Local Molecular Motion of Polystyrene Model Compounds Measured by Picosecond Pulse Radiolysis. 2. Multicomponent Fluorescence Decay Curves of Diastereomeric Styrene Trimers

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ABSTRACT: The dynamics of intramolecular excimer formation in isotactic (mm), syndiotactic (rr), and heterotactic (mr) 4,6,8-triphenylundecanes (PS3), which are diastereomeric trimer model compounds of polystyrene, were investigated by picosecond pulse radiolysis. The monomeric fluorescence of rr PS3 decays single exponentially with a time constant of 7.4 ns, while those of mm PS3 and mr PS3 decay dual exponentially with time constants of ~0.5 and 4 ns. The multicomponent fluorescence decays are influenced by local molecular motion (conformational change). The results suggest that the phenyl groups do not rotate independently around the carbon–carbon bonds of the backbone but that their rotation involves a cooperative motion of backbone chain bonds. The existence of singlet energy migration is established by the fact that the monomeric fluorescence decay curve of mr PS3 does not have as long a decay constant as the curves of the racemic isomers r PS2 and rr PS3 have.

Introduction

Intramolecular excimer formation between side-chain chromophores in macromolecules is an important aspect of photophysics.[1] The dynamics of excimer formation are influenced by the configuration and conformation of macromolecules as well as by energy migration. Attempts have been made to clarify these processes by studying intramolecular excimer formation in diastereomeric dimer model compounds with symmetric alkyl end groups.[2–7] However, there is a big gap between a polymer and its dimer models. For example, the monomer fluorescence of meso styrene dimer with propyl ends decays dual exponentially with time constants of 0.5 and 6 ns,[3b] while the fluorescence of atactic oligostyrenes[8] and polystyrenes[9] decays single exponentially with a time constant of 0.8–1 ns.

Measurements of transient fluorescence of diastereomeric trimer model compounds should give information on both the dynamics of conformational changes and singlet energy migration. Bokobza et al. studied the photostationary fluorescence of all-meso and all-racemic styrene trimers and tetramers with methyl end groups.[2a,b] Monnerie, Jasse, and co-workers investigated conformational changes in styrene trimers and tetramers, using ultrasonic relaxation[10] and UV,[11] IR,[12] and Raman spectroscopy.[13] Sato and Tanaka used ^{13}C NMR to study end-group effects in diastereomeric styrene oligomers (n = 2–5).[14] Studies of the photophysical properties of trimers without alkyl end groups have been reported on 1,3,5-triphenylpentane[15] and 1,3,5-trinaphthylpentane (TNP).[16] Transient measurements have been published only for TNP.[17]

We have shown that there is an alkyl-end-group effect on intramolecular excimer formation by comparing fluorescence decay time constants of styrene dimers with methyl, propyl, and pentyl ends.[3b] The methyl end group cannot restrain the motion of the phenyl rings and the excimer can be formed easily, while a bulkier end group can restrict the conformational change of the phenyl group around the main chain and retard excimer formation. Since the motion of midchain phenyl rings of polystyrene is restricted by steric hindrance, styrene trimers with propyl ends should be better model compounds of polystyrene than trimers with methyl ends. We report here on the transient fluorescence of diastereomeric styrene trimers with propyl end groups.

Experimental Section

The synthesis of meso, meso (mm), meso, racemic (mr), and racemic, racemic (rr) 4,6,8-triphenylundecanes (PS3) with purity >98% has been reported.[14,18] Fluorescence measurements were carried out in cyclohexane (Wako, luminasol grade). All sample solutions were degassed by freeze–pump–thaw cycles under high vacuum.

Fluorescence spectra and fluorescence excitation spectra were measured on a Hitachi F-3000 spectrofluorometer. Fluorescence decay curves were obtained with a picosecond pulse radiolysis system, using as an exciting source a pulsed electron beam (10 ps, fwhm).[19] The emission in the longer time range (>20-ns full time scale, channel width 39.06 ps) was measured at ~20 °C with a photomultiplier (HTV 1194UX (UV)) and a sampling oscilloscope (Tektronix 7704A) through a grating monochromator (Ritsu Oyo Kogaku MC-10N) or an interference filter (280 nm, 287 nm for monomeric singlet, and 340 nm for excimer). This method is denoted DPO (data processing oscilloscope). Fluorescence decay in the shorter time range (<5-ns full time scale; channel width 20 ps/channel) was measured with a gated streak camera (HTV C979) followed by a silicon-intensified target tube (SIT C1000-18), a microprocessor (C1098), a TV monitor, and a recorder. Only interference filters were used in these measurements.

Details of our method for calculating time constants have been reported.[3b] First we analyzed fluorescence decay curves with full time scale ranges of 50 and 100 ns by a nonlinear least-squares method, excluding several initial channels where signals are distorted by both Cerenkov radiation (which overlaps the emission of monomer singlet and excimer at very short times) and instrumental response. After determining the decay profile at longer times, we used the streak camera data to calculate the short-lifetime component by the reconvolution method. We used the

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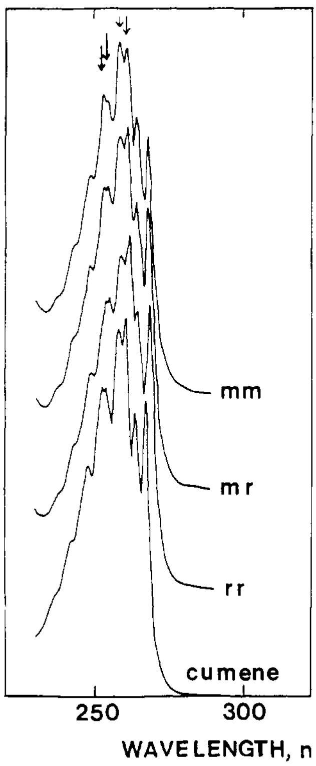


Figure 1. UV absorption spectra of cumene and mm, mr, and rr PS3 in cyclohexane at room temperature.

Durbin–Watson factor (DW)[20] to assess the validity of the trial fitting function. DW is calculated from

$$D = \sum_{i=2}^{N}(R_i - R_{i-1})^2 / \sum_{i=1}^{N} R_i^2$$

where the weighted residual $R_i = (Y_i - F_i)/Y_i^{1/2}$, Y_i and F_i are the values of the experimental data and trial decay function corresponding to time channel i, and N is the number of experimental points. For the best fit, the value of DW approaches 2.0. The calculated equations were normalized by setting $\sum A_i = 1$. Since the dynamic range of the streak camera is quite narrow and the decay is somewhat complicated, the preexponential term of the shortest lifetime component may be overemphasized. We did not examine the possibility that monomer emission might decay according to a relationship with a time-dependent term such as $t^{1/2}$.

Results

Figure 1 shows the UV absorption spectra of mm, mr, and rr PS3, and their monomer model, cumene in cyclohexane. Each UV spectrum is different, although the spectrum of mr PS3 nearly coincides with that of cumene. Large differences are seen at the doublet peaks 253.3–254.8 and 259.0–261.1 nm. The absorption intensity at the lower peaks of these doublets increases with increasing meso content of the trimers, while that at higher peaks of the doublets increases with increasing racemic content. Similar results have been reported on meso and racemic diphenylpentanes.[2a]

The corrected fluorescence spectra of PS3 diastereomers have two peaks near 285 and 330 nm. The efficiency of intramolecular excimer formation increases in the order r PS2 < rr PS3 < m PS2 < mr PS3 < mm PS3. This order suggests that (1) it is hard to form excimer in all-racemic isomers and (2) excimer is formed in the trimer more easily than in the dimer. An important result is that the efficiency of the excimer formation in mr PS3 is a little higher than that in m PS2, even though the rotation of phenyl groups around the main chain in m PS2 should be less sterically hindered than in mr PS3.

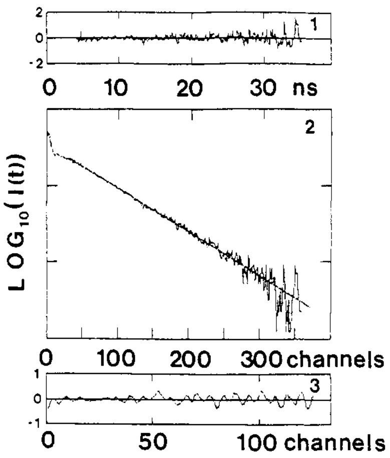


Figure 2. Monomeric fluorescence decay of rr PS3 in cyclohexane at 280 nm obtained by DPO (97.66 ps/channel) (2), plots of weighted residuals (1), and autocorrelation of residuals (3) for single-exponential fits (exp($-t/7.3$ ns)).

Figure 2 shows the decay curve of monomer emission of rr PS3 together with the weighted residuals and autocorrelation of residuals for single-exponential fits. Figure 2 suggests that the monomeric fluorescence of rr PS3 decays according to

$$I_M(t) = \exp(-t/\tau_1)$$

with time constant $\tau_1 = 7.4 \pm 0.4$ ns. If the excimer dissociates under these conditions, the monomer fluorescence should not decay single exponentially. Accordingly, this decay profile means that the excimer of rr PS3 dissociates very little (or not at all) at 20 °C. It is difficult to obtain the exact value of the rise time of the excimer emission by removing the Cerenkov light and the overlap of the monomer fluorescence decay, but the decay curve at 340 nm is fitted well to

$$I_{340}(t) = (0.7 \pm 0.2)[\exp(-t/20 \pm 5 \text{ ns}) - \exp(-t/8 \pm 2 \text{ ns})] + (0.3 \pm 0.1) \exp(-t/8 \pm 2 \text{ ns})$$

Thus, the excimer emission rises single exponentially with the same time constant (7.4 ns) as that of the monomer fluorescence decay, since the monomer fluorescence overlaps the excimer emission at 340 nm by ~30%. Thus, the shortening of the fluorescence lifetime of the phenyl moiety from 27 ns (cumene) to 7.4 ns (rr PS3) is due to intramolecular excimer formation.

We have reported that the monomer fluorescence of racemic styrene dimers with propyl and pentyl ends decays single exponentially [$\tau_1 = 11$ ns (propyl) and 13 ns (pentyl)].[3] Since the time constant of rr PS3 is about half that of racemic dimer compounds, we suggest that excimer formation depends on the number of pairs capable of attaining the excimer conformation between two adjacent phenyl groups (PS2, 1; PS3, 2).

Figure 3 shows the fluorescence decay of mm PS3 at 290 nm over the long-time range. The fluorescence near the monomer peak of mm PS3 decays triple exponentially with time constants less than 1, 4, and 20 ns; this is also true of styrene dimers.[3] The fluorescence at 340 nm, consisting only of the excimer signal, decays single exponentially with a time constant of 21 ns, the same value obtained for r PS2 and rr PS3. Thus, the longest component in the fluorescence decay at 290 nm is due to overlapping of excimer fluorescence at this wavelength.[3b] Accordingly, the monomer fluorescence of mm PS3 decays dual exponentially (eq 1) with time constants of 0.4 ± 0.2 and 4.0 ± 0.5 ns.

$$I_M(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2), \quad A_1 + A_2 = 1 \quad (1)$$

Table I
Fluorescence Decay Profiles of mm, mr, and rr PS3 in Cyclohexane[a]

sample	λ, nm	A_1	τ_1, ns	A_2	τ_2, ns	A_3	τ_3, ns	DW	method
mm PS3	290	0.36	3.9			0.084	23	1.4	DPO
		0.27	3.7			0.075	24	1.2	DPO
		0.31	3.9	0.62	0.36	0.072	23	0.69	SC
		0.30	3.7	0.62	0.36	0.083	24	0.69	SC
		0.32	4.1	0.61	0.35	0.074	24	0.55	SC
	340						21	0.72	DPO
mr PS3	290	0.28	3.6			0.061	23	1.2	DPO
		0.23	4.7			0.043	31	1.2	DPO
		0.36	3.6	0.56	0.63	0.079	23	0.53	SC
	340						21	0.92	DPO
rr PS3	280	1.0	7.3					1.1	DPO
	290	1.0	7.6					1.1	DPO
	340						21	1.0	DPO

summary

sample	λ, nm	A_1	τ_1, ns	A_2	τ_2, ns	A_2/A_1	$\sum A_i\tau_i$
mm PS3	290	0.3 ± 0.1	4.0 ± 0.5	0.7 ± 0.2	0.4 ± 0.2	2.3	1.5
mr PS3	290	0.4 ± 0.1	4.0 ± 0.5	0.6 ± 0.2	0.6 ± 0.2	1.5	2.0
rr PS3	290	1.0 ± 0.1	7.4 ± 0.4				7.4
m PS2	290	0.3 ± 0.1	6.0 ± 1.0	0.7 ± 0.2	0.5 ± 0.2	2.6	2.2
r PS2	290	1.0 ± 0.1	11 ± 1				11

[a] Fluorescence decays are from the equation $I(t) = \sum A_i \exp(-t/\tau_i)$; rise components were not calculated for excimer fluorescence at 340 nm.

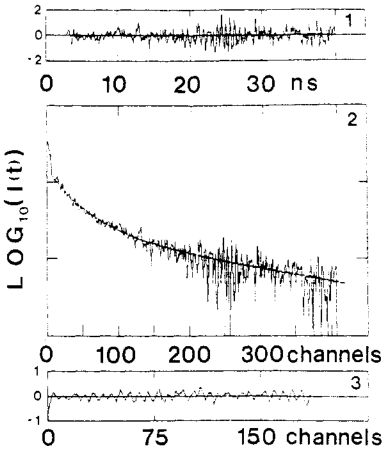


Figure 3. Monomeric fluorescence decay of mm PS3 in cyclohexane at 290 nm obtained by DPO (97.66 ps/channel) (2), plots of weighted residuals (1), and autocorrelation of residuals (3) for dual-exponential fits calculated after 2.9 ns ($I(t) = 0.28 \exp(-t/3.7\ \text{ns}) + 0.074 \exp(-t/24\ \text{ns})$).

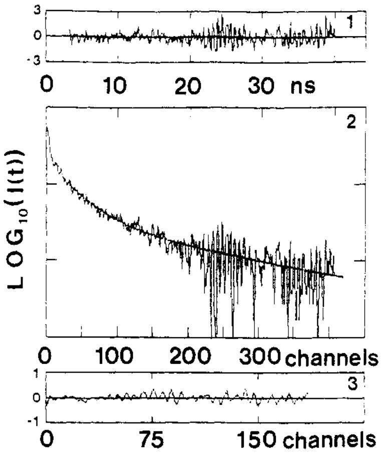


Figure 4. Monomeric fluorescence decay of mr PS3 in cyclohexane at 290 nm obtained by DPO (97.66 ps/channel) (2), plots of weighted residuals (1), and autocorrelation of residuals (3) for dual-exponential fits calculated after 2.9 ns ($I(t) = 0.28 \exp(-t/3.6\ \text{ns}) + 0.061 \exp(-t/23\ \text{ns})$).

The calculated decay parameters are summarized in Table I. Although the Durbin–Watson factors appear to be distorted by the regular correlation induced by correction of the time axis in the analysis of streak camera data, the parameters in Table I represent the best fit of the calculations.

Figure 4 shows the fluorescence decay of mr PS3 at 290 nm over the long-time range. The fluorescence near the monomer peak of mr PS3 also decays triple exponentially with time constants less than 1, 4, and 20 ns, like mm PS3. Since the longest component is due to overlapping of the excimer fluorescence at this wavelength, the monomer fluorescence of mr PS3 decays dual exponentially (eq 1) with time constants of 0.6 ± 0.2 and 4.0 ± 0.5 ns. The difference in the photostationary fluorescence spectra of mm and mr PS3 is thought to be mainly induced by the difference between the preexponential terms A_1 and A_2. Since each integration ($\sum A_i\tau_i$) of monomer fluorescence decay of the isomers (m PS2, r PS2, mm PS3, mr PS3, and rr PS3) corresponds to each intensity of the steady-state fluorescence spectrum, our analysis appears to be consistent.

Discussion

The formation of an intramolecular excimer in vinyl-type polymer systems requires (1) formation of the excimer conformation (tt, meso diad; g^-t/tg^-, racemo diad)[21] by local motion such as a crankshaft transition and (2) the influx of excitation energy into the excimer conformation by singlet energy migration.[22] We discuss these in reverse order.

Energy Migration in Trimers. Although it has been suggested that there is no singlet energy migration among phenyl groups in polystyrene,[23] our results establish that such singlet energy migration takes place. Each phenyl group in an oligomer molecule should be excited in the same way. Thus, in mr PS3, at least 33% of the total excitation energy is absorbed by the phenyl group at an end in the racemic diad. If the excitation energy is localized at one phenyl group during its lifetime, this energy must decay just like the excitation energy absorbed by a phenyl group in r PS2 or rr PS3; all-racemic compounds show the same decay profile of fluorescence, a single exponential with a long decay constant. Since the intensity of monomer fluorescence of r PS2 is about 10

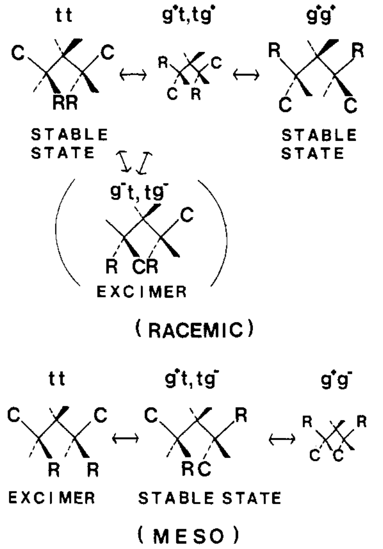


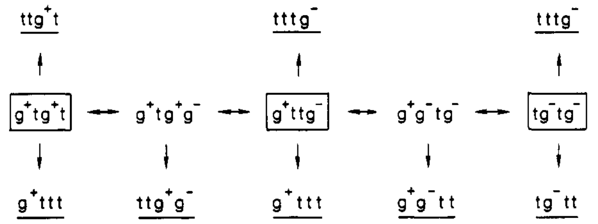
Figure 5. Main conformational changes in meso and racemic diads (C, main chain; R, phenyl group).

times greater than that of m PS2, the contribution of the long lifetime component derived from the racemic diad would be large if the excitation energy is localized in the racemic diad during its lifetime. However, since no time constant as long as that of r PS2 (11 ns) or rr PS3 (7 ns) is observed in mr PS3, singlet energy migration must occur.[24] The absence of a long decay component implies that the excitation energy can totally cover a styrene trimer within at least 4 ns.

Local Motion in Trimers. In low molecular weight compounds, the formation of an excimer conformation should be the rate-determining process for excimer formation;[8] excitation energy appears able to migrate into an excimer conformation before the conformer changes to another. Thus, once an excimer conformer is formed, excitation energy belongs to the excimer state; the dissociation of excimer need not be taken into account. We discuss here the conformational changes of each diastereomer of PS3.

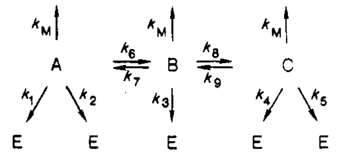
Figure 5 shows the main conformational changes in meso and racemic diads.[21] In a meso diad, since the conformational change from the most stable conformer (g^+t/tg^-) to an excimer (tt) should occur readily, excimer formation should give information about the dynamics of conformational changes. However, excimer formation in the all-racemic isomers r PS2 and rr PS3 is not a good probe for the dynamics of conformational changes, because an excimer conformer in a racemic diad is a deviation from the possible conformational changes ($tt \leftrightarrow g^+t/tg^+ \leftrightarrow g^+g^+$). This is confirmed by the experimental results from both steady-state and transient fluorescence spectra, which show that the efficiency of excimer formation in r PS2 and rr PS3 is much lower than that in isomers with one or more meso diads (m PS2, mm PS3, and mr PS3). The fact that the monomer fluorescence of r PS2 and rr PS3 decays single exponentially also suggests that the transient measurements of the monomer fluorescence cannot pick up the details of the main conformational changes ($tt \leftrightarrow g^+t/tg^+ \leftrightarrow g^+g^+$) because these conformational changes occur much more quickly than the change to form the excimer conformer (g^-t/tg^-). First let us examine the dynamics of excimer formation in isomers having more than one meso diad.

Scheme I
Conformational Changes during the Lifetime of an Excited Phenyl Singlet in mm PS3 under Assumptions 1 and 2[a]



[a] ☐, quite stable conformer; —, excimer conformer.

Scheme II
Kinetic Scheme for Excimer Formation in mm PS3[a]



[a] k_M is the sum of the rate constants k_{FM} (for radiative deactivation) and k_{IM} (for nonradiative deactivation) from excited phenyl monomer. k_i (i = 1–9) is the rate constant for conformational change. A is [tg^-tg^-/g^+tg^+t]. B is [$g^+g^-tg^-/g^+tg^+g^-$]. C is [g^+ttg^-]. E is excimer.

As shown in Figure 5, the stable conformers are g^+t/tg^- in a meso diad, and tt and g^+g^+ in a racemic diad, while the excimer conformers are tt in a meso diad and g^-t/tg^- in a racemic diad. In styrene dimers with methyl ends, the population of g^+t/tg^- in the meso isomer is about 100%, while in the racemic isomer the populations of tt and g^+g^+ are 71–76% and 23–29%, respectively.[25,26]

In mm PS3, the stable conformation can be considered to be tg^-tg^-, g^+ttg^-, and g^+tg^+t, because it should be a combination of g^+t and tg^-, which are the most stable conformers in the meso diad; tg^-g^+t is excluded because of steric hindrance. Pivcova et al. reported that the populations of g^+ttg^- and tg^-tg^-/g^+tg^+t are 0.22 and 0.78, respectively, in an all-meso styrene trimer with methyl ends.[25]

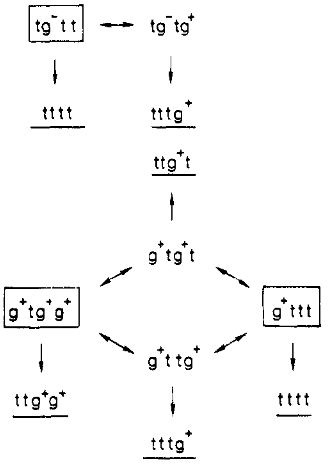
In mr PS3, the stable conformation can be considered to be tg^-tt, g^+ttt, and $g^+tg^+g^+$, because it should be a combination of g^+t and tg^-, the stable conformers in the meso diad, and tt and g^+g^+, the stable conformers in the racemic diad; $tg^-g^+g^+$ is excluded because of steric hindrance. Pivcova et al. reported that the populations of tg^-tt, g^+ttt, and $g^+tg^+g^+$ are 0.44, 0.41, and 0.15, respectively, in a heterotactic styrene trimer with methyl ends.[25]

Since we can assume possible excimer conformations, we can estimate both the initial and final distribution of conformers. The problem is how the conformational changes occur from the irradiation time until the excitation energy deactivates.

Schemes I and III show the possible conformational changes in mm PS3 and mr PS3 under the assumptions that (1) side-chain phenyl groups can rotate independently around each carbon–carbon bond of the backbone and (2) conformational changes occur stepwise by way of this independent rotation. Several conformers are excluded because of high steric hindrance: $g^+g^-g^+g^-$, $g^+g^-g^+t$, and $tg^-g^+g^-$ in mm PS3; tg^-g^+t, $g^+g^-g^+t$, $tg^-g^+g^+$, $g^+g^-g^+g^+$, $g^+g^-tg^+$, and g^+g^-tt in mr PS3. Scheme I can be simplified as Scheme II because of the symmetry of some conformers. The conformers in Schemes I and III are assumed to be important even if the conformational changes occur cooperatively.

In previous work,[3b] we concluded that (1) conformational change from g^+t/tg^- to tt in m PS2 is as quick as 0.7 ns but that (2) once another conformer (g^+g^-) is formed it takes as much as 6 ns for the backward conformational

Scheme III
Conformational Changes during the Lifetime of an Excited Phenyl Singlet in mr PS3 under Assumptions 1 and 2[a]



[a] ☐, quite stable conformer; —, excimer conformer.

change to occur; two decay times (0.5 and 6 ns) were observed in the monomer fluorescence decay of m PS2. The 6-ns decay is attributed to the path to form a conformer from which any excimer conformers can be formed. The transient fluorescence of mm PS3 and mr PS3 has two decay times (0.5 and 4 ns) like that of m PS2. However, Schemes I and III show that excimer conformers can be formed directly from any possible conformers of mm PS3 or mr PS3, which argues against any decay component as long as 4 ns. Moreover, Scheme I shows that there are two paths to form an excimer conformation from the three most stable conformers of mm PS3, while Scheme III shows that there is only one path to form an excimer conformation from the three stable conformers of mr PS3. Nevertheless, both transient and photostationary fluorescence results do not show a large difference between the efficiency of excimer formation in mm PS3 and mr PS3.

We tried to calculate rate constants for conformational changes in mm PS3 according to Scheme II (see Appendix section), but we could not reproduce the experimental decay function. For example, rate constants for the formation of excimer conformers, k_2, k_3, k_4, and k_5, were assumed to be similar because all of them correspond to the same conformational change of the phenyl group at an end [(g^+t/tg^-) → tt]. If the values of these rate constants are identical with the estimated value for m PS2 [1.5×10^9 s^{-1} (0.7 ns)], all of the decay constants must be this large, and it is impossible to obtain a decay constant of 2.5×10^8 s^{-1} (4 ns).

Accordingly, our experimental results conflict with the conclusions derived from styrene dimers under our assumptions 1 and 2.

On the contrary, the following simple assumptions give good concordance with our results on PS2 and PS3. (1) The decay constant ($1/\tau_1$) is expressed by the sum of k_M (Scheme II) and k_{DM} (rate constant for total excimer formation); $1/\tau_1 = k_M + k_{DM}$. (2) The lifetime of dilute cumene (27 ns) can be substituted into k_M. Values of k_{DM} are calculated to be 5.4×10^7 s^{-1} (r PS2) and 9.8×10^7 s^{-1} (rr PS3), isomers without any meso diads, and 1.3×10^8 s^{-1} (m PS2) and 2.1×10^8 s^{-1} (mm PS3 and mr PS3), isomers with more than one meso diad. Since the number of pairs capable of attaining the excimer conformation between two adjacent phenyl groups is $n - 1$ for n-mer, we divided each k_{DM} by $n - 1$. The resulting value is the rate constant for excimer formation per one pair of adjacent phenyl groups (k_r). Consequently, the values of k_r for dimers and trimers coincide: for isomers without any meso diads, 5.4×10^7 s^{-1} (PS2) and 4.9×10^7 s^{-1} (PS3); for isomers with more than one meso diad, 1.3×10^8 s^{-1} (PS2) and 1.1×10^8 s^{-1} (PS3).

The coincidence between mm PS3 and mr PS3 under our latter assumptions strongly suggests that conformational changes do not occur only by independent rotation around each carbon–carbon bond of the backbone chain but rather by a cooperative motion of backbone chain bonds. Excimer is formed mainly in a meso diad even in mr PS3.[27] If the side chain can rotate around each carbon–carbon bond of the backbone *independently*, the efficiency of excimer formation in mm PS3 might be 2 times as high as that in mr PS3 because mm PS3 has two meso diads. However, the experimental results show that the longer time constant (τ_1) of mm PS3 is the same as that of mr PS3. The fact that the efficiency of the excimer formation depends on the number of phenyl groups (or the number of the bonds), not on the number of meso diads, indicates a cooperative motion because the frequency of a cooperative motion in a molecule should be proportional to the number of carbon–carbon bonds in the backbone chain. The failure to reproduce the experimental fluorescence decay function under the assumption of independent rotation also indicates a cooperative motion, such as a three-bond jump[28] or a crankshaft transition,[29] in the backbone chain of PS3.

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Appendix

The rate equations for kinetic Scheme II are

$$\begin{aligned} \dot{A} &= I_a - XA + k_7B \\ \dot{B} &= k_6A - YB + k_9C \\ \dot{C} &= I_c + k_8B - ZC \end{aligned} \tag{A-1}$$

where

$$\begin{aligned} X &= k_M + k_1 + k_2 + k_6 \\ Y &= k_M + k_3 + k_7 + k_8 \\ Z &= k_M + k_4 + k_5 + k_9 \end{aligned}$$

In the case of pulse excitation, I_a and I_c are supposed to be represented by a δ function. Then by solving eq A-1 with the initial condition that $[A] = a$, $[B] = 0$, and $[C] = 1 - a$ at $t = 0$, we obtain the decay function of the monomer fluorescence, $I_M(t)$:

$$\begin{aligned} I_M(t) &= k_{FM}[M^*](t) \\ &= k_{FM}\sum_{i=1}^{3} C_iS_i \exp(-\lambda_it) \end{aligned} \tag{A-2}$$

where

$$C_i = k_7(Z - \lambda_i) + k_8(X - \lambda_i) - (X - \lambda_j)(Z - \lambda_i)$$

and

$$S_i = \frac{(1 - a)(Z - \lambda_j)(Z - \lambda_k) - ak_8(X - \lambda_j)(X - \lambda_k)}{k_7k_8(X - Z)(\lambda_i - \lambda_j)(\lambda_k - \lambda_i)}$$

$$\lambda_i\lambda_j\lambda_k = \lambda_1\lambda_2\lambda_3$$

and

$$\lambda_1 + \lambda_2 + \lambda_3 = X + Y + Z$$

$$\lambda_1\lambda_2 + \lambda_1\lambda_2 + \lambda_1\lambda_2 = XY + YZ + ZX - k_6k_7 - k_8k_9$$

$$\lambda_1\lambda_2\lambda_3 = XYZ - k_6k_7Z - k_8k_9X \qquad \text{(A-3)}$$

$$\lambda_1 > \lambda_2 > \lambda_3 > 0$$

It is not a big problem that there should exist three decay constants under these assumptions, even if the experimental results show only two decay constants, because they are not always detectable due to too small preexponential terms or too small time constants, etc.

We tried to search for a set of rate constants to satisfy the above equations under the next assumptions: (1) The monomer lifetime of cumene in CH can be substituted into k_M (27 ns). (2) The value of 2,4,6-triphenylheptane[24] can be substituted into a; that is to say, $[A](tg^-tg^-/g^+tg^+t) = 0.78$ and $[C](g^+ttg^-) = 0.22$ at $t = 0$. (3) The rate constants for the formation of excimer conformers, k_2, k_3, k_4, and k_5, are assumed to be similar to each other because all of them correspond to the same conformational change of the phenyl group at an end $((g^+t/tg^-) \rightarrow tt)$, while k_1 corresponds to that of the phenyl group at the center.

The values of the reciprocal of some rate constants were changed from 0.3 to 20 ns by 0.1 ns. The third decay component was taken into account; for example, if the value of the third decay time is close to either 0.5 or 4 ns, its preexponential term is added to the preexponential term of the decay component of 0.5 or 4 ns. Nevertheless we could not find out any reasonable and consistent rate constants to reproduce the experimental decay functions.

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