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Rates for intramolecular excimer formation of poly(α-methylstyrene) measured by using picosecond pulse radiolysis

Hideyuki Itagaki[1],*, Masakazu Washio[2], and Seiichi Tagawa[3]

[1]Department of Chemistry, Faculty of Education, Shizuoka University 836 Ohya, Shizuoka 422, Japan
[2]Sumitomo Heavy Industries, 63-30 Yuhigaoka, Hiratsuka 254, Japan
[3]Research Center for Nuclear Science and Technology, University of Tokyo, Tokai-mura, Ibaraki 319-11, Japan

Summary

The rate constants for intramolecular excimer formation, k_{DM}, of poly(α-methylstyrene) with different molecular weight were determined by using picosecond pulse radiolysis. Values of k_{DM} for poly(α-methylstyrene) are a little smaller than those for polystyrene with nearly same molecular weight. It appears to be mainly due to steric hindrance by methyl substituent of main chain.

Introduction

We have studied intramolecular excimer formation of atactic polystyrenes (1), diastereoisomers of styrene dimers (2,3), styrene trimers (4,5), and styrene tetramers (6) by using picosecond pulse radiolysis in order to observe dynamically the local motions of polystyrenes in fluid solution. All through these studies, we could conclude the followings: (i) The excimer in oligostyrenes (or polystyrene) is formed mainly in meso diad. (ii) There definitely exists singlet energy migration in styrene trimer and tetramer systems. (iii) All the side-chain phenyl groups do not rotate independently around the carbon-carbon bonds of the backbone chain, but their rotation involves a cooperative motion of backbone chain bonds such as a crankshaft transition (7-10) or a three-bond jump motion (11).

We believe that the accumulation of the quantitative data on intramolecular excimer formation in various polymer systems is required for the clarification of the detail of both the excimer formation process and local molecular motion in macromolecules with higher molecular weight. Poly(α-methylstyrene) (PMS) has a similar structure to polystyrene but its main chain appears to be more stiff due to the methyl substituent. The comparison of rates for excimer formation between polystyrene and PMS would give information on local molecular motion of side-chain chromophores around the main polymer chain. We have already reported that the molecular weight dependence of PMS on the ratio of excimer to monomer fluorescence intensity using photostationary measurements and that it increases with increasing degree of polymerization up to ca. 50 after which the plateau value does not change (12). The present paper describes the transient profiles of PMS with a variety of chain lengths in cyclohexane solution by using picosecond pulse radiolysis.

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*To whom offprint requests should be sent

Table I Properties of the Polymer Samples

samples	M_w	M_w/M_n	DP
PMS140	1.64×10^4	1.66	140
PMS 82	9.68×10^3	1.64	82
PMS 39	4.55×10^3	1.63	39
PMS 29	3.43×10^3	1.27	29
PMS 20	2.33×10^3	1.19	20
PMS 11	1.31×10^3	1.10	11

Experimental

The preparation of PMS's with symmetrical pentyl end groups were reported already (12). The properties of the PMS samples used for the measurements were listed in Table I. The degree of polymerization, DP, was derived from its universal molecular weight, M_w ($DP=M_w/118$).

Fluorescence 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 (1,13,14). The emission in the longer time range (above 10 ns as the full time scale) was measured at 293K by using a photomultiplier [HTV 1194UX(UV)] with a sampling oscilloscope (Tektronix 7704A) through an interference filter of 280-, 287- (monomeric singlet), or 340-nm (excimer). The fluorescence decay curve in the shorter time range was measured through the same interference filters as above method 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 (6.4 ns as the full time scale; channel width = 25 ps). We analyzed fluorescence decay curves by the deconvolution method after O'Connor and Phillips (15) using the emission decay curve of water as an exciting pulse profile. We used the Durbin-Watson factor (DW) (16,17) to assess the validity of the trial fitting function. DW is calculated from

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

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 calculation value corresponding to the time channel i, and N is the number of experimental points. For the best fit, the value of DW approaches 2.0.

Transient fluorescence measurements were carried out in luminasol cyclohexane supplied by Wako. 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 about 1mM as the base molar concentration of phenyl group, while those used for the photostationary measurements were about 0.2mM.

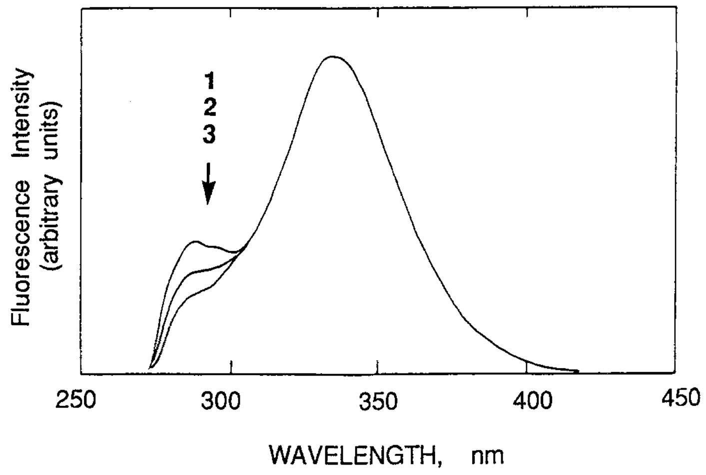


Figure 1
Fluorescence spectrum of PMS29 (1), PMS39 (2), and PMS140 (3) in degassed cyclohexane solution (excitation wavelength, 259 nm). The spectra are normalized at excimer peak.

Results and Discussion

Figure 1 shows the corrected fluorescence spectra of PMS39 in degassed cyclohexane solution. The peak near 285- and 330-nm have been assigned to phenyl monomer singlet and excimer emission, respectively.

We measured decay curves of both monomer and excimer fluorescence by means of picosecond pulse radiolysis. Although there should exist a rise component in transient profile of excimer fluorescence, it is very difficult to obtain the exact rise curve with a time constant shorter than 2 ns by removing the Cherenkov light. Thus we did not examine the initial rise of excimer fluorescence and determined the decay functions by excluding several initial channels. The decay curves at 340 nm of all PMS samples except PMS11 were found to be fitted very well to a single exponential function with a time constant of 11 ns (Table II). It means that the excimer of higher molecular weight PMS dissociates very little (or not at all) at room temperature, because all the PMS with a DP being larger than 20 have the same value of excimer lifetime, in spite of their monomer lifetimes being different from one another (see Scheme I). The longer fluorescence lifetime of PMS11 at 340 nm (15 ns) would be due to the dissociation process of excimer. Since oligostyrenes do not show the excimer dissociation at all (1-6), this dissociation is assumed to be induced by higher energy barrier of PMS main chain.

Table II Transient Results of PMS

samples	τ_D (ns)	DW	τ_M (ns)	DW	k_{DM} ($10^7 s^{-1}$)
PMS 140	10 ± 1	1.61	1.1 ± 0.1	1.64	87
PMS 82	10 ± 1	1.54	1.3 ± 0.3	1.45	73
PMS 39	11 ± 1	1.34	1.6 ± 0.3	2.09	59
PMS 29	11 ± 1	1.49	1.7 ± 0.3	1.74	55
PMS 20	10 ± 1	1.59	2.6 ± 0.3	1.37	35
PMS 11	15 ± 1	1.22	5.4 ± 0.3	1.91	8.2

With regard to decay profiles of fluorescence at 280- and 287-nm, they are fitted very well to either a single exponential with a short time constant (1-5 ns) or sum of dual exponentials with time constants of 1-5 ns and 11 ns. Since the component of 11 ns should be due to the overlap of excimer fluorescence in this wavelength region, it is concluded that there is one decay component for monomer fluorescence of all the PMS samples in cyclohexane. Table II lists time constants of both monomer and excimer fluorescence together with each best DW values.

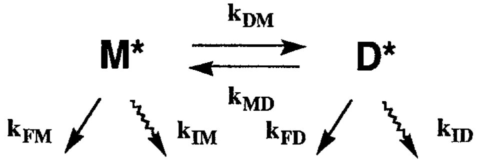
The transient results as shown above indicate that the kinetics of excimer formation in PMS system obeys to the conventional model shown in scheme I. In the case of PMS with DP≥20, the lifetime of monomer fluorescence can be described as eq 1, since excimer dissociation can be neglected.

$$\tau_M = (k_{FM} + k_{IM} + k_{DM})^{-1} \qquad (1)$$

Therefore the values of k_{DM} can be calculated by substituting the values of k_{FM} and k_{IM} for cumene in cyclohexane ($k_{FM} + k_{IM} = 3.7 \times 10^7\ s^{-1}$) into eq 1. On the other hand, if excimer dissociation cannot be neglected, two time constants should be described as follows.

$$\tau_M, \tau_D = \frac{1}{2}[X + Y \pm \{(Y - X)^2 + 4k_{DM}k_{MD}\}^{1/2}] \qquad (2)$$

where $X = k_{FM} + k_{IM} + k_{DM}$ and $Y = k_{FD} + k_{ID} + k_{MD}$. In the case of PMS11, k_{DM} and k_{MD} were calculated to be $8.2 \times 10^7\ s^{-1}$ and $4.2 \times 10^7\ s^{-1}$, respectively, from eq 2 by using the next values; $k_{FM} + k_{IM} = 3.7 \times 10^7\ s^{-1}$ (cumene in cyclohexane) and $k_{FD} + k_{ID} = 9.1 \times 10^7\ s^{-1}$ (average value of excimer of PMS with DP≥20 in cyclohexane). The calculated values of k_{DM} are summarized in Table II.



Scheme I k_{FM} and k_{IM} = rate constants for radiative and for nonradiative deactivation from excited phenyl monomer; k_{FD} and k_{ID} = rate constants for radiative and for nonradiative deactivation from excimer; k_{DM} and k_{MD} = rate constant for excimer formation and for excimer dissociation.

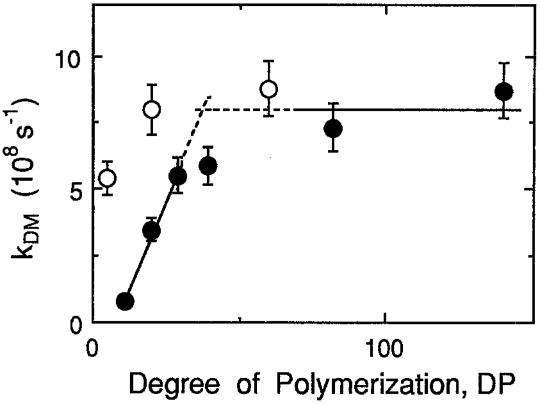


Figure 2
Molecular weight dependence of k_{DM} of PMS in cyclohexane at room temperature together with some k_{DM}'s of polystyrene.

Figure 2 shows the dependence of k_{DM} on the degree of polymerization together with k_{DM} of some polystyrene samples in cyclohexane (1). The results can be summarized as follows: (i) The values of k_{DM} obtained for PMS increases very much with molecular weight up to DP=50 after which the molecular weight dependence is not so large. (ii) The value of k_{DM} for PMS is smaller than that for polystyrene with the nearly same molecular weight. (iii) The difference of k_{DM} between PMS and polystyrene is more apparent when molecular weight is small, however, it is not so large when molecular weight is higher.

The result (i) obtained by this transient measurements precisely agrees with the photostationary results (1). The result (ii) suggests that the local motion of side-chain phenyl ring around the main chain of PMS is more restricted than that of polystyrene mainly due to the steric hindrance induced by the introduction of methyl group into the main chain. The existence of higher steric effect would be supported by the fact that the time constant of 15 ns, which is due to dissociation of excimer, is observed in phenyl fluorescence decay of PMS11, although polystyrene and PMS with higher molecular weight does not show excimer dissociation at all at room temperature.

It is not easy to clearly explain the reason of the result (iii). We have already shown that the phenyl fluorescence of diastereomeric oligostyrenes decays dual exponentially with time constants of 0.5 and a few nanoseconds, in addition to the long lifetime component due to the overlapping of excimer fluorescence (2-6), suggesting that there exist two different relaxation processes of local motion in nanosecond time range and that one is definitely due to a cooperative motion of back bone chain bonds. Thus there is a possibility that some phenyl groups could rotate independently around the carbon-carbon bonds of the backbone. Since this rotation strongly depends on the barrier energy between conformers, in the lower molecular weight region where independent rotation could be possible, excimer formation would be influenced by the stiffness of PMS main chain in comparison with polystyrene. However local motion of PMS main chain includes a cooperative motion that does not differ very much from polystyrene and this cooperative motion appears to become more important for higher molecular weight polymers. Therefore the difference of k_{DM} value between PMS and polystyrene is explained to decrease when molecular weight increases.

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