the Green function is written as (cf. eq 20b and 22)

$$g_K{}^{\mu}(\xi,\xi';\tau) = \sum_p (1/N_p)\psi_p(\mu,\xi)\psi_p(\mu,\xi')e^{-\lambda_p\Theta\tau}$$
$$= \sum_p\sum_n\sum_l (1/N_p)A_{p,n}A_{p,l}P_n(\xi)P_l(\xi')e^{-\lambda_p\Theta\tau} \quad \text{(G12)}$$

where N_p is the normalization constant. From eq G12, we immediately have the apparently similar result to eq 24b:

$$G^1(\tau) = G_D(\tau)\sum_p\sum_n\sum_l (1/N_p)e^{-\lambda_p\Theta\tau}A_{p,n}A_{p,l}(i)^n(-i)^l b_n(k)b_l(k) \quad \text{(G13)}$$

Equation G13 is Gierke's result. His theory is mathematically equivalent to ours, because eq G10, G11, and A2 give the recurrence formula for $A_{p,n}$ which has the same form as that for $U_p(n)$ derived from substitution of eq 19b into eq 12. Both λ_p and $A_{p,n}$ can be computed one by one by use of formulas for spheroidal wave functions.[34] We computed the necessary number of λ_p and $U_p(n)$ at once by the matrix method. Gierke's theory is superior to any other theories in the sense that it can give an exact analytical expression of $G^1(\tau)$ for relatively small μ^2 values. In machine computation of $G^1(\tau)$ for large μ^2 (or $\bar{\mu}^2$) values, Gierke's method and ours will require almost the same amount of task. If subroutines for matrix calculations are available, our method provides a very simple way.

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(22) Due to this definition of **M**, all vectors and matrices appearing in the text have sizes $((N/2) + 1)$ and $((N/2) + 1)^2$, respectively. However, subscripts specifying their elements are taken to be even integers. For examples, A_4 and $B_{0,6}$ should read the 2nd element of a vector **A** and the 3rd element of the 0th line of the matrix **B**, respectively.
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Absorption Spectrum of the Triplet State and the Dynamics of Intramolecular Motion of Polystyrene

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ABSTRACT: Transient absorption spectra in the wavelength range between 220 and 900 nm have been measured in the KrF excimer laser (248 nm) photolysis of polystyrene in cyclohexane solutions. Although the absorption spectrum with the shoulder around 300–350 nm and a small tail around 400 nm had been correlated to the triplet state of polystyrene,[1] the $T_n \leftarrow T_1$ absorption spectrum of polystyrene with a single peak at 230 nm, two shoulders around 250–270 and 300–350 nm, and a small tail in the wavelength region longer than $\lambda = 400$ nm is identified clearly in the present work, in addition to the excimer absorption band at 520 nm with a lifetime of 20 ns, which had been reported previously by us.[1,2] The lifetime of the triplet state of polystyrene is 110 ns and is a clue to the internal rotation of polystyrene, because the lifetime of the triplet state of polystyrene is determined by self-quenching on the basis of intramolecular interaction between triplet- and ground-state chromophores. Comparison of the present results with literature values for internal rotation, measured by other techniques, is also presented.

Introduction

A number of papers have been published on photoinduced[3] and radiation-induced[4] reactions of polystyrene, because it is the simplest polymer with aromatic chromophores and photoinduced and radiation-induced main-chain cleavage of polystyrene is very important in

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commercial use. Recently, polystyrene derivatives, such as chloromethylated,[5,6] chlorinated,[7] and iodinated[8] polystyrene, have been used for electron, X-ray, and deep-UV resists.

To understand these reactions a detailed knowledge of the absorption spectra of reactive intermediates is required. Although a number of papers have been published on the fluorescence spectroscopy, only a few papers have been published on the absorption spectra of reactive intermediates at room temperature, such as excimers[1,2,9–11] and the charge-transfer complex of polymer repeating units with chlorine atoms,[1,9–11] in photoinduced and radiation-induced reactions of polystyrene and poly(α-methylstyrene) in solution. Very recently, absorption spectra of reactive intermediates in photoinduced[12] and radiation-induced[13] reactions of chloromethylated polystyrene have also been observed.

The fluorescence[14–18] and absorption[1,2,11,19] spectra of excited singlet states of benzene, toluene, xylene, polystyrene, and poly(α-methylstyrene) are similar, although relative fluorescence intensities of the monomer excited singlet states ($^1B_{2u}$) and the excimer states ($^1B_{1g}$) are different due to the difference of the solute concentrations and the interaction of the excited states with the ground states of benzene or phenyl groups.[2]

The lifetime of the lowest triplet state of polystyrene ($^3B_{1u}$) is expected to be determined by the intramolecular interaction between triplet- and ground-state chromophores, because the lowest triplet state of benzene ($^3B_{1u}$) is quenched by the interaction with the ground state.[20–22] Therefore, the lifetime of the triplet state should be a clue in the study of the internal motion of polystyrene.

Recently the absorption spectrum correlated to the triplet state of polystyrene and its decay curve[1] and the $T_n \leftarrow T_1$ absorption spectrum of the triplet state of benzene in the wavelength range between 220 and 850 nm[19] have been observed by us, in addition to the $S_n \leftarrow S_1$ (due to one-photon absorption)[2,17,18] and the dimer cation radical (due to two-photon ionization)[23] absorption spectra of benzene and related compounds.

The absorption spectra of the transient species in the wavelength range between 220 and 900 nm, especially the $T_n \leftarrow T_1$ absorption spectrum of polystyrene, in the 248-nm photolysis of polystyrene in cyclohexane solution and the dynamics of intramolecular motion of polystyrene are investigated in the present work.

Experimental Section

Details of the laser photolysis system have been reported elsewhere.[19] Polystyrene in cyclohexane solution in a 1 × 1 × 2 cm quartz cell was excited by a 248-nm pulse from a KrF excimer laser (Lambda Physik EGM 500). The width of the pulse was 15 ns (full width at half-maximum (FWHM)). Transient spectra were monitored point by point by using a conventional nanosecond laser photolysis method.

Polystyrene was a standard sample ($\bar{M}_w = 1.65 \times 10^4$) with a very narrow molecular weight distribution ($\bar{M}_w/\bar{M}_n < 1.06$) and was used without further purification. Cyclohexane (Merck Spectrograde) was used without further purification.

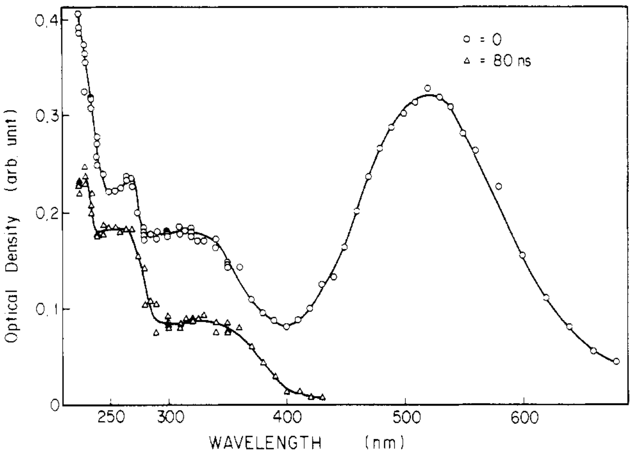

Figure 1. Transient absorption spectra observed in the 248-nm laser photolysis of 1 base mM deaerated solution of polystyrene in cyclohexane immediately (○) and at 80 ns (△) after 15-ns pulses.

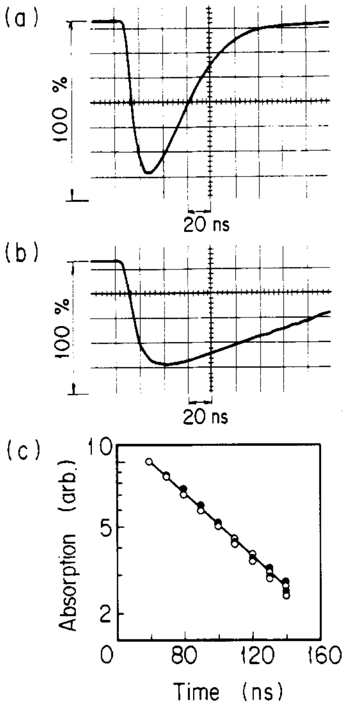

Figure 2. Decay curves of the transient absorption at 520 nm (a) and at 230 nm (b) observed in the 248-nm laser photolysis of 1 base mM deaerated solution of polystyrene in cyclohexane. The first-order plots of the decrease of the optical absorption at 230 nm (○) and at 260 nm (●) are also shown (c).

Results and Discussion

(a) $T_n \leftarrow T_1$ Absorption Spectrum. Transient absorption spectra and the decay curves at 520 and 235 nm, observed in the 248-nm laser photolysis of a 1 base mM deaerated solution of polystyrene in cyclohexane, are shown in Figures 1 and 2, respectively. The absorption spectrum observed immediately after a 15-ns laser pulse has a clear peak at 520 nm and several absorption bands in the wavelength region shorter than 400 nm. The transient species with the absorption maximum at 520 nm has an absorption spectrum and a lifetime of 20 ns, like those of the singlet excimer of polystyrene reported previously.[1,2] The absorption spectrum observed at 80 ns after excitation has a single peak at 235 nm, two shoulders around 250–270 nm and 300–350 nm, and a small tail around 420 nm. Although the lowest excited singlet state ($^1B_{2u}$) of polystyrene due to the $S_1 \leftarrow S_0$ transition of the benzene ring is excited by 248-nm light (other parts of the polystyrene molecule (CH and CH_2) do not absorb light in the range above 200 nm), the $S_n \leftarrow S_1$ absorption has not been observed by the nanosecond laser photolysis system[1,2] because of the short lifetime (about 1 ns) measured by fluorescence spectroscopy.[10,24,39] The absorption spectrum observed at 80 ns after excitation was assigned to the triplet state of polystyrene, since the absorption spectrum is very similar to that of the triplet state of benzene[19,25] and the lifetime was shortened by oxygen for the whole spectral region. The lowest excited singlet state ($^1B_{2u}$) is transformed by intersystem crossing to the triplet state ($^3B_{1u}$). The shoulder near 420 nm in the absorption spectrum presumably corresponds to the lowest allowed $T_n \leftarrow T_1$ absorption band, which was measured by a microsecond flash photolysis method.[26] But an additional shoulder around 250–270 nm was observed in our spectrum of the $T_n \leftarrow T_1$ absorption of polystyrene, compared with that of benzene.[19] Although the absorption spectrum with the shoulder around 300–350 nm and the small tail around 420 nm was previously correlated to the triplet state of polystyrene,[1] the $T_n \leftarrow T_1$ absorption spectrum of polystyrene in the wavelength region between 220 and 900 nm was identified clearly in the present work.

(b) Lifetime of the Triplet State. The lifetime of the triplet state of polystyrene is independent of the solute concentration and of the intensity of the excitation light and was determined to be 110 ns, as shown in Figure 2c. The short lifetime of the triplet state of polystyrene is believed to be due to self-quenching arising from intramolecular interaction between triplet- and ground-state chromophores of polystyrene, since the triplet state of benzene has a lifetime of 1 μs in 10^{-2} M benzene in cyclohexane and is quenched by the interaction of the triplet state with the ground state of benzene.[20-22]

Intramolecular motions of polystyrene in dilute solution have been studied by several authors using different measuring techniques.[27-39] However, they are generally summarized as consisting of two modes of molecular motion.[37] The faster one (the local segmental motion of the chain) is 0.5–1 ns and the slower one (arising from slower modes of the chain involving about 20 monomer units) is 20 ns at room temperature. The 7-ns time for the formation of the excimer conformation, the basis of picosecond pulse radiolysis data, was correlated to the former motion, but was assumed to be required for the several steps of this motion necessary to attain the excimer conformation after random walk sampling of several conformations.[38]

The fact that the lifetime of the triplet state of polystyrene is longer than the formation time of the excimer conformation may be due to the interaction range between triplet- and ground-state chromophores being shorter than the interaction range between excited singlet- and ground-state chromophores. The lifetime of 110 ns of the triplet state of polystyrene may be correlated to the slower mode of intramolecular motions, which assume the conformation for self-quenching of the triplet state.

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