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Local Molecular Motion of Polystyrene Model Compounds Measured by Using Picosecond Pulse Radiolysis. 1. Diastereoisomeric Styrene Dimers: Multicomponent Fluorescence Decay Curves, Concentration Dependence, and Alkyl End-Group Effect on Excimer Formation

Hideyuki Itagaki,[*†] Kazuyuki Horie,[‡] Itaru Mita,[‡] Masakazu Washio,[§] Seiichi Tagawa,[§,⊥] Yoneho Tabata,[§] Hisaya Sato,[‖] and Yasuyuki Tanaka[‖]

Department of Chemistry, Faculty of Education, Shizuoka University, 836 Ohya, Shizuoka 422, Japan, Institute of Interdisciplinary Research, Faculty of Engineering, University of Tokyo, Komaba, Meguro-ku, Tokyo 153, Japan, Nuclear Engineering Research Laboratory, Faculty of Engineering, University of Tokyo, Tokai-mura, Ibaraki 319-11, Japan, Research Center for Nuclear Science and Technology, University of Tokyo, Ibaraki 319-11, Japan, and Faculty of Engineering, Tokyo University of Agriculture and Technology, Koganei, Tokyo 184, Japan.
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ABSTRACT: The dynamic process of intramolecular excimer formation in meso and racemic 4,6-diphenylnonanes (PS2(propyl)), diastereoisomeric dimer models of polystyrene, was investigated by using a picosecond pulse radiolysis technique. In dilute cyclohexane solution, the monomeric fluorescence of racemic PS2(propyl) decays single exponentially with a time constant of 11 ns, while that of meso PS2(propyl) was found to decay dual exponentially with time constants of 6 and 0.5 ns. These multicomponent fluorescence decays were found to be explicable by the local motion of conformational change. In conclusion, each time required for the conformational change $(g^+t/tg^-) \rightarrow tt$, $(g^+t/tg^-) \rightarrow g^+g^-$, and $g^+g^- \rightarrow (g^+t/tg^-)$ in meso PS2(propyl) is estimated to be 0.7, 2.5 and 6 ns, respectively, at room temperature. The proposition that fluorescence decay of diastereoisomeric dimers is influenced by molecular motion (conformational change) is also valid for explaining the profile of the transient fluorescence spectra of racemic PS2(propyl). The present result is an indication that multicomponent fluorescence decay observed in some polymer systems may be mainly due to the conformational change motion in meso dyads. The concentration dependence of the time constants of meso and racemic PS2(propyl) was also measured. In addition, an alkyl end-group effect on intramolecular excimer formation in styrene dimers is found to exist by comparing time constants of styrene dimers with methyl ends, propyl ends, and pentyl ends.

Introduction

Recently many investigators have published papers concerning intramolecular excimer formation in aromatic dimers compounds.[1-15] There are three main reasons for studying dimeric compounds: (1) to understand the photophysical interaction between chromophores in excited states since the encounter probability of rings increases greatly in dimeric compound such as diarylpropanes,[1-3] (2) to clarify complex photophysical processes in polymer systems because the structure of these dimeric compounds are identical with those of polymer dyands,[4-11] and (3) to investigate the end-to-end cyclization rate of polymer molecules in terms of the theory of polymer so-

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[†] Shizuoka University.

[‡] Institute of Interdisciplinary Research, University of Tokyo.

[§] Nuclear Engineering Research Laboratory, University of Tokyo.

[⊥] Research Center for Nuclear Science and Technology, University of Tokyo.

[‖] Tokyo University of Agriculture and Technology.

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lution.[12-14] Diarylpropanes are appropriate compounds for studying photophysical interactions between chromophores but are not sufficient as a polymer model because (1) a polymer has many configurations (tacticity) they do not have and (2) the motion of side-chain chromophores of macromolecules is limited because of their being packed into a smaller volume; this is not restricted by the lack of bulky end groups such as pentyl groups. Thus interest in the study of dimeric diastereoisomers with symmetric alkyl end group has increased in recent years.[4-11] In particular, transient measurements of the fluorescence of diastereoisomeric dimers as models of polymers will give important information on the dynamics of the local motion of side chains, using the excimer as a probe.

Since Longworth and Bovey,[15] several authors have reported that the excimer is more easily formed in meso than in racemic dimeric diastereoisomers. These results suggest that in the meso isomer the excimer conformation (tt) is easily formed by a pathway with small steric hindrance from the most stable ground-state conformation (g^+t,tg^-), where almost all oligomers are at the initial stage of excitation, but in the racemic isomer the excimer conformer (g^-t,tg^-) cannot be formed without passing over the higher rotational energy barrier from the most stable conformers (tt,g^+g^+). De Schryver et al.[4c] reported that the rate constant of excimer formation of *meso*-diphenylpentane (styrene dimer with methyl end: PS2(methyl)) is 25 times larger than that of racemic PS2(methyl) at room temperature.

We have studied intramolecular excimer formation of atactic oligostyrenes[16] and diastereoisomers of diphenyltridecanes (styrene dimer with pentyl end: PS2(pentyl))[11] using picosecond pulse radiolysis in order to observe dynamically the local motions of macromolecules. The monomeric fluorescence of racemic PS2(pentyl) decays single exponentially with a time constant of 13 ± 1 ns, while that of meso PS2(pentyl) was found at first to decay dual exponentially with time constants of 3.5 and 0.5 ns. However, the concentrations of the solutions used in the transient measurements were 0.06–0.09 base molar, at which concentrations excimer may be intermolecularly formed. In this paper we have investigated the concentration dependence of excimer formation and/or the multicomponent decay of phenyl fluorescence. In addition we now report and discuss the alkyl end-group influence (symmetric methyl, propyl, and pentyl end groups) on the time required for excimer formation.

Experimental Section

The details of the synthesis and identification of meso and racemic 4,6-diphenylnonane (PS2(propyl)) have already been

$C_nH_{2n+1}\text{–}(C(C_6H_5)HCH_2)_2\text{–}C_{n-1}H_{2n-1}$

$n = 1$, PS2(methyl); $n = 3$, PS2(propyl); $n = 5$, PS2(pentyl)

reported by Sato and Tanaka.[17] Fluorescence measurements were carried out in luminasol cyclohexane (CH) supplied by Nako Co. and used without further purification. All sample solutions were degassed by freeze–pump–thaw cycles under high vacuum. The concentrations of the solutions used in the transient measurements were from 3 mM to 0.2 M for meso PS2(propyl) and from 0.2 mM to 0.5 M for racemic PS2(propyl) (the unit of concentration here is not base molar but molar).

Fluorescence spectra and fluorescence excitation spectra were measured on a Hitachi F-3000 spectrofluorometer. Fluorescence decay curves were obtained by using a picosecond pulse radiolysis system, details of which have been already reported.[11,16,18] The emission in the longer time range (above 20 ns as the full time scale; channel width = 39.06 ps) was measured at ca. 20 °C by using a photomultiplier [HTV 1194UX (UV)] with a sampling oscilloscope (Tektronix 7704A) through a grating monochromator (Ritsu Oyo Kogaku MC-10N) or an interference filter of 280, 287 (monomeric singlet), or 340 nm (excimer). The above method is abbreviated as the DPO (data processing oscilloscope) method below. The fluorescence decay curve in the shorter time range (below 5 ns as the full time scale; channel width = 20 ps) was measured by using the gated streak camera (HTV C979) followed by a silicon-intensified target tube (SIT C1000-18), a microprocessor (C1098), a TV monitor, and a recorder. In the measurements using a streak camera, the wavelength of emission was separated only by using interference filters.

Our method of calculating time constants is as follows. First we analyzed fluorescence decay curves whose full time scale range is 50 and 100 ns (or 20 ns in some cases), because 100 ns is long enough to calculate the longest lifetime obtained in our measurements. We tried to fit these experimental data to three types of equations (single exponential, sum of two exponentials, and sum of three exponentials) by using a nonlinear least-squares method, excluding several initial channels where signals are distorted by both Cerenkov radiation (which overlaps the emission of both monomer singlet and excimer at very short times) and instrumental response. We used the Durbin–Watson factor (DW)[19] 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 the time channel i, and N is the number of experimental points. For the best fitting, the value of DW approaches 2.0.

After determining the decay profile at longer times, we used the streak camera data to exactly calculate the short-lifetime component by using the reconvolution method. For example, the fluorescence of 40 mM meso PS2(propyl) at 280 nm obtained by a DPO method was determined to decay as $0.85 \exp(-t/4.4 \text{ ns}) + 0.15 \exp(-t/24 \text{ ns})$ (DW = 1.42; preexponential terms are normalized by using the sum of only these two terms). On calculating the streak camera data obtained under the same conditions, we used this relationship as a base curve and also used the data of water as an exciting pulse profile. Thus the whole profile shown in Table I (DW = 1.7) was obtained. The calculated equations shown in the present paper are normalized in such a way that $\Sigma A_i = 1$. Since the dynamic range of the streak camera is quite narrow and the decay is somewhat complicated, the exactness of the preexponential terms might seem to be a problem. The preexponential term of the shortest lifetime component might be overemphasized.

We did not examine the possibility that the monomer emission might decay according to a relationship having a time dependent term such as $t^{1/2}$.

Results

Figure 1 shows the corrected fluorescence spectra of racemic PS2(propyl) (A) and meso PS2(propyl) (B) at a concentration low enough that intermolecular excimer formation can be neglected. The excitation wavelength is 250 nm and the spectra were measured at 25 °C. The peaks near 285 and 330 nm have been assigned to phenyl monomer singlet and excimer emission, respectively; the fluorescence excitation spectra between 270 and 400 nm coincide with the absorption spectra. Figure 1 shows that meso PS2(propyl) presents a greater ratio of excimer to normal fluorescence intensity than racemic PS2(propyl). As described in the Introduction, similar results were reported for other diastereoisomeric dimers.[4-11]

Figure 2 shows the decay curve of monomer emission of racemic PS2(propyl) (0.2 mM) together with the weighted residuals and autocorrelation of residuals for single-exponential fits. Figure 2 suggests that the monomeric fluorescence of racemic PS2(propyl) decays according to

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

Table I
Fluorescence Decay Profiles of Meso and Racemic PS2(propyl) in Cyclohexane[a]

[M], mM	wavelength, nm	A_1	τ_1, ns	A_2	τ_2, ns	A_3	τ_3, ns	DW
			Meso PS2(propyl)					
200	200	0.73	0.31	0.20	2.7	0.066	17	1.46[b]
		0.82	0.43	0.14	2.7	0.045	17	2.00[c]
	287	0.74	0.37	0.17	3.0	0.088	15	1.55[b]
		0.79	0.52	0.14	3.0	0.071	15	1.89[c]
		0.78	0.47	0.15	3.0	0.077	15	1.56[c]
	340						19	1.00
40	280	0.77	0.37	0.19	4.4	0.034	24	1.67[b]
		0.82	0.30	0.15	4.4	0.027	24	1.78[c]
	287	0.72	0.36	0.23	4.1	0.051	20	1.46[b]
		0.84	0.32	0.13	4.1	0.028	20	1.74[c]
	340						23	0.92
20	280	0.70	0.56	0.23	5.5	0.069	22	1.60[b]
		0.65	0.38	0.27	5.5	0.081	22	1.80[c]
	287	0.69	0.49	0.23	5.7	0.082	21	1.51[b]
		0.61	0.44	0.29	5.7	0.10	21	1.56[c]
		0.68	0.38	0.24	5.7	0.084	21	1.58[c]
	340						24	0.82
3	280	0.68	0.47	0.25	6.0	0.075	22	1.40[c]
	287	0.61	0.49	0.29	5.7	0.10	21	0.50[b]
		0.66	0.66	0.25	5.7	0.089	21	1.02[c]
	340						23	0.80

Racemic PS2(propyl)

[M], mM	wavelength, nm	τ_1, ns	τ_2, ns	τ_3, ns	DW
500	280		2.2		0.59
	340			23	0.27
20	280		9.4		1.88
			10		1.56
	340			22	1.46
4	280		11		1.12
			11		1.49
	340			24	1.01
0.2	280		10		0.95
			11		1.30
	340[d]				

[a] Fluorescence decays due to equation $I(t) = \sum A_i \exp(-t/\tau_i)$; rise components were not calculated concerning excimer fluorescence at 340 nm. The shortest component was calculated by using streak camera data of [b] 20 ps/channel scale and [c] 12 ps/channel scale. [d] Time constants could not be determined due to a weak signal.

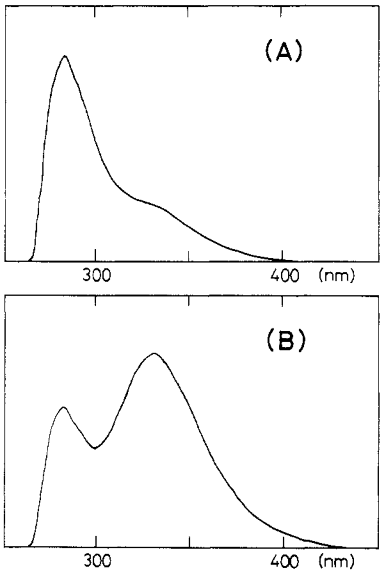


Figure 1. Fluorescence spectra of racemic PS2(propyl) (A) and meso PS2(propyl) (B) in CH (excitation wavelength, 250 nm).

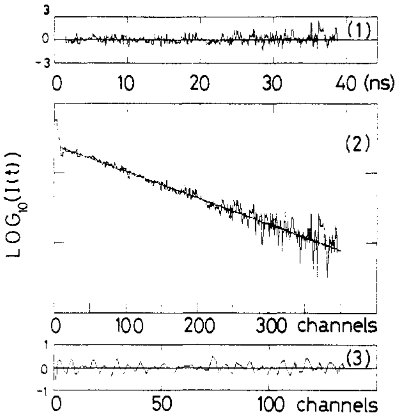


Figure 2. Monomeric fluorescence decay of racemic PS2(propyl) in CH (0.2 mM) at 280 nm obtained by using a DPO method (97.66 ps/channel) (2), plots of weighted residuals (1), and autocorrelation of residuals (3) for single-exponential fits (exp($-t$/11 ns)). The rapid decay at very short times is due to Cerenkov radiation.

with time constant τ = 11 ± 1 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 racemic PS2(propyl) dissociates very little (or not at all) at 20 °C. It is difficult to obtain the exact rise curve of the excimer emission by removing the Cerenkov light and the overlap of the monomer fluorescence decay, but the decay curve at 340 nm may be fitted very well to

$$I_{340}(t) = 0.77[\exp(-t/22\text{ ns}) - \exp(-t/11\text{ ns})] + 0.23\exp(-t/11\text{ ns})$$

This is a reasonable result because the intensity of monomer fluorescence is found to be about 25% of that of the fluorescence at 340 nm from the photostationary results. Accordingly, the excimer emission rises single exponentially with the same time constant (11 ns) as that

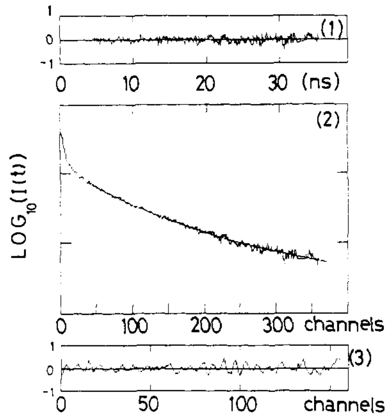


Figure 3. Monomeric fluorescence decay of meso PS2(propyl) in CH (20 mM) at 280 nm obtained by using a DPO method (97.66 ps/channel) (2), plots of weighted residuals (1), and autocorrelation of residuals (3) for dual-exponential fits calculated after 4.9 ns ($I(t) = 0.26 \exp(-t/6.1 \text{ ns}) + 0.060 \exp(-t/24 \text{ ns})$).

of monomer fluorescence decay. This means that the shortening of the fluorescence lifetime of the phenyl moiety from 27 ns (the monomer model cumene) to 11 ns (racemic PS2(propyl)) is due to intramolecular excimer formation.

We measured the concentration dependence of the time constants of racemic PS2(propyl) fluorescence. The monomer fluorescence at 0.2 mM to 0.5 M is found to decay single exponentially (eq 1) within experimental error, and the time constants change with concentration. In particular, the time constant of monomer fluorescence at 0.5 M is shortened to 2.2 ns because excimer is formed both intra- and intermolecularly. The time constants obtained are summarized in Table I.

Figure 3 shows the fluorescence decay of meso PS2-(propyl) at 280 nm over the long time range obtained by using a DPO method. We conclude that the fluorescence near the monomer peak of the meso styrene dimer with propyl end groups is found to decay triple exponentially with time constants of 0.5, 6, and 23 ns; this is also true of meso PS2(pentyl).[11]

The fluorescence at 340 nm, consisting only of the excimer signal, decays single exponentially with a time constant of 23 ns; thus the longest component is due to the overlapping of excimer fluorescence at this wavelength. The reasons are as follows: (1) The steady-state fluorescence spectra of meso PS2(propyl) suggests that excimer fluorescence overlaps even in the monomeric fluorescence region, while the intensity of monomeric fluorescence is very low (see Figure 1B). (2) The component with a time constant of 23 ns is not observed in racemic PS2(propyl) monomer fluorescence decay, though the lifetime of excimer fluorescence of racemic dimer precisely coincides with that of meso compound. This means that the time constant of 23 ns is only due to the lifetime of excimer (sum of k_{FD} and k_{ID}). (3) The preexponential term ratio of the longest component (A_3) to the middle one (A_2) of monomer fluorescence of dilute meso PS2(propyl) solution is 0.35 at 287 nm and 0.30 at 280 nm, while the ratio of A_1 to A_2 is nearly the same at 280 nm and at 287 nm (2.6). It also suggests that the component with the longest lifetime is due to the overlapping of the excimer fluorescence. Thus, the monomer fluorescence of meso PS2(propyl) decays dual exponentially with the time constants of 0.5 ± 0.2 and 6 ± 1 ns, while the excimer fluorescence (340 nm) rises very quickly and decays with time constant of 23 ± 1 ns.

We also measured the concentration dependence of the time constants of meso PS2(propyl) fluorescence. The monomer fluorescence decay curves are all found to consist of three components, including the overlapping of excimer fluorescence, although at high concentration the excimer could be formed intra- and intermolecularly. The equations which fit best are summarized in Table I.

Discussion

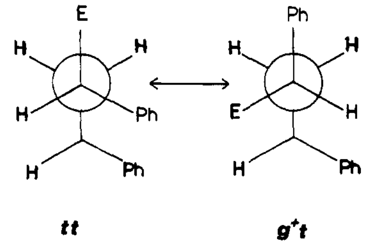
Kinetics of Intramolecular Excimer Formation. The monomer fluorescence of meso PS2(propyl) decays dual exponentially with time constants of 0.5 and 6 ns, while that of racemic PS2(propyl) decays single exponentially with an 11-ns constant at concentrations dilute enough that intermolecular excimer formation can be neglected. Since the fluorescence lifetime of cumene, a monomer model, is 27 ns, a possible qualitative explanation is that the shortening of the lifetime is due to the existence of an escape process from the excited monomer state, that is excimer formation; the shorter values for the meso compound suggest that excimer formation is more effective in the meso dimer than in the racemic dimer. However, the most important question is why there are two time constants in the monomer fluorescence decay of meso PS2, because monomer fluorescence must decay single-exponentially under the condition that dissociation of the excimer can be neglected in terms of general Birks[20] and Klöpffer[21] kinetics.

The formation of an intramolecular excimer in polymer systems needs two important processes; one is the formation of the excimer conformation (tt, meso diad; g^-t/tg^-, racemo diad) by local motion such as a crankshaft transition, and another is the influx of excitation energy into the preformed excimer conformation by singlet energy migration.[22] However, since the singlet energy migration does not influence excimer formation in dimer compounds, excimer formation is due only to the limited molecular motion of phenyl rings connected with the main chain. This means that rate constant for excimer formation is identical with that for the motion of phenyl rings to achieve the required geometry. Thus the probelms to be recognized in our systems, where the probe is phenyl and its excimer fluorescence and the time resolution are over 20 ps, are (1) what type of molecular motion influences the excimer formation process (and how fast it is) and (2) whether its relaxation has the form of an exponential equation or a more complicated form such as $a + bt^{-1/2}$ type because of the diffusion process being influenced by spatial distribution.

Here we assume that all relaxation processes occur exponentially. This also means that we assume that all rate constants observed in our experiments are independent of time.

Before considering the reason why there are two time constants for the meso dimer, we discuss the main conformational change shown in Figure 4.

Figure 4 shows the main conformational change of the diastereoisomeric dimers. The conformational change between tt and g^+t in the meso dimer may be shown as follows.



The rotation around the carbon–carbon bond requires three groups (Ph (phenyl), E (alkyl end group), and H) to

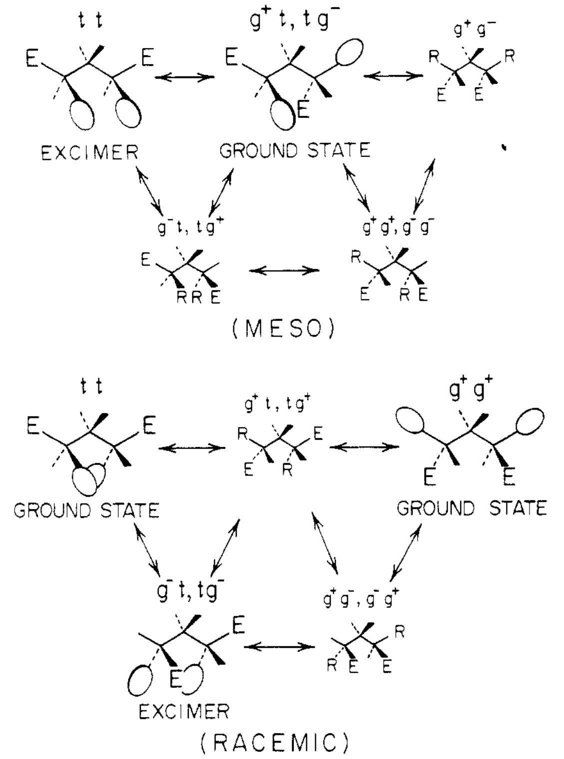


Figure 4. Main conformational changes for meso and racemic PS2 (E, propyl end group; R, phenyl group).

pass over each of three steric hindrance (H, H, and carbon with phenyl group). Here we define this conformational change as Ph(H), E(H), H(Ph,H). By using this description, we can estimate the similarity of barrier energies. In Figure 4, the path having the same description of the rotational energy barrier is placed in the same corresponding position in each meso and racemic structure. Of course, we must bear in mind that the total energy barrier is different between tt → g$^+$t and g$^+$t → tt because the stability of each conformer is different. The conformational changes which occur readily are those in which the smallest group, H, i.e., C–H bond, passes over the bulkiest group (H(Ph,H) or H(E,H)), while those including Ph(Ph,H), E(Ph,H), Ph(E,H), or E(E,H) occur with difficulty. For example, excimer formation in the racemic dimer is supposed to occur mainly via the process tt → g$^-$t/tg$^-$ or g$^+$t/tg$^+$ → g$^-$t/tg$^-$, but the energy barrier is expressed as H(H), E(H), Ph(Ph,H), or H(H), Ph(H), E(Ph,H) and includes a larger factor. Thus it is explicable that the excimer is difficult to form in the racemic dimer.

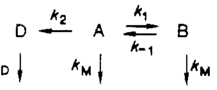
On the other hand, the most stable conformers are g$^+$t/tg$^-$ in the meso dimer and tt and g$^+$g$^+$ in the racemic dimer.[23,24] Concerning the racemic dimer, the bulkier the alkyl end group, the greater is the population of the tt conformer.

There are two possible explanations for the existence of two time constants in the monomer fluorescence of the meso dimer:

(I) The first is the case where the conformational changes shown in Figure 4 are so slow that we can only observe at most one conformational change during the fluorescence lifetime of phenyl group. In this case, excimer formation by way of more than one other conformation, such as g$^+$t → g$^+$g$^-$ → g$^+$t → tt, can be neglected. However, the reorientation of phenyl rings, which is a faster relaxation process, could influence the fluorescence decay.

(II) The second is the case where the conformational changes shown in Figure 4 are so rapid that the process g$^+$g$^-$ ↔ g$^+$t/tg$^-$ can occur repeatedly before the formation of excimer conformation (tt) in the meso dimer. Under these conditions, the monomer fluorescence will decay dual exponentially, while reorientational motion cannot be observed separatedly.

Scheme I[a]



[a] k_M = the sum of rate constants k_{FM} (for radiative deactivation) and k_{IM} (for nonradiative deactivation) from excited phenyl monomer; k_D = the sum of rate constants k_{FD} (for radiative deactivation) and k_{ID} (for nonradiative deactivation) from excimer; k_1, k_{-1}, and k_2 = rate constants for conformational change.

In the beginning we thought that the fastest component (0.5 ns) might come from the reorientational motion of the phenyl ring.[11] However, it does not seem at present to be fully correct to assign the time constant of 0.5 ns to reorientation motion for the following reasons: (1) The preexponential term of component with time constant of 0.5 ns is found to be about 70% of the whole fluorescence intensity at $t = 0$. If this percentage shows the population of excimer conformation (tt) at $t = 0$, the results are quite different from the values obtained for meso PS2(methyl) by NMR[23] and energy calculations.[24] (2) The reorientational correlation times of phenyl groups in PS2(methyl) were measured to be 24 ps at room temperature by means of Raman line-shape analysis,[25] while the relaxation time corresponding to 0.5 ns was observed in meso PS2(methyl) by using the ultrasonic absorption method.[26]

It is also pointed out that special "cooperative" motions in backbone chain bonds allow the rotation of phenyl groups in polystyrene.[27] Thus, we must exclude explanation I.

Next let us discuss explanation II. In this case, molecular motion is assumed to be so rapid that we can observe the equilibrium reaction of conformational change. It is also assumed that once the excimer conformation is formed in a dimer molecule, it should remain as an excimer. In other words, excimer dissociation can be neglected (see Results).

In the case of meso PS2(propyl), the main conformational change influencing our experiments is tt ↔ g$^+$t/tg$^-$ ↔ g$^+$g$^-$; thus, we must consider the kinetics of Scheme I. A and B are excited monomer states of g$^+$t/tg$^-$ and g$^+$g$^-$ conformers, respectively, while D is the excimer state (tt). The rate equations for this scheme are given in eq 1. In

$$\dot{A} = I_a - (k_1 + k_2 + k_M)A + k_{-1}B$$

$$\dot{B} = I_b + k_1 A - (k_{-1} + k_M)B$$

$$\dot{D} = k_2 A - k_D D \tag{1}$$

the case of pulse excitation, I_a and I_b are assumed to be represented by a δ-function. Then by solving eq 1 with initial conditions [A] = a and [B] = b at $t = 0$ (the fraction of tt conformer at $t = 0$ is c; $a + b + c$ is assumed to be 1), we obtain

$$A(t) = (\lambda_1 - \lambda_2)^{-1}[(a(l - \lambda_2 + k_M) - k_{-1}(a + b)) \exp(-\lambda_1 t) + (k_{-1}(a + b) - a(l - \lambda_1 + k_M)) \exp(-\lambda_2 t)] \tag{2a}$$

$$B(t) = (k_{-1}(\lambda_1 - \lambda_2))^{-1}[(a(l - \lambda_2 + k_M) - k_{-1}(a + b)) \times (l + k_M - k_{-1} - \lambda_1) \exp(-\lambda_1 t) + (k_{-1}(a + b) - a(l - \lambda_1 + k_M))(l + k_M - k_{-1} - \lambda_2) \exp(-\lambda_2 t)] \tag{2b}$$

where

$$\lambda_1 = k_M + [l + (l^2 - 4k_{-1}k_2)^{1/2}]/2 \quad (3a)$$

$$\lambda_2 = k_M + [l - (l^2 - 4k_{-1}k_2)^{1/2}]/2 \quad (3b)$$

$$l = k_1 + k_{-1} + k_2 \quad (4)$$

and also

$$\lambda_1 + \lambda_2 = l + 2k_M \quad (5)$$

$$\lambda_1\lambda_2 = k_M^2 + k_M l + k_{-1}k_2 \quad (6)$$

The time dependence of excited monomer ($[M^*](t)$) is expressed as

$$[M^*](t) = A(t) + B(t) = A_1 \exp(-\lambda_1 t) + A_2 \exp(-\lambda_2 t) \quad (7)$$

where

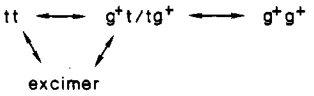
$$A_1 = (k_M - \lambda_1 + l)[a(l + k_M - \lambda_2) - k_{-1}(a + b)]/[k_{-1}(\lambda_1 - \lambda_2)] \quad (8)$$

$$A_2 = (k_M - \lambda_2 + l)[-a(l + k_M - \lambda_1) + k_{-1}(a + b)]/[k_{-1}(\lambda_1 - \lambda_2)] \quad (9)$$

It is clear that the monomer fluorescence of meso PS2 will decay dual exponentially under this condition. If values of each conformer population (a, b, and c) can be obtained, rate constants for the conformational change k_1, k_{-1}, and k_2 can be calculated by substituting the values obtained by our experiment ($\lambda_1 = (0.5\ \text{ns})^{-1}$, $\lambda_2 = (6\ \text{ns})^{-1}$, $k_M = (27\ \text{ns})^{-1}$ (cumene in CH), $A_1 = 0.72$, and $A_2 = 0.28$) into eq 5, 6, 8, and 9. Figure 5 shows the calculated values of these rate constants when the values of a and b change. The population of g^+t/tg^- is thought to be close to 100% while the fraction of other conformers are assumed to be at most 10%.[23d,24] Thus the estimated values are as follows: $k_1 = 4 \times 10^8\ \text{s}^{-1}$ ($1/k_1 = 2.5$ ns), $k_{-1} = 1.7 \times 10^8\ \text{s}^{-1}$ (6 ns), and $k_2 = 1.5 \times 10^9$ (0.7 ns). Especially when the population calculated for meso PS2(methyl) can be applied to the present dimer ($a = 0.955$, $b = 0$, $[tt] = 0.045$),[24b] the estimated values are $k_1 = 4.7 \times 10^8\ \text{s}^{-1}$ ($1/k_1 = 2.1$ ns), $k_{-1} = 1.8 \times 10^8\ \text{s}^{-1}$ (5.7 ns), and $k_2 = 1.5 \times 10^9$ (0.7 ns). This results suggest that the fast component depends mainly on the conformational change $g^+t/tg^- \rightarrow tt$, while the component with a time constant of 6 ns appears mainly due to the backward conformational change from g^+g^- being slow.

The profile of monomer fluorescence decay in the meso styrene dimer can be explained by assuming the foregoing kinetic scheme, Scheme I. Our assumption is that the fluorescence decay curves observed in these experiments are influenced mainly by local molecular motion. However, if the treatment applied to the meso dimer is ironically construed, the introduction of two different conformers might be regarded as the trick to make the number of excited monomer states the same as that of the time constants, as the time constants observed correspond to more excited states than should exist. Thus it is very important whether our treatment holds for the racemic PS2 or not.

In the case of racemic PS2(propyl), the main conformational change is



thus the kinetic scheme which we have to consider is as in Scheme II. P, Q, and R are excited monomer states in tt, g^+t/tg^+, and g^+g^+ conformers, respectively, while D is the excimer state (g^-t/tg^-). Excimer dissociation can be

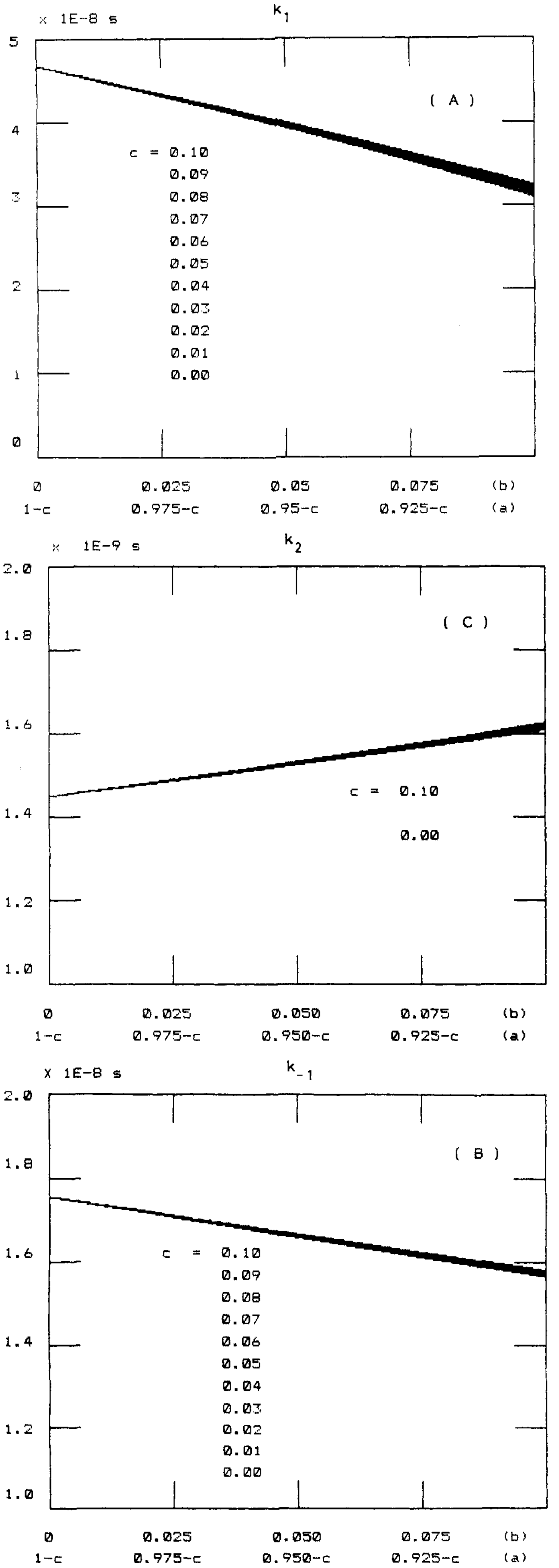
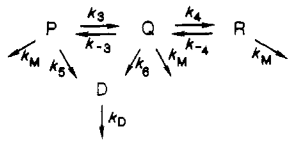


Figure 5. Rate constants for conformational changes of meso PS2(propyl) calculated by using kinetic Scheme I (a, b, and c are the population of conformers g^+t/tg^-, g^+g^-, and tt, respectively, at time = 0).

Table II
Simulation of the Monomer Fluorescence Decay Profile of Racemic PS2(propyl) under Kinetic Scheme II

k_3^{-1}, ns	k_{-3}^{-1}, ns	k_4^{-1}, ns	k_{-4}^{-1}, ns	k_5^{-1}, ns	k_6^{-1}, ns	A_1	τ_1, ns	A_2	τ_2, ns	A_3	τ_3, ns
0.8	1.5	0.5	0.6	0	6.6	−0.010	0.29	−0.0076	0.72	1.02	11
1.0	1.2	0.7	0.5	0	7.1	−0.0096	0.2	−0.012	0.75	1.02	11
0.5	4.6	0.7	0.7	0	8.6	−0.026	0.31	0.016	0.52	1.01	11
6.1	1.0	0.6	0.6	14	0	0.00071	0.25	−0.0021	1.6	1.00	11
5.1	0.4	0.9	3.0	13	0	0.00085	0.26	0.0037	2.9	1.00	11
1.0	0.6	0.9	0.6	9.0	0	0.0043	0.24	0.0093	0.69	0.99	11

Scheme II[a]



[a] k_M = the sum of k_{FM} and k_{IM}; k_D = the sum of k_{FD} and k_{ID}; k_3, k_{-3}, k_4, k_5, and k_6 = rate constants for conformational change.

neglected because there is no decay component with the same time constant in monomer fluorescence decay as that of excimer fluorescence. The excimer formation path by way of g^-g^+/g^+g^- can be neglected due to their instability and the large energy required to form them.

If we assume three monomer states, then the total monomer fluorescence ought to decay as the sum of three exponentials. Nevertheless, the experimental decay is found to be best fit by a single exponential equation. The possible explanation is (1) the other two time constants are too short to be observed in our system or (2) the preexponential terms of the other two decay components are too small to be observed in our system. The problem is whether the experimental fluorescence decay curve can be produced by assigning reasonable values to rate constants for conformational change (k_3, k_{-3}, k_4, and k_{-4}). Thus we considered whether there may exist conditions such that under the kinetic Scheme II the monomer fluorescence might appear to decay single exponentially. The general solution calculated under the above kinetic scheme is shown in the Appendix. To search for pairs of rate constants giving the experimental decay curve, the following method was used: (1) $\lambda_3 = (11\ \text{ns})^{-1}$ and $k_M = (27\ \text{ns})^{-1}$ were fixed; (2) the values of the reciprocal of k_3, k_{-3}, k_4, and k_4 were changed from 0.3 to 7.0 ns by 0.1 ns, respectively; (3) the population of conformers at $t = 0$ was assumed to be [P] = 0.75, [Q] = 0, [R] = 0.25;[23d] (4) either $k_5 = 0$ or $k_6 = 0$ were assumed in order to check which path is dominant.

Some pairs of rate constants that could give an apparent single exponential monomer fluorescence decay are summarized in Table II. Although the values themselves are meaningless, this simulation suggests the following: (1) The observed experimental fluorescence decay curve may appear even under the kinetics of Scheme II. (2) It is impossible to determine which conformational change is dominant in the excimer formation process, k_5 or k_6, from this experiment. (3) As the time constant of monomer fluorescence in racemic dimer is expressed as eq A-3, it is impossible to calculate each rate constant for conformational change in the case of racemic PS2.

In conclusion, the fluorescence decay of meso and racemic PS2(propyl) is influenced mainly by conformational change, and some relaxation times required for conformational change can be obtained by fitting these decay curves.

We now consider the concentration dependence of the fluorescence decay curves. These experiments were carried out because of the possibility (1) that the previous PS2(pentyl) data[11] are distorted by intermolecular excimer formation or (2) that the decay profile for the racemic dimer might approach that of the meso dimer. Since intermolecular excimer formation accompanies intramolecular excimer formation with increasing concentration, the decay profile should change. The time constant of racemic PS2(propyl) is found to be shorter, showing nearly the same concentration dependence as the longer one of the meso dimer, while the shorter time constant of the racemic PS2(propyl) corresponding to 0.5 ns of the meso dimer does not appear even in concentrated solution. The qualitative explanation possible in our high-concentration experiments is that the intermolecular excimer formation process by the diffusional encounter of two molecules would become faster than the intramolecular one by conformational changes (6 ns (meso) and 11 ns (racemic)) and come to be the more dominant process in place of these conformational changes, though intramolecular excimer formation by conformational change from g^+t/tg^- to tt in the meso dimer still remains faster than intermolecular excimer formation. However, it is very difficult to exactly analyze the molecular motion from these data including intra- and intermolecular reaction, and thus it seems that further discussion here is not fruitful. All we can present here is that intermolecular excimer formation will be influenced by concentrations above 0.02 M, suggesting that the concentration of our previous data[11] is high (0.09 base molar (0.05 M)) for meso PS2(pentyl) and that the data might be distorted by intermolecular excimer formation. The values obtained for meso PS2(pentyl) will be omitted when the end group effect on excimer formation is discussed in the next section.

Table III
End Group Effect on Decay Constants of Monomer Fluorescence Decay of Styrene Dimers in Cyclohexane[a]

	ref	λ,[d] s^{-1}	$\lambda - k_M$, s^{-1}	$1/(\lambda - k_M)$, ns
racemic PS2(methyl)	4(c)	1.4×10^8 [b]	9×10^7	11
racemic PS2(propyl)		9.1×10^7	5.3×10^7	11
racemic PS2(pentyl)	11	75×10^7	3.9×10^7	25
meso PS2(methyl)	4(c)	*c*	2×10^9	0.5
meso PS2(propyl)		2.0×10^9	2.0×10^9	0.5
		1.7×10^7	1.3×10^8	7.7

[a] Except ref 4c in isooctane at 20 °C. [b] From Figure 2 in ref 4c. [c] Decay constant could not be measured directly. Other values were calculated by extrapolating the data at low temperatures to 20 °C. [d] Decay constant.

End-Group Effect upon Excimer Formation and Molecular Motion. Fluorescence decay profiles for styrene diastereoisomeric dimers have been reported for methyl end[4c] and pentyl end,[11] in addition to propyl end in this paper. The lifetimes reported are summarized in Table III.

We conclude that there clearly exists an end-group effect on the intramolecular excimer formation, although our previous data for meso and racemic PS2(pentyl) seem to include an intermolecular excimer formation process, as was described in the previous section; the concentration of even racemic PS2(pentyl) was a little high to be 0.06 base molar (0.03 M). The pentyl end group is so bulky that it can restrict the conformational motion of the phenyl ring around the main chain and it retards the excimer formation time, while the methyl end group cannot restrain the motion of phenyl rings and excimer can be formed easily. This result suggests that (1) the motion of phenyl ring is restricted by the steric hindrance of alkyl end group and (2) the motion of midchain phenyl rings of polystyrene might be restricted more than that of styrene dimers.

De Schryver et al.[4c] reported detailed results concerning the fluorescence properties of meso and racemic PS2(methyl). At that time the resolution time of their equipments for measuring transient fluorescence was not sufficiently short that they could observe the decay profile of the meso PS2(methyl) except in the temperature range between 178 and 225 K. The excimer formation rate constant at 20 °C was stated as 2×10^9 s^{-1} (0.5 ns) by extrapolating the data in this temperature region. At these low temperatures, the main kinetic scheme is supposed to be $g^+t/tg^- \rightarrow tt$ because other conformational changes (e.g., $g^+t/tg^- \leftrightarrow g^+g^-$) are very slow, and thus it was assumed that the single-exponential fluorescence decay would occur with a time constant corresponding to our fastest value.

Monnerie et al.[26] also reported a relaxation time of meso and racemic PS2(methyl) at temperatures between −20 and −50 °C by using an ultrasonic method as a part of their intensive work on polystyrene and its model oligomers. They concluded that the relaxation should be observed at 204 MHz (4.9 ns) in the $g^+t/tg^- \rightarrow tt$ process of meso PS2(methyl) and at 575 MHz (1.7 ns) in $tt \leftrightarrow g^+g^+$ of racemic PS2(methyl) at room temperature.[28] This result supports the conclusion that the conformational change $tt \leftrightarrow g^+t/tg^+ \leftrightarrow g^+g^+$ in the racemic PS2(methyl) is fast. However, the assignment of the relaxation at 204 MHz (4.9 ns) is found to be wrong, compared with our data. This relaxation should correspond either to our 6-ns time constant or to the conformational $g^+t/tg^+ \rightarrow g^+g^+$. The small difference in magnitude of the constants is assumed to be due to the bulkiness of alkyl end group.

Conclusion

Fluorescence decay curves of diastereoisomeric styrene dimers are found to be influenced mainly by the conformational changes shown in Figure 4. When both the populations of conformers and the possibility of conformational changes occurring are taken into account, kinetic Scheme I would apply to the meso dimer while kinetic Scheme II would apply to the racemic dimer. Consequently the times required for the conformational changes $(g^+t/tg^-) \rightarrow tt$, $(g^+t/tg^-) \rightarrow g^+g^-$, and $g^+g^- \rightarrow (g^+t/tg^-)$ in meso PS2(propyl) are estimated to be 0.7, 2.5, and 6 ns, respectively, at room temperature. These values are consistent with those obtained for meso PS2(methyl) by using an ultrasonic method.

Recently it has become of major interest that the conventional kinetic scheme for intramolecular excimer formation by Birks[20] and Klöpffer[21] may not be applicable to some polymer systems, because the decay curves of some polymers have been found to be fit better by a linear combination of three exponentials, although there should be only two decay constants in a monomer–excimer fluorescence system. The present result suggests that multicomponent fluorescence decay curves observed in some polymer systems may be mainly due to conformational change processes in the meso diad, since the contribution of the racemic diad is assumed not to be so important in excimer formation in polymer systems.[29]

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Appendix

The rate equations for kinetic Scheme II are given in eq A-1. In the case of pulse excitation, I_p, I_q, and I_r are

$$\dot{P} = I_p - (k_3 + k_5 + k_M)P + k_{-3}Q$$

$$\dot{Q} = I_q + k_3P - (k_{-3} + k_4 + k_6 + k_M)Q + k_{-4}R$$

$$\dot{R} = I_r + k_4Q - (k_{-4} + k_M)R$$

$$\dot{D} = k_5P + k_6Q - k_DD \qquad \text{(A-1)}$$

supposed to be represented by a δ-function. Then by solving eq A-1 with initial condition that [P] = p, [Q] = q, and [R] = r at t = 0, we obtain

$$P(t) = \sum_{i=1}^{3}[k_{-3}/(Z - \lambda_i)]S_i \exp(-\lambda_i t)$$

$$Q(t) = \sum_{i=1}^{3}S_i \exp(-\lambda_i t)$$

$$R(t) = \sum_{i=1}^{3}[k_4/(Y - \lambda_i)]S_i \exp(-\lambda_i t) \qquad \text{(A-2)}$$

where

$$X = k_{-3} + k_4 + k_6 + k_M \qquad Y = k_{-4} + k_M$$
$$Z = k_3 + k_5 + k_M$$

and

$$S_i = \{A_i(Y - \lambda_i)(Z - \lambda_i)[p(Z - \lambda_j) \times (Z - \lambda_k) + qk_{-3}k_4(Y - Z) - rk_{-3}(Y - \lambda_j)(Y - \lambda_k)]\}/[k_{-3}k_4(Z - Y)A_1A_2A_3] \qquad (\lambda_i\lambda_j\lambda_k = \lambda_1\lambda_2\lambda_3)$$

where

$$A_1 = \lambda_2 - \lambda_3 \qquad A_2 = \lambda_3 - \lambda_1 \qquad A_3 = \lambda_1 - \lambda_2$$

and

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

$$\lambda_1\lambda_2 + \lambda_2\lambda_3 + \lambda_3\lambda_1 = XY + YZ + ZX - k_3k_{-3} - k_4k_{-4}$$

$$\lambda_1\lambda_2\lambda_3 = XYZ - k_3k_{-3}Y - k_4k_{-4}Z \qquad \text{(A-3)}$$

where $\lambda_1 > \lambda_2 > \lambda_3 > 0$. Accordingly the time dependence of excited monomer ([M*](t)) is expressed as

$$[M^*](t) = P(t) + Q(t) + R(t) = \sum_{i=1}^{3}[1 + k_4/(Y - \lambda_i) + k_{-3}/(Z - \lambda_i)]S_i \times \exp(-\lambda_i t) \qquad \text{(A-4)}$$

Registry No. PS2(propyl), 75761-01-2; (±)-PS2(propyl), 75761-00-1; polystyrene, 9003-53-6.

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Role of Symmetry in the Formation of *n*-Paraffin Solid Solutions

Douglas L. Dorset

Electron Diffraction Department, Medical Foundation of Buffalo, Inc., Buffalo, New York 14203.

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ABSTRACT: Single-crystal electron diffraction patterns from epitaxially crystallized binary solids of n-$C_{32}H_{66}$/n-$C_{36}H_{74}$ and n-$C_{33}H_{68}$/n-$C_{36}H_{74}$ have been reanalyzed to determine the symmetry rules for solid solution formation. For these orthorhombic structures, the symmetry alternates sequentially between the $Pca2_1$ space group of the even-chain structure and the $A2_1am$ space group (or possibly twinned Aa) of the odd-chain structure with increasing concentration of the longer chain component, irrespective of whether the solid is comprised of even–even or odd–even chain combinations. Similar structural features are found for a commercial multicomponent paraffin wax. The sequence of lamellar spacings is regulated by archetypical crystal packing(s) for any concentration region so that, in the microcrystalline state, increase in lamellar thickness is steplike and not a smooth function like Vegard's law. In this sense, the solid solutions are not continuous, even when the chain length difference is small and the pure components have the same crystal structure.

Introduction

Because of its importance for understanding the physical behavior of various polydisperse linear chain molecules (e.g., lipids, polymers), the solid solubility of binary n-paraffin aggregates has been an object of continued interest for at least 60 years. With an overview of calorimetric and diffraction data as reviewed by Mnyukh,[1] Kitaigorodskii formulated rather strict rules for the formation of continuous solid solutions. The first rule states that the molecular size difference (which can be inversely stated as a parameter of geometrical similarity[2]) cannot be too large.[2,3] Expression of this rule is verified by the characteristics of phase diagrams in Mnyukh's review; hence, if the paraffin chain lengths are too different, a eutectic is formed. The upper limit for length difference permitted for solid solution formation is discussed by several authors.[4,5]

The second rule considers molecular and/or crystal symmetry. According to Kitaigorodskii, if the molecules are not asymmetric (as in the case of linear paraffins), then the addition of solute A to crystal solvent B must not raise the symmetry of B. Addition will either lower the symmetry of B or leave its symmetry unchanged. For this reason, proposed solid solubility of even- with odd-chain