Local Molecular Motion of Polystyrene Model Compounds Measured by Picosecond Pulse Radiolysis. 3. Diastereomeric Styrene Dimer, Trimer, and Tetramer in Poly(methyl methacrylate) Solid Solution

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ABSTRACT: The photophysical properties of diastereomeric oligostyrenes, meso (*m*) and racemic (*r*) 4,6-diphenylnonanes (PS2); *mm*-, *mr*-, and *rr*-4,6,8-triphenylundecanes (PS3); and *mmm*-, *mmr*-, *mrm*-, *rrm*-, and *rrr*-4,6,8,10-tetraphenyltridecanes (PS4), in poly(methyl methacrylate) (PMMA) were studied by photostationary and transient measurements. The fluorescence spectra of PS2, PS3, and PS4 with meso diads exhibited excimer fluorescence even in PMMA solid solution where conformational changes are restricted, suggesting that the population of tt, an excimer conformer, in the meso diad is noticeable even in low molecular weight compounds such as PS2, PS3, or PS4. Monomer fluorescence of oligostyrenes in PMMA decayed single exponentially with the same time constant as that of cumene. The observed monomer fluorescence is assumed to come from a molecule that has no excimer conformer while a molecule having excimer conformers does not exhibit monomer fluorescence. Fluorescence polarization measurements at 77 K and at room temperature demonstrated that the reorientational motion of phenyl groups was not perfectly restricted in PMMA solid solution. The efficiency of the energy migration among the phenyl rings in PS2, PS3, and PS4 was not so outstanding that it could induce the fluorescence depolarization.

Introduction

Excimer fluorescence is a powerful tool for monitoring molecular motions and ordered structures of macromolecules both in fluid and solid solutions.[1] In particular the excimer probe method has been suggested to be applied for the direct measurements of dynamic local motion of macromolecules; unfortunately this trial appeared to be prevented by complicated polymer structural features such as the configuration and the conformation as well as by complicated polymer photophysical properties such as energy migration.

The formation of an intramolecular excimer in vinyl-type polymer systems requires two important processes: one is the formation of the excimer conformations (Figure 1: 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.[2] In low molecular weight compounds, the formation of an excimer conformation should be the rate-determining process for excimer formation,[3] thus direct measurement of local motion using the excimer probe method is expected to be possible in the case of oligomers. Therefore in order to exclude the influence induced by polymer structure, we started with the studies using diastereomeric styrene oligomers, model compounds of polystyrene. We measured the dynamic process of intramolecular excimer formation in diastereomers as shown in Figure 2 (PS2,[4] PS2(pt),[5] PS3,[6] PS3(pt),[7] and PS4[8]) together with that in atactic oligostyrenes from dimer to tridecamer with symmetric propyl ends[3] by picosecond pulse radiolysis.

All through the studies of the oligostyrenes, we could conclude the following: (1) The excimer in oligostyrenes (or polystyrene) is formed mainly in the meso diad. It coincides with both the theoretical prediction for the polymer system[9] and the experimental results of diastereomeric dimers that the excimer is more easily formed in the meso than in the racemic isomer,[10] which was first reported by Longworth and Bovey.[11] (2) There exists singlet energy migration in styrene trimer and tetramer systems. This is shown by the fact that monomer fluorescence decay curves of heterotactic isomers (*mr* PS3, *mmr* PS4, *mrm* PS4, and *rrm* PS4) do not have as long a decay lifetime as the curves of all-racemic isomers. (3) The phenyl groups do not rotate independently around

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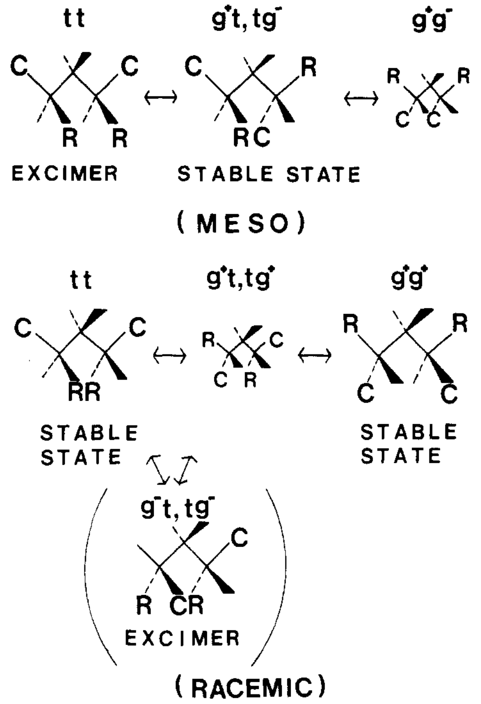

Figure 1. Main conformational changes for meso (top) and racemic (bottom) diads (C, main chain; R, phenyl group).

Table I
Purity of Oligostyrene Diastereomers

r PS2	>99%	*rrr* PS4	95%
m PS2	>99%	*rrm* PS4	83%[a]
rr PS3	>98%	*mmr* PS4	90%
mr PS3	>98%	*mrm* PS4	85%
mm PS3	>98%	*mmm* PS4	90%

[a] Including 17% *rmr* PS4.

the carbon–carbon bonds of the backbone chain, but their rotation involves a cooperative motion of backbone chain bonds such as a crankshaft transition[12] or a three-bond jump motion.[13]

The present paper will describe the photophysical properties of diastereomeric oligostyrenes in poly(methyl methacrylate) solid solution. Since the dynamic motion of oligostyrenes is restricted in the solid solution, we obtain information on singlet energy migration and the stable conformation of molecules at the temperature of casting.

Experimental Section

The diastereoisomeric oligostyrenes used in the present study were meso (*m*) and racemic (*r*) 4,6-diphenylnonanes (PS2); *mm*-, *mr*-, and *rr*-4,6,8-triphenylundecanes (PS3); and *mmm*-, *mmr*-, *mrm*-, *rrm*-, and *rrr*-4,6,8,10-tetraphenyltridecanes (PS4). The details of the synthesis and identification of the isomers have already been reported by Sato and Tanaka.[14] Each purity of the compounds is shown in Table I. Biphenyl, *n*-octadecylbenzene, and pyrene were purified by repeated recrystalization. The plastic solutions of PS2, PS3, PS4, biphenyl, *n*-octadecylbenzene (OB), and pyrene were obtained by casting on a Pyrex glass plate or in a beaker from ca. 8% spectrosol THF solution of poly(methyl methacrylate) (PMMA) containing the above compounds. The films were removed from either the casting plates or the beakers after preliminary drying for several days at room temperature; then all films were dried by extensive pumping under vacuum at 40 °C. The drying time was at least 3–4 days. The thickness of the films was ca. 50 μm for the photostationary measurements and ca. 1–5 mm for the transient measurements from pulse radiolysis.

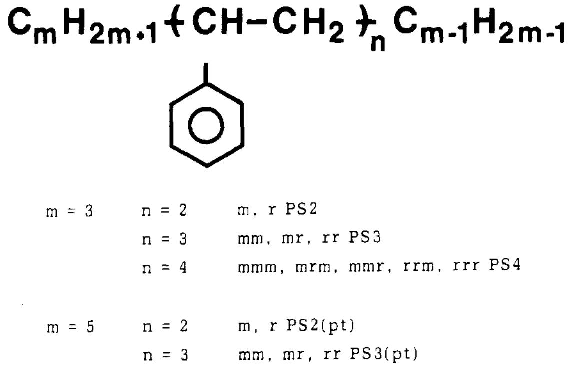

Figure 2. Structure of oligostyrenes.

Fluorescence spectra, fluorescence excitation spectra, and fluorescence polarization spectra were measured on a Hitachi F-3000 spectrofluorometer. Fluorescence polarization was measured for oligostyrenes, OB, biphenyl, anthracence, and pyrene in PMMA solid solution both at room temperature and at 77 K. Excitation wavelengths were 250 nm for diastereomeric oligostyrenes and OB, 270 nm for biphenyl, 340 nm for anthracene, and 330 nm for pyrene. The values of anisotropy were determined by averaging the values for each 2 nm between 280 and 300 nm for oligostyrenes and OB, between 300 and 330 nm for biphenyl, and between 380 and 410 nm for pyrene. For anthracene, the anisotropy at 400 nm was measured on a Hitachi 650-60 spectrofluorometer. Fluorescence decay curves were obtained with a picosecond pulse radiolysis system, using as an exciting source a pulsed electron beam (10 ps, fwhm) comprising a specially designed linear accelerator.[15] The emission of diastereomeric oligostyrenes in PMMA was measured at ca. 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). Details of our method for calculating time constants have been already reported.[4] The calculated equations were normalized by setting $\sum A_i = 1$; $I(t) = \sum A_i \exp(-t/\tau_i)$.

Results and Discussion

Fluorescence of Diastereomeric Oligostyrenes in PMMA. Figure 3 shows fluorescence spectra of all-meso isomers (*m* PS2(pr), *mm* PS3(pr), and *mmm* PS4(pr)) in PMMA together with cumene, a monomer model compound, in cyclohexane (CH) solution. The spectra were normalized at 290 nm. Rough difference spectra (Figure 3B) were obtained by subtracting the spectrum of cumene from each spectrum of the isomers, although fluorecence at 290 nm may not always consist of only monomer fluorescence. The difference spectra demonstrate that the isomers having meso diads exhibit excimer fluorescence even in PMMA solid solution, because (1) dilute cumene does not display excimer fluorescence, (2) the peak wavelength of rough difference spectra (330 nm) precisely agrees with that of excimer fluorescence of poly- and oligostyrenes, and (3) the fluorescence excitation spectra of oligostyrenes in PMMA coincide with their absorption spectra.

Figure 3 clearly indicates that the intensity of excimer fluorescence increases with an increase of the number of meso diads in the isomers. The conformations of the oligomers in PMMA are considered to be fixed completely at the moment when the films were cast at 40 °C. Since the excimer conformation of the meso diad is tt (see Figure 1), the results mean that the population of tt in the meso diad is noticeable even in low molecular weight compounds such as PS2, PS3, or PS4. With regard to meso styrene dimer with methyl ends, Stegen and Boyd[16] calculated the population of tt to be 0.045, while Pivcova et al.[17] reported it to be close to zero. Sato et al.[18] recently determined the population of tt in the meso diad of PS2

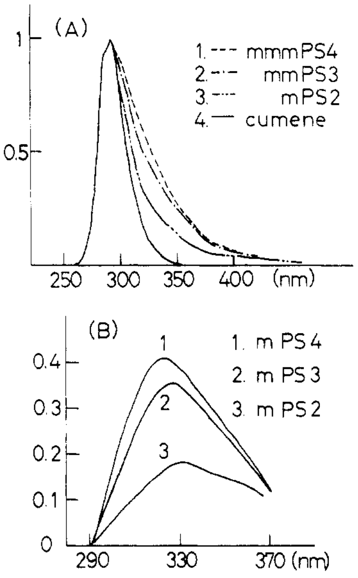

Figure 3. (A) Fluorescence spectra of all-meso PS2, PS3, and PS4 in PMMA together with cumene in cyclohexane (4) at 20 °C. Spectra were normalized at 290 nm. (B) Difference spectra obtained by subtracting (A) − 4 (cumene) from each spectrum of the isomers (A-1,2,3).

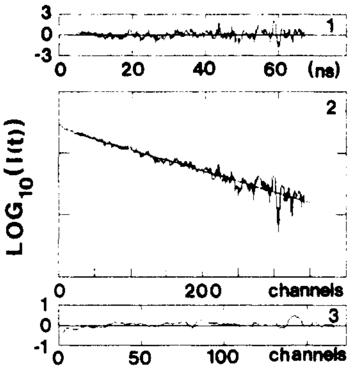

Figure 4. Monomeric fluorescence decay of *mm* PS3 in PMMA at 290 nm at 20 °C (0.1953 ns/channel) (2), plots of weighted residuals (1), and autocorrelation of residuals (3) for single-exponential fits ($\exp(-t/25\text{ ns})$).

and PS3 in deutrium chloroform to be 4–5% by calculating the NMR data. Thus the fluorescence results ascertain that even dimers can have the conformation tt in the meso structure.

An excimer in a solid solution system is assumed to be formed by the influx of excitation energy into an excimer conformation that is already fixed at the casting time. In order to examine the dynamic process of excimer formation of the isomers in PMMA solid solution, we measured fluorescence spectra of oligostyrenes in PMMA at 77 K where even the rotation of the phenyl ring is assumed to be restricted. Consequently the spectra at 77 K do not exhibit excimer fluorescence and precisely agree with one another, although the spectra at room temperature are different from one another as shown in Figure 3. This result establishes that the formation of excimer even in solid solution requires the motion of phenyl ring. Since the rotation of phenyl ring is possible in PMMA at room temperature, an excimer would be formed by this motion of a phenyl ring in an excimer conformation (mainly meso tt).

Figure 4 shows the fluorescence decay curve of *mm* PS3 in PMMA solid solution at 290 nm. The fluorescence was found to decay single exponentially with a time constant of 26 ns. The value of 26 ns is identical with that of cumene in dilute CH solution (27 ns). Since the fluorescence intensity of 1-pentylbenzene (PB), a monomer model compound, in CH is not so different (94%) from that of PB in ethyl acetate, a solvent mimicking PMMA polarity, the decay times of both monomer and excimer fluorescence of oligostyrenes in CH appear to be close to those of oligostyrenes in PMMA. The decay curve of the fluorescence at 340 nm, whose emission is assumed to consist of predominantly the monomer fluorescence with a small amount of excimer fluorescence, was also fit to a single-exponential function with a time constant of 27 ns. The fluorescence decay at 340 nm could consist of two exponential terms; however, it is not possible to fit the experimental data to a dual exponential function with time constants of 27 ns, the lifetime of the monomer fluorescence of oligostyrenes in PMMA, and 23 ns, the lifetime of the excimer of oligostyrenes in CH. No special rising component could be observed in the present experiments. Taking into account the overlapping of both the Cerenkov light and the scattering light, it can be concluded that there is no rising component whose time constant is more than 1 ns. The decay parameters of some isomers in PMMA are summarized in Table II together with those in CH solution.

Table II
Decay Parameters of Monomer Fluorescence of Diastereomeric PS2, PS3, and PS4 in PMMA and in CH at 20 °C[a]

samples	A_1	τ_1, ns	A_2	τ_2, ns	ref
mmm PS4 in PMMA	1.0 ± 0.1	26 ± 3			
mrm PS4 in PMMA	1.0 ± 0.1	28 ± 4			
mm PS3 in PMMA	1.0 ± 0.1	26 ± 2			
mr PS3 in PMMA	1.0 ± 0.1	27 ± 3			
mmm PS4 in CH	0.4 ± 0.1	2.0 ± 0.4	0.6 ± 0.1	0.7 ± 0.2	8
mmr PS4 in CH	0.4 ± 0.1	2.0 ± 0.4	0.6 ± 0.1	0.7 ± 0.2	8
mrm PS4 in CH	0.3 ± 0.1	2.0 ± 0.5	0.7 ± 0.2	0.6 ± 0.2	8
rrm PS4 in CH	1.0 ± 0.2	2.0 ± 0.4			8
rrr PS4 in CH	1.0 ± 0.1	8.2 ± 0.5			8
mm PS3 in CH	0.3 ± 0.1	4.0 ± 0.5	0.7 ± 0.2	0.4 ± 0.2	6
mr PS3 in CH	0.4 ± 0.1	4.0 ± 0.5	0.6 ± 0.2	0.6 ± 0.2	6
rr PS3 in CH	1.0 ± 0.1	7.4 ± 0.4			6
m PS2 in CH	0.3 ± 0.1	6 ± 1	0.7 ± 0.2	0.5 ± 0.2	4
r PS2 in CH	1.0 ± 0.1	11 ± 1			4

[a] Fluorescence decays due to the equation $I_M(t) = \sum A_i \exp(-t/\tau_i)$ where $\sum A_i = 1$.

The monomer fluorescence of all racemic isomers (*r* PS2, *rr* PS3, and *rrr* PS4) and *rrm* PS4 in CH fluid solution was determined to decay single exponentially

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

within experimental error.[6,8] On the other hand all the diastereomers but these four isomers in CH solution were found to decay double exponentially

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

but appeared to decay triple exponentially due to the overlapping of excimer fluorescence. The longer time constants (τ_1) are about 6 (PS2), 4 (PS3), and 2 ns (PS4), while the shorter time constants (τ_2) are almost identical with each other.

In the case of the CH fluid solution, any phenyl group in an oligomer is capable of forming an excimer or an excimer conformer, thus the excimer formation process is in equilibrium. However, in the case of the solid solution, the excimer is thought to be formed only in a molecule where an excimer conformer is already fixed. If excitation energy can reach an excimer conformer in an oligomer, excimer fluorescence would be observable, but

Table III
Anisotropy of Aromatic Compounds and Oligostyrenes in PMMA at Room Temperature and 77 K

sample	at room temp	at 77 K
mmm PS4	0.05 ± 0.02	0.13 ± 0.02
mrm PS4	0.09 ± 0.02	0.12 ± 0.04
rrm PS4	0.07 ± 0.02	0.12 ± 0.03
rrr PS4	0.09 ± 0.02	0.11 ± 0.04
mm PS3	0.08 ± 0.03	0.15 ± 0.02
mr PS3	0.08 ± 0.01	0.17 ± 0.05
m PS2	0.09 ± 0.03	0.14 ± 0.03
n-octadecylbenzene	0.09 ± 0.03	0.13 ± 0.03
biphenyl	0.34 ± 0.02	0.29 ± 0.03
anthracene[a]	0.13	0.14
pyrene	0.07 ± 0.02	0.08 ± 0.03

[a] Measured on a Hitachi 650-60 fluorescence spectrofluorometer.

if there are no excimer conformers in an oligomer, the possibility of forming an excimer is zero because no conformational change is expected. The reason we could not observe any other lifetime than 27 ns, which is identical with the value of cumene in CH, is that almost all monomer fluorescence comes from an oligomer that has no excimer conformers.

In conclusion, the excimer in PMMA solid solution is formed by means of singlet energy migration and reorientational rotation of the phenyl group in an oligomer that has excimer conformers fixed already.

Fluorescence Polarization of Oligostyrenes and Dyes in PMMA. Fluorescence polarization was measured for oligostyrenes, OB, biphenyl, and pyrene in PMMA solid solution both at room temperature and at 77 K. The values of anisotropy are summarized in Table III.

In general when a chromophore is excited by polarized light, the emission of the chromophore will be observed to be polarized if (1) the molecular motion of the chromophore is slow enough and (2) energy transfer and/or energy migration do not take place. Thus the measurements of the emission anisotropy give information on molecular motions and/or energy transportation. The fluorescence anisotropy, r, is defined as

$$r = (I_p - I_v)/(I_p + 2I_v)$$

where the I_p and I_v denote the measured intensities when the observing polarizer is parallel and perpendicular, respectively, to the direction of the polarized excitation. When motion of a chromophore is fast enough or excitation energy can hop among molecules, the anisotropy of the emission falls to zero.

MacCallum and Rudkin[19] reported that the emission of styrene/phenyl acetylene copolymer (PSPA) in PMMA was not depolarized, concluding that singlet energy migration did not exist. The presence of singlet energy migration among phenyl groups is already proved.[6,8] However, with regard to the fluorescence anisotropy experiments for polystyrene or its derivatives, clear evidence to the contrary has not been presented so far, because the monomer fluorescence intensity of polystyrene is too weak to correctly measure fluorescence polarization. The monomer fluorescence of our oligostyrenes is so strong (see Figure 3) that it can give correct information of fluorescence polarization without being interfered by scattering light.

The values of the anisotropy of oligostyrenes in PMMA are 0.07–0.09 at room temperature. They are not so small that the emission is not depolarized completely; however, they are smaller than the values at 77 K. Thus it can be ascertained that the emission of the phenyl singlet of oligostyrenes is depolarized significantly. Since the conformational changes as shown in Figure 1 are considered to be restricted in PMMA solid solution, the cause of this depolarization is assumed to be singlet energy migration among phenyl groups and/or reorientational motion of phenyl rings, which may take place in a region with free volume in PMMA films. Some motions of PMMA such as the rotation of the ester group or the rotation of the α-methyl group are allowed to occur even at room temperature, thus some motions of a chromophore in PMMA may occur by means of some motions of the host PMMA. In order to examine the effect of motions of PMMA on a guest molecule, we measured (1) the dependence of molecular size of a guest molecule on anisotropy and (2) the anisotropy of dyes in PMMA at 77 K where local motions of PMMA are perfectly stopped except vibrational motions.

The anisotropy values of biphenyl, anthracene, and pyrene, whose molecular sizes are different, are large enough that their fluorescence is determined to be polarized. Moreover, each chromophore showed nearly the same value of anisotropy both at room temperature and at 77 K where no molecular motions are possible except some vibrational motions. The results suggest that any motion of these chromophores to influence the fluorescence anisotropy is restricted in PMMA solid solution even at room temperature.

However, the anisotropy value of OB, a monomer model of oligostyrenes at 77 K, was found to be large compared with that at room temperature. This behavior is identical with that of oligostyrenes and different from that of other chromophores used in the present study. It shows that (1) the reorientational motion of the phenyl ring in PMMA is not perfectly restricted at room temperature and by means of this motion the fluorescence anisotropy decreases from 0.13 to 0.09 and (2) the singlet energy migration taking place in the oligostyrenes does not depolarize any more. Item 2 does not deny the presence of energy migration, though the efficiency of the energy migration is assumed not to be so high in this system.

One could consider the possibility of the occurrence of some phase separation of oligostyrenes during the film casting. However, the phase separation does not appear to take place in our system because (1) the anisotropies of the compounds with phenyl group at 77 K are identical with each other and (2) no trace of intermolecular excimer formation induced by the phase separation[20] is observed.

It should be noted that values of anisotropy are nearly independent of the tacticity of the isomers. It is reasonable because the observed monomer fluorescence is assumed to come from a molecule that has no excimer conformer, while a molecule having excimer conformers does not exhibit monomer fluorescence; thus it does not matter whether an isomer has meso diads or not. It coincides with the transient results that the monomer fluorescence of oligostyrenes has the same time constant as that of cumene in CH solution. Furthermore, not that no significant difference was observed among the dimers, the trimers, and the tetramers.

Conclusion

In a meso diad, the repulsion force between two phenyl rings shortens the presence time of the excimer conformer (tt); however, the conformational change from the most stable conformer (g^+t/tg^-) to tt occurs quite readily. Actually, the fluorescence spectra of oligostyrene diastereomers in PMMA films clearly showed that the population of the tt conformer in the meso diad was noticeable. The excimer in the solid solution is formed by the influx of singlet excitation energy into the excimer conformer, i.e., the tt conformer in the meso diad, which is fixed at the film-casting time. If an oligomer in PMMA that absorbs a photon does not have an excimer conformer, it exhibits only monomer fluorescence. Thus the monomer fluorescence of PS2, PS3, and PS4 in PMMA was found to behave like a monomer model compound. The emission of oligostyrenes in PMMA was depolarized significantly but not as much. Since the temperature dependences of the anisotropy of both oligostyrenes and OB coincided with each other, the depolarization of phenyl fluorescence is due to the reorientational motion of the phenyl rings, which is not perfectly restricted in PMMA solid solution at room temperature. The efficiency of the energy migration among phenyl rings is found to be not so outstanding in the present system.

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Registry No. mPS2, 75761-01-2; rPS2, 75761-00-1; mmPS3, 75801-33-1; mrPS3, 75801-32-0; rrPS3, 75761-02-3; mmmPS4, 125172-53-4; mrmPS4, 125276-04-2; mmrPS4, 125276-05-3; rrmPS4, 125276-06-4; rrrPS4, 125276-07-5.