtained in isooctane are reported in Table II. The rate constant of formation, which at room temperature is 25 times larger than for 1, and of fluorescence of the excimer are of the same order of magnitude

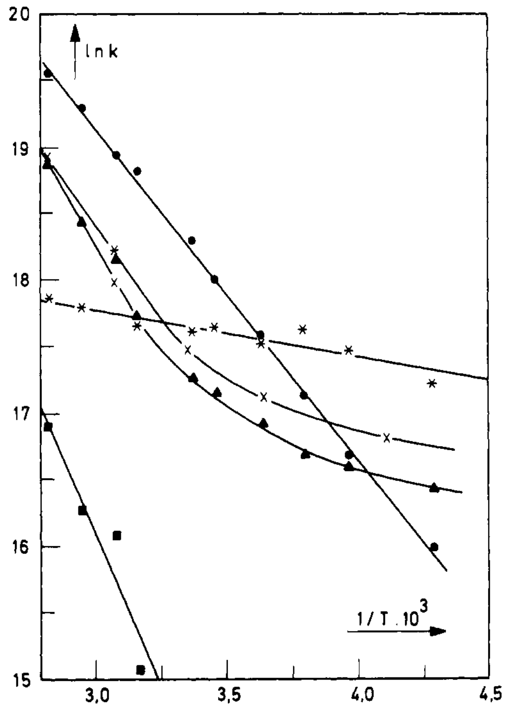

Figure 3. Logarithm of the rate constants of 1 in isooctane as a function of $1/T$: (●) k_{DM}; (■) k_{MD}; (▲) k_{IM}; (*) k_{ID}; (×) k_M.

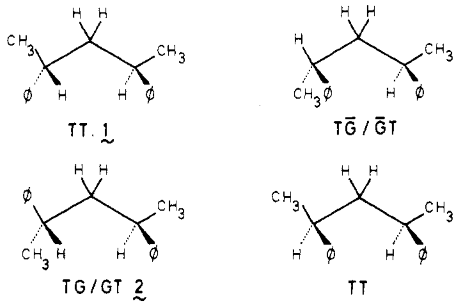

Figure 4. Conformations of 1 and 2 in the ground and excited states.

Table II
Specific Characteristics of 2 in Isooctane

$k_{DM}{}^a = 2 \times 10^9$ s^{-1}	$A_{DM} = 10^{11}$	$E_{DM} = 2.3$ kcal mol^{-1}
$k_{FD} = 1.3 \times 10^6$ s^{-1}		
$k_D = 4 \times 10^7$ s^{-1}	$A_D = 5 \times 10^7$	$E_D = 0.1$ kcal mol^{-1}

[a] At 20 °C.

as those obtained for isotactic polystyrene.[12]

The difference in activation energy of excimer formation between *rac*- and *meso*-2,4-diphenylpentane can be related to the rotational barriers between, respectively, TT → T$\bar{G}$/$\bar{G}$T for the racemic and TG/GT → TT for the meso compound (Figure 4). Force field calculation[9d,e] on the meso isomer indicates a possible pathway for TG/GT → TT in the ground state with a barrier of approximately 3 kcal mol^{-1}. Acoustic measurements[9c] indicate an activation enthalpy of 3.2 kcal mol^{-1} for the same process. Excited-state stabilization of the phenyl–phenyl interaction could lower the barrier to the experimentally obtained one. Although NMR[9a] indicates the presence of two conformations in the racemic isomer, they could not be distinguished from the experimentally obtained decay curves. Force field calculation[9d] indicate a minimal barrier of 6 kcal mol^{-1} in the ground state to reach the T$\bar{G}$/$\bar{G}$T conformation of the racemic isomer from the TT conformation. The

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observation in atactic polystyrene can now be related to the much faster excimer formation of the meso sequences as compared to the racemic ones. Values of rate constants or activation energies obtained for atactic polymers hence only reflect polymer composition.

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Mechanochemical Effects in a Poly(α-amino acid)

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ABSTRACT: The relationship between chain conformation and the physical and mechanical properties of a poly(α-amino acid) has been investigated. In order to eliminate intermolecular effects, cross-linked polymers were prepared and the properties investigated in the swollen state. In water, films of poly[(2-hydroxyethyl)-L-glutamine] take the random coil conformation and the mechanical behavior is elastomeric. In methanol, the chains are α-helical and plastic deformation is observed. The helical content was varied by using water–methanol mixtures and by increasing the number of methylene groups in the side chain. Elastomeric behavior was observed in the coil-to-helix transition region. This was interpreted in terms of the high chain flexibility of the interrupted helix.

Introduction

The relationship of individual chain characteristics such as conformation and mobility to the physical and mechanical properties of the condensed state is of fundamental importance. Only rarely, as in the case of rubber elasticity, has a quantitative theory been developed which successfully describes this relationship. In general, the effects of molecular properties and supermolecular or morphological features are difficult to separate.

The poly(α-amino acids) can provide new insight into this important area. These polymers exhibit chain conformations which have been well characterized in solution and the solid state. Poly(L-glutamic acid) and poly(L-lysine) have been lightly cross-linked with glycerol and formaldehyde, respectively.[1,2] Reversible dimensional changes of the water-swollen network were observed to accompany the pH-induced helix-to-coil transition.

The helix-to-coil transition has been described in terms of the interrupted helix model. As the helical content decreases from unity and the fraction of randomly coiled residues increases, the entire chain segment can no longer be a rigid rod but becomes flexible at the points where the randomly coiled residues interrupt the helical sections. The shape of such a chain segment may be pictured as a broken rod which consists of rigid rods connected by short flexible joints.

Experimental support for the interrupted helix as the predominant molecular structure in the region of the helix-to-coil transition is provided by measurements of size-dependent properties such as limiting viscosity number and the radius of gyration. Okita et al.[3] found that the limiting viscosity of poly[(3-hydroxypropyl)-L-glutamine] in water–methanol mixtures increased gradually with increasing helicity until a helix content of about 75% was reached; then the viscosity showed a sharp rise. Miyake et al.[4] observed a broad minimum followed by a sharp rise in the curve of intrinsic viscosity vs. helical fraction for a high molecular weight sample of poly[(2-hydroxyethyl)-L-glutamine] in 2-propanol–water mixtures. Ohta et al.[5] observed that the mean-square radius of gyration showed the same dependence on helicity as the viscosity for this system.

The viscosity vs. helicity curves have features quite similar to the theoretical curves for the molecular dimensions vs. helicity first presented by Nagai[6] and later by Miller and Flory.[7] This suggests a close relationship between the intrinsic viscosity and the molecular dimensions of interrupted helices. The minimum has also been pre-

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