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# Molecular weight dependence of excimer formation of poly(α-methylstyrene)

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## Summary

The molecular weight dependence of the fluorescence properties of poly(α-methylstyrene) (PMS) was investigated in cyclohexane solution. The ratio of excimer to monomer fluorescence intensity increases with increasing degree of polymerization up to ~ 50 after which the plateau value does not change. This molecular weight dependence of the excimer formation appears to be related to that of the local motion of PMS in fluid solution.

## Introduction

Excimer fluorescence is a powerful tool for monitoring molecular motions and ordered structures of macromolecules both in fluid and solid solutions. An intramolecular excimer in vinyl-type polymer systems is formed between adjacent side-chain chromophores and its formation needs two important processes: one is the formation of the excimer conformations (tt in meso diad; $g^-t/tg^-$ in racemo diad) by local motion such as a crankshaft transition, and the other is the influx of excitation energy into the preformed excimer conformation by singlet energy migration (1-3). In low molecular weight region, the formation of the excimer conformation is the rate-determining process for the excimer formation (4), thus we have measured directly the local motion of atactic and diastereomeric oligostyrenes in fluid solution by using the transient measurements of the excimer fluorescence (4-10). However, the detail of the excimer formation process is still not clear in macromolecules with higher molecular weight.

The molecular weight dependence of fluorescence measurements should give important information about polymer photophysics. Each chromophore attached to a polymer molecule is assumed to be in a similar environment independent of the molecular weight. Thus the variation of molecular weight should provide information about excimer formation process of single chain without introducing a new parameter. However, normally this information is difficult to obtain since one needs a series of samples with a variety of chain lengths, each with narrow molecular weight distribution. Thus although the data should be accumulated on the molecular weight dependence of excimer formation, relatively little work has appeared so far: polystyrene (4, 11-15), poly(1-vinylnaphthalene) (16), poly(2-vinylnaphthalene) (17-19), poly(1-naphthyl methacrylate)(20), poly(2-isopropenylnaphthalene) (21), and poly(N-carbazole) (22). In this paper we show the molecular weight dependence of excimer formation of poly(α-methylstyrene) (PMS) in order to clarify the formation process involving singlet energy migration.

## Experimental

PMS with symmetrical pentyl end groups were prepared by living anionic polymerization of α-methylstyrene in tetrahydrofuran (THF) at -78 °C initiated by n-butyllithium and terminated by 1-bromopentane, following to the way of Fujimoto et al. (23). The obtained polymers were purified by repeated dissolution and precipitation with THF and methanol, respectively.

Molecular weight and molecular weight distribution of PMS was measured on a Toyo Soda HLC-802 UR gel permeation chromatograph (GPC) and/or on a Varian 5020 high pressure liquid chromatograph with a Dupont PSM Bimodal II column pair with toluene as the eluting solvent. Polystyrene (PS) standards were used to determine the calibration curve of molecular weight versus elution volume. A universal molecular weight (M) of PMS can be calculated by the following equations using the intrinsic viscosity η (24).

$$\eta_{PS} M_{PS} = \eta_{PMS} M_{PMS} \quad \text{(at the same GPC elution volume)} \tag{1}$$

$$\eta = KM^{\alpha} \tag{2}$$

where K and α are constants characteristic of the polymer solvent system. The values of K and α used were obtained by averaging several reference values(25): PMS, $K = 7.44 \times 10^{-3}$ ml/g and a = 0.74 in toluene at 25 °C; PS, $K = 8.76 \times 10^{-3}$ ml/g and a = 0.75 in toluene at 25 °C. Table I lists the properties of the polymer samples used in the present study. The degree of polymerization, DP, was derived from its universal molecular weight (DP = M/118).

Table I Properties of the Polymer Samples

| Samples | $M_w$ | $M_w/M_n$ | DP |
|---|---|---|---|
| PMS11 | $1.31 \times 10^3$ | 1.10 | 11 |
| PMS20 | $2.33 \times 10^3$ | 1.19 | 20 |
| PMS29 | $3.43 \times 10^3$ | 1.27 | 29 |
| PMS39 | $4.55 \times 10^3$ | 1.63 | 39 |
| PMS82 | $9.68 \times 10^3$ | 1.64 | 82 |
| PMS140 | $1.64 \times 10^4$ | 1.66 | 140 |

Fluorescence spectra and fluorescence excitation spectra were measured on a Hitachi F-3000 spectrofluorometer. Fluorescence measurements were carried out in aerated luminasol cyclohexane (CH) supplied by Wako Co. and used without further purification. The excitation wavelength was chosen to be 250 nm. The optical density of the sample solutions at 250 nm was kept to be less than 0.06.

## Results and Discussion

Figure 1 shows the corrected fluorescence spectra of PMS29 in CH at room temperature. 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 spectrum. The ratios of excimer to monomer fluorescence intensity ($I_E/I_M$) reported in this paper were those of the intensity at the excimer peak to that at the

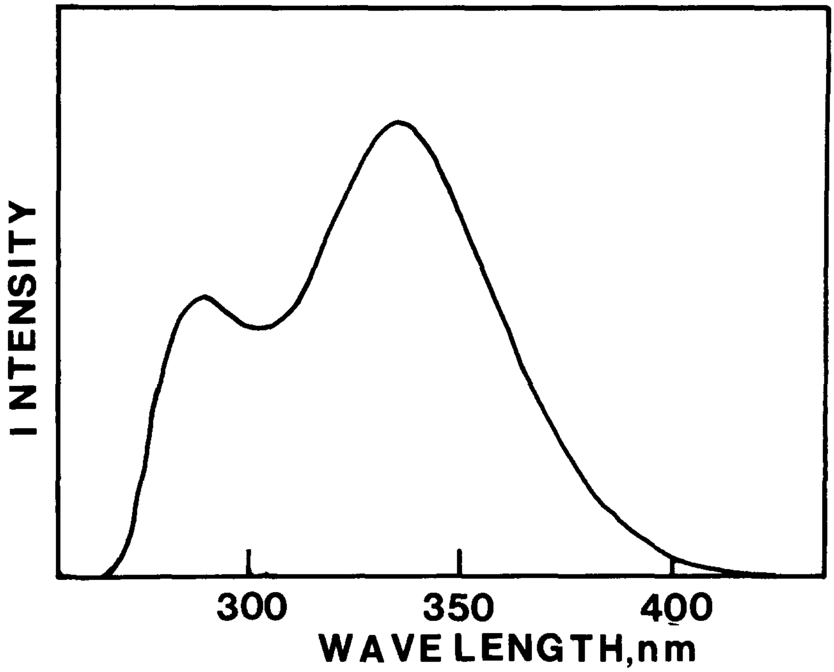

Figure 1. Fluorescence spectrum of PMS29 in aerated CH solution (excitation wavelength, 250 nm).

monomer peak. This rough treatment is after Torkelson et al. (13). Here $I_E/I_M$ means the efficiency of excimer formation. Figure 2 shows the dependence of $I_E/I_M$ of PMS on the degree of polymerization. The values of $I_E/I_M$ show an increase with molecular weight up to DP = ~ 50 after which the plateau value does not change.

We discuss the molecular origin of the molecular weight dependence of the excimer formation.

First it is possible to assume that this dependence is induced by the presence of a random hopping process of singlet energy migration among the phenyl groups. Since the possibility of formation of excimer conformation in a polymer molecule is expected to be proportional to the number of monomer units and the excitation energy could migrate into this excimer conformation, the efficiency of the excimer formation should increase in proportion to the degree of polymerization. However, the number of phenyl rings covered by the energy migration should be limited, thus the efficiency is assumed to be independent of molecular weight above a degree of polymerization. If this explanation is valid, it follows that the number of phenyl rings covered by the energy migration is about 50 monomer units in the case of PMS.

By the way we have already presented in the case of atactic oligostyrenes that the number of the phenyl rings covered by the singlet energy migration is seven or eight by measuring the emission decay curves using a picosecond pulse radiolysis technique (4). Oligostyrenes are assumed to be rod-like, thus the energy migration would occur between the adjacent phenyl rings in the low

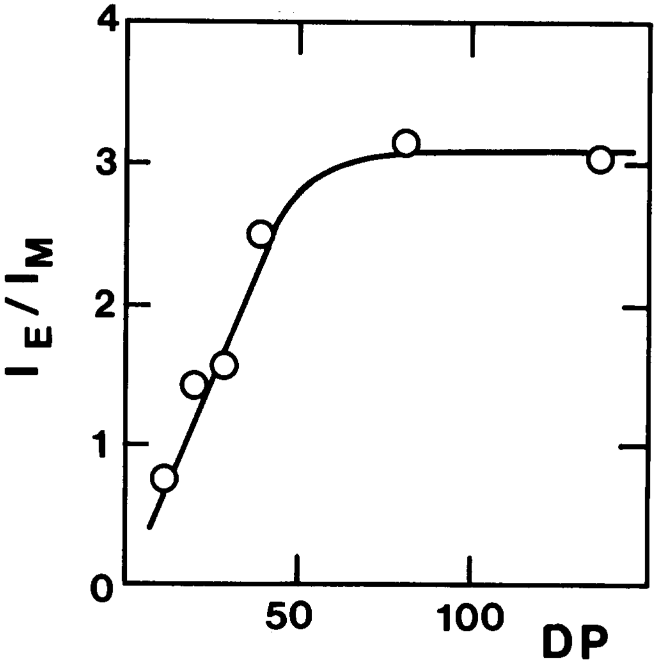

Figure 2. The ratio of excimer to monomer fluorescence ($I_E/I_M$) of PMS in CH versus the degree of polymerization.

molecular weight region. On the other hand it is possible in the higher molecular weight region that the energy migration takes place between three-dimensional non-adjacent phenyl rings. However since the dramatic increase of the efficiency could not be anticipated, it is not so likely that the excitation energy can migrate among 50 monomer units of PMS during the lifetime of the excitation.

Another possible explanation is that this dependence is related to the molecular weight dependence of the local motion of PMS. Lauprêtre et al. (26) reported the molecular weight dependence of $^{13}C$ spin-lattice relaxation times of PMS in $CDCl_3$ at 30°C. Although they measured only 5 samples ($M_w$ = 2.3 x $10^3$, 3.4 x $10^3$, 1.5 x $10^4$, 5.0 x $10^4$, and 5.0 x $10^5$), all the relaxation times but of the methyl carbon and of the main-chain methylene carbon depends on molecular weight below 1.5 x $10^4$, but is constant above it. It demonstrates that the molecular weight dependence of two different physical measurements for PMS solution is almost identical with each other and that there exists a mode of molecular motion that depends on molecular weight below $M_w$ = 1 x $10^4$. Accordingly it is more likely that the molecular weight dependence of the excimer formation of PMS is mainly due to that of the local motion of PMS.

In any event the accumulation of the data on the molecular weight dependence of excimer formation is quite necessary in order to clarify the detail of the excimer formation process in macromolecules with higher molecular weight. From this standpoint, we present the molecular weight dependence of excimer formation of

PMS in this paper.

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