Photoisomerization of Spirobenzopyran in Polystyrene Film

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ABSTRACT: The photoisomerization mechanism of 1,3,3-trimethylindolino-6′-nitrospirobenzopyran in a polystyrene film was studied by means of a transient absorption measurement system with a pulsed laser and a streak camera. The results in polystyrene were compared with those in toluene. The excited triplet state of the cisoid open form ($^3X^*$) was found in polystyrene at 440 nm. The slow isomerization process via $^3X^*$ was also found in polystyrene in addition to the fast process via excited singlet state $^1X^*$. These were similar to the case of degassed toluene. Microviscosity environments produced a different effect in the process having a conformational change from the cisoid open form to a colored merocyanine form. The rise time of the transient absorbance of the merocyanine species was 1.2 ns, 10 times as long as that in toluene.

Introduction

Organic photochromic compounds are widely expected to offer new functional materials such as erasable photomemories[1] and photomechanical or photoresponsive devices that take advantage of polarity and geometrical changes induced by irradiation.[2–4] In particular, spiropyrans belong to the most attractive class of organic photochromic compounds due to their high photosensitivity and drastic color change. Therefore a large number of studies have been carried out concerning the photochemical and photophysical properties as well as their industrial application. This type of photoisomerization has been studied by means of laser flash photolysis[5–14] and time-resolved Raman scattering.[15,16] In these earlier works some complicated mechanisms have been proposed to explain the dynamics of the spiropyrans in solution.

Nitrospirobenzopyran (colorless form, SP) in solvents is isomerized to the ring-opened merocyanine form (MC) by UV irradiation. It was reported that a cisoid isomer (X) which was formed after rupture of the C–O bond in the benzopyran ring was present as an intermediate.[10–14] In addition, the species in the excited triplet state took part in the process considerably[5–10] and aggregates were formed.[7,10,13,14,17–19]

When the photochromic compounds (spiropyran derivatives) are applied to functional materials, they are mostly required to be treated under solid conditions such as in polymer films. There are some studies on the photoisomerization in solid matrices. The thermal decoloration in polymer[2,18–22] and the formation of J aggregates in the LB films were reported.[23] No study has yet been carried out on the primary process of photoisomerization in solid matrices. The results of thermal decoloration in solid matrices showed that the mechanism of the photoisomerization was quite different from that expected in homogeneous solution, due to the polymeric environments which consist of macroscopic and microscopic values of polarity, viscosity, and glass transition temperature. In other words, the use of spiropyrans as probes in polymer matrices can lead to a variety of useful information.[4] The study on the isomerization behavior of photochromic compounds in matrices enables us to estimate the molecular environments. The mechanism of the coloration process in solution is not always applicable to that in the solid. Therefore it is attractive to study the characteristic behavior of photoisomerization under solid conditions. Moreover, elucidation of the photoisomerization mechanism is very important for development of new functional materials.

In this study we have developed a transient absorption measurement system with a pulsed laser and a streak camera[24–26] to investigate the photoisomerization of spiropyran in polystyrene, a glassy commercial polymer. Also, the results were compared with those in toluene, which was a solution model of polystyrene.

Experimental Section

Materials. 1,3,3-Trimethylindolino-6′-nitrospirobenzopyran (SP, Tokyo Kasei) was recrystallized from hexane. Polystyrene (M_w = 120 000, Wako Chemicals) was reprecipitated with methanol. Toluene (Wako Chemicals) was purified by distillation.

Sample Preparation. A polystyrene film containing 1×10^{-4} mol/g of SP (40-μm thickness) was prepared by casting a toluene solution containing 3% polystyrene on a glass plate. The film was evacuated at room temperature for 2 days and then heated in vacuo at 50 °C for 8 h to eliminate the residual solvent. The sample in toluene (1×10^{-3} mol/dm^3) in a flow cell with a 4-mm optical path length was bubbled with oxygen or argon for 10 min.

Laser Photolysis. The block diagram for the microsecond time-resolved absorption spectrometer is shown in Figure 1. The third harmonic (355 nm, 5-ns fwhm) of a Q-switched Nd:YAG laser (Quanta-Ray, DCR3F) was used as a light source for excitation. The probe light was a xenon lamp (Hamamatsu Photonics, L2195). The change in absorbance induced by the laser was monitored with a combination of polychromator (Jobin Yvon, HR320, 300 grooves/mm grating) and a streak camera system (Hamamatsu Photonics, C1587, C3140, C3610). The streak trigger was synchronized with each light source by using a homemade timing controller. The two-dimensional streak camera system used in the present study enables us to measure not only temporal but also spectral changes in the transient absorption with a single laser shot.[24] This system permitted us to measure a wavelength range of ca. 200 nm. Therefore two spectra (400–575 nm and 510–700 nm) were chosen in order to observe the visible region.

The block diagram for the picosecond time-resolved absorption spectrometer is shown in Figure 2. The third harmonic (355 nm, 30-ps fwhm) of a mode-locked Nd:YAG laser pulse (Matsui, YGM-

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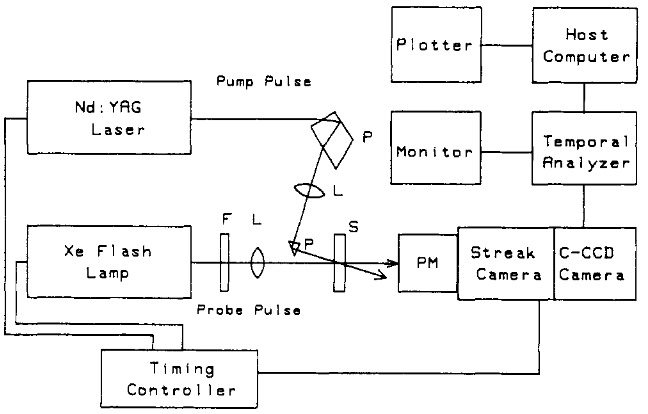

Figure 1. Block diagram of the nanosecond time-resolved absorption spectroscopy apparatus. S, sample; P, prism; L, lens; F, filter; PM, polychromator.

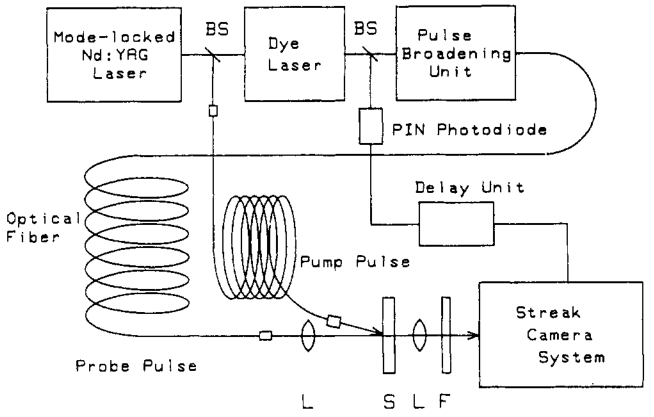

Figure 2. Block diagram of the picosecond time-resolved absorption spectroscopy apparatus. S, sample; BS, beam splitter; L, lens; F, filter.

500) was used as a light source for excitation. The picosecond UV light pulse was split by a beam splitter. One part of the pulse was used for the excitation of the sample after passing through an optical fiber, while the other part was used for the pumping of a dye laser. The output pulse of the dye laser was converted to a probe light pulse with a duration of several nanoseconds by a pulse-broadening unit. The pulse-broadening unit was comprised of two eight-branch optical fiber couplers and optical fibers with different lengths. The dye laser pulse was divided into eight by one of the fiber couplers and each beam was transmitted by optical fibers with different path lengths. Then the divided pulses were bundled into one by the other fiber coupler. Ethanol solutions of coumarin 2, coumarin 153, and rhodamine 6G (Eastman Kodak) were used for the generation of the probe lights at 440, 520, and 570 nm, respectively. A part of the dye laser output pulse was split off by a beam splitter and directed into a PIN photodiode to generate a trigger signal for the streak camera. The timing of the trigger is electrically adjusted with a delay unit. In this system the instrumental resolution time was estimated to be less than 50 ps.

It was confirmed that the kinetics values did not depend on the intensity of the light sources.

Results and Discussion

1. Microsecond Time-Resolved Spectroscopy. Transient absorption spectra following the 355-nm excitation of SP in polystyrene film are shown in Figure 3. The spectrum 0.3 μs after the excitation exhibits two characteristic absorption bands: one is located in the 500–700-nm wavelength region (band I) and is attributed to the colored form of SP (merocyanine structure, MC), while the other is located in the 430–470-nm wavelength region (band II). The intensity of band II decreases with increasing delay time, and absorbance in the 600–650-nm region (band III) increases with delay time (see Figure 3a–e). The species with absorption band III slowly relaxes to a stable photoproduct which exhibits an absorption maximum yield at 620 nm and a shoulder at 560 nm (see Figure 3f). The same characteristic spectra were found in the photolysis of SP in argon-degassed toluene (see Figure 4). On the other hand, absorption bands II and III were not observed in oxygen-saturated toluene solution (Figure 5). The spectrum 9.0 μs after the excitation was the same as it was in the steady state. This result indicates that the photoisomerization was completed within several microseconds in oxygen-saturated toluene.

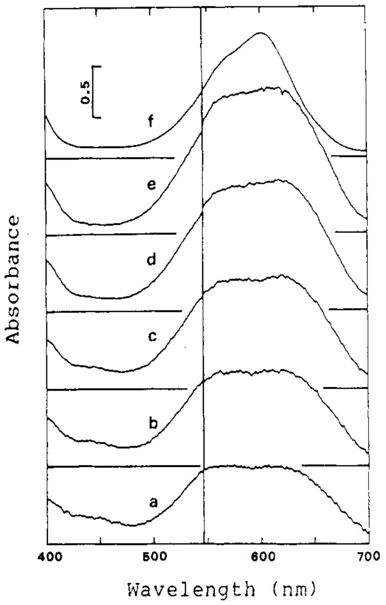

Figure 3. Time-resolved spectrum following the 355-nm excitation of SP in polystyrene (a–e) and steady-state absorption spectrum of photoproduct formed by the irradiation of SP in polystyrene at 330–380 nm (f). Delay times are (a) 0.3, (b) 0.6, (c) 1.0, (d) 3.0, and (e) 9.0 μs.

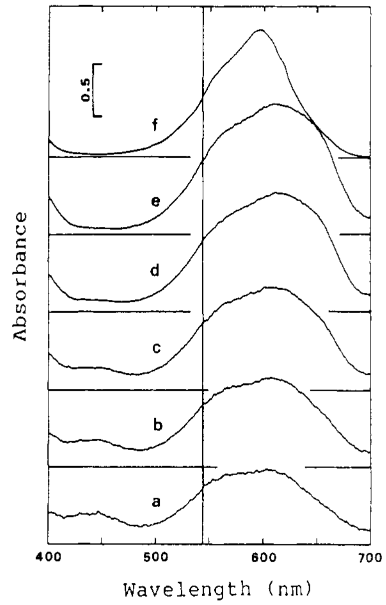

Figure 4. Time-resolved spectrum following the 355-nm excitation of SP in argon-degassed toluene (a–e) and steady-state absorption spectrum of photoproduct formed by the irradiation of SP in argon-degassed toluene at 330–380 nm (f). Delay times are (a) 0.3, (b) 0.6, (c) 1.0, (d) 3.0, and (e) 9.0 μs.

The time dependence of absorbance following the excitation of SP monitored at a specific wavelength is shown in Figure 6. It was found that the reactions in this

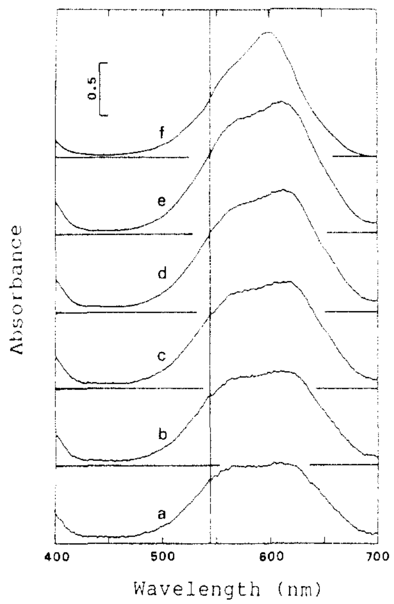

Figure 5. Time-resolved spectrum following the 355-nm excitation of SP in oxygen-saturated toluene (a–e) and steady-state absorption spectrum of photoproduct formed by the irradiation of SP in oxygen-saturated toluene at 330–380 nm (f). Delay times are (a) 0.3, (b) 0.6, (c) 1.0, (d) 3.0, and (e) 9.0 μs.

time region proceeded in the same way both in polystyrene (Figure 6A) and in argon-degassed toluene (Figure 6B). The rise time at all measured wavelengths (440, 540, and 640 nm) were less than the resolution time of our apparatus in Figure 1 (0.1 μs). In polystyrene film and argon-degassed toluene solution, the time constants for the decay of absorbance at 440 nm were measured to be 1.6–1.8 μs. In oxygen-saturated toluene (Figure 6C), the signal was weak because of the rapid decay (<0.1 μs). Therefore the absorption band at 440 nm (band II) was attributed to a species in the excited triplet state. In the photolysis of SP in oxygen-saturated toluene, the triplet species was quenched but the absorption at 540 nm due to the formation of MC was greater than that in argon-degassed toluene. These results are consistent with the behavior of SP reported in nonpolar solvents.[10] Therefore it is concluded that the triplet species found in polystyrene and toluene is not ^{3}SP* but the cisoid open form of SP in the excited triplet state (^{3}X*). At 540 nm, the absorbance curves of all samples reached a plateau after a fast rise time. The absorption at 540 nm was attributed to the colored form (MC) and MC aggregates (AG).[10,19] At 640 nm, the slow rise time component was found in addition to the initial fast rise time component (<0.1 μs) attributable to the formation of MC in polystyrene and in argon-degassed toluene (Figure 6A,B, respectively). Its rise time (1.6–1.8 μs) agreed well with the decay time at 440 nm. These results indicate that the species with absorption band III (600–650 nm) is formed from ^{3}X*. Lenoble and Becker suggested that the process leading to a species at 640 nm was a bimolecular reaction between ^{3}X* and MC instead of a ground-state molecule SP.[10] The slowly formed species with absorption at 640 nm is not MC but metastable aggregate, because the shoulder peak at 640 nm is not observed in a steady-state spectrum (Figures 3f and 4f).

Since diffusivity of colored species in a polystyrene matrix is negligible and reverse isomerization to the initial colorless form is much slower than in toluene (several minutes), we were able to obtain the characteristic absorption at 640 nm after it had fallen to the steady-state colored form. The lifetime of the metastable aggregate was ca. 0.5 s.

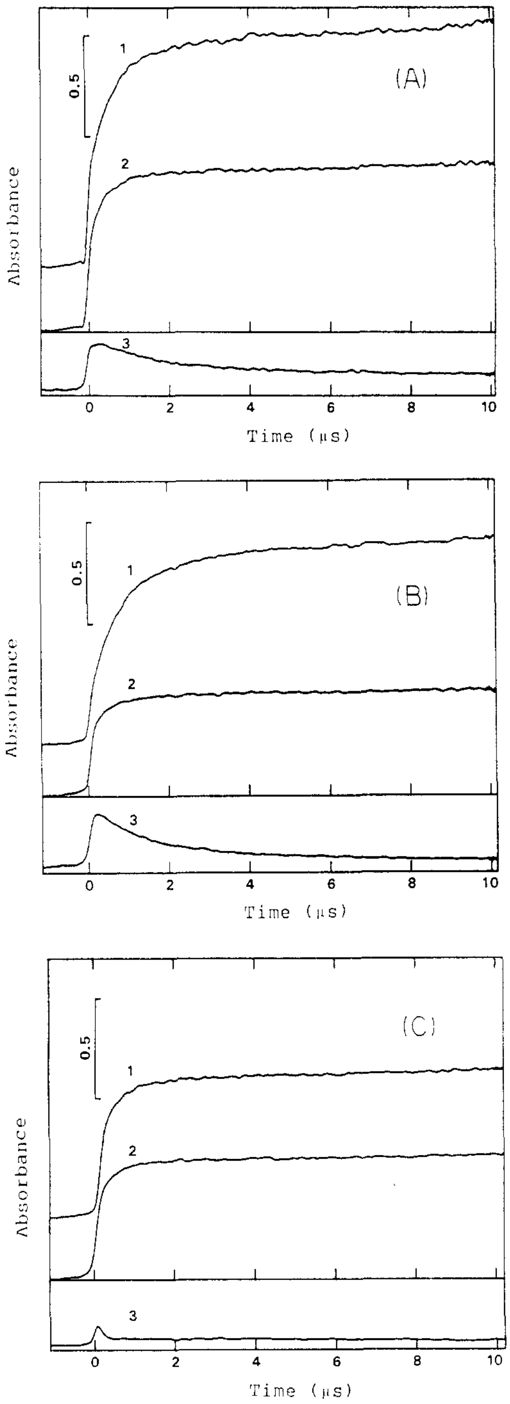

Figure 6. Time dependence of absorbance following the 355-nm excitation of SP in polystyrene (A), argon-degassed (B), and oxygen-saturated (C) toluene. Monitoring wavelengths for curves 1, 2, and 3 are 640, 540, and 440 nm, respectively.

2. Picosecond Time-Resolved Spectroscopy. The behavior of isomerization in the nanosecond time region was observed with the picosecond laser system shown in Figure 2. The kinetics of the absorbance of SP in argon-degassed toluene solution and in polystyrene film are shown in Figures 7 and 8, respectively. There were no significant differences between argon-degassed and oxygen-saturated toluene solutions in this time region. The buildup of absorbance monitored at 440 nm indicated the formation of ^{3}X* and that at 570 nm indicated either MC or aggregate of MC (AG).

The time dependence absorbance curves were considered to obey first-order kinetics. A time constant which was the reciprocal of the kinetic rate constant (k^{-1}) was

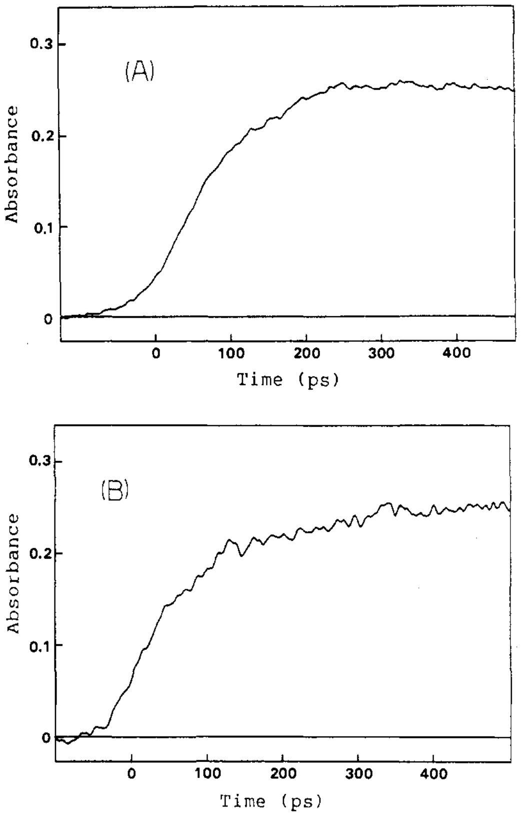

Figure 7. Time dependence of absorbance following the 355-nm excitation of SP in toluene. Monitoring wavelengths for curves A and B are 440 and 570 nm, respectively.

estimated by a best fitting procedure and a least-squares method. Both in toluene and in polystyrene, time constants for the rise were measured to be ca. 100 ps at 400 nm (see Figures 7A and 8A), and almost the same value was also measured at 570 nm in toluene (see Figure 7B). In polystyrene, an interesting absorbance profile was observed at 520 nm. A short-lived species with a lifetime of ca. 1.1 ns was observed after a fast rise (100 ps) as shown in Figure 8B. The value of the time constant at 570 nm (1.2 ns as shown in Figure 7C) agreed well with the lifetime observed at 520 nm. This result indicates that the short-lived species in the absorption at 520 nm can be attributed to a precursor of MC. In an earlier report, a transient species with an absorption band at 530 nm was attributed to the ground state of the cisoid-open form of SP (X) by Kalisky and Williams. The species X was formed within 300 ps when the SP derivative in methylcyclohexane was excited at 353 nm.[14] We also attribute the short-lived species at 520 nm to X. On the other hand, in toluene, no characteristic behavior was observed at 520 nm as shown in Figure 8B, but the absorption profile was almost the same as what was observed at 570 nm. This is mainly because the lifetime of X is much shorter than the formation time (100 ps) and because a weak signal of X cannot be detected due to the superimposing on the absorbance of MC.

3. Mechanism of Photoisomerization. The isomerization mechanism of SP can be summarized by previous studies[10-14] with some modifications as shown in Figure 9. The time constants for the rises at 440 nm are equal to those at 520 nm (100 ps) both in toluene and in polystyrene. These results show that both $^3X^*$ and X are formed from a common precursor, i.e., the cisoid open-ring species in the excited singlet state ($^1X^*$). It is concluded that the $^3X^*$ with an absorption at 440 nm is produced via $^1X^*$ (processes 1 and 4) and not via $^3SP^*$.

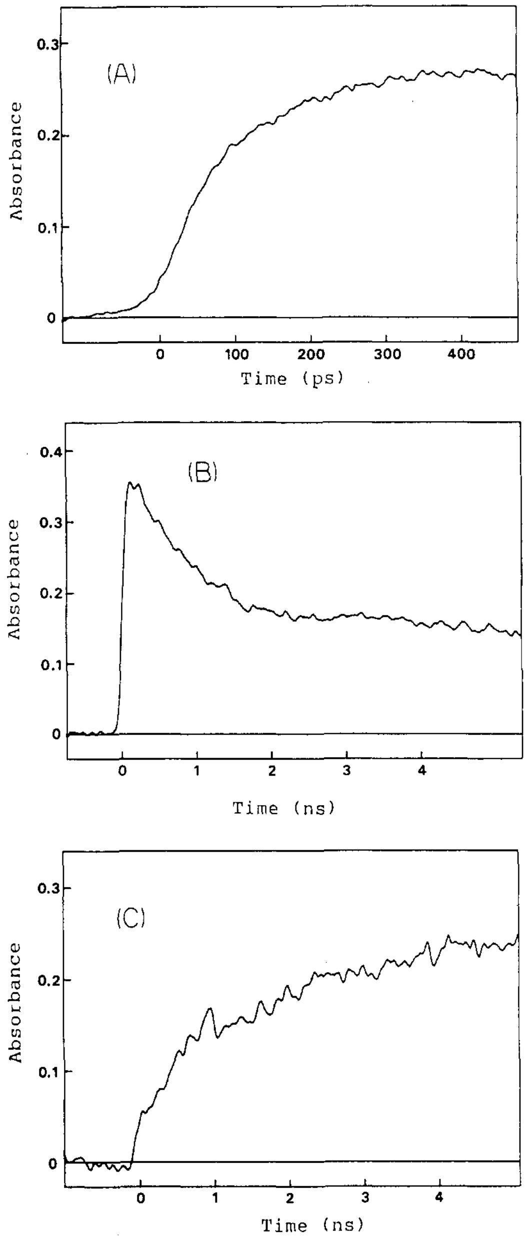

Figure 8. Time dependence of absorbance following the 355-nm excitation of SP in polystyrene. Monitoring wavelengths for curves A, B, and C are 440, 520, and 570 nm, respectively.

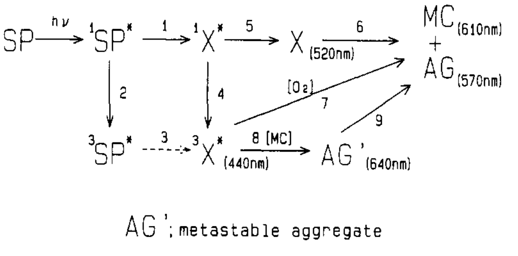

Figure 9. Photoisomerization mechanism of spirobenzopyran. SP, 1,3,3-trimethylindolino-6′-nitrospirobenzopyran: X, cisoid open-ring form; MC, merocyanine form; AG, aggregated MC; AG′, metastable aggregate.

This mechanism is supported by the recent triplet energy transfer experiments.[27]

The rise time at 570 nm was attributed to the formation of MC and MC aggregates (AG) from $^1X^*$ and X in the ground state in the nanosecond time domain (processes 1, 5, and 6). The time constants obtained for formation of MC were 1.2 ns and 110 ps in polystyrene film and in toluene solution, respectively. The latter time constant agreed well with the formation time of $^3X^*$, i.e., the lifetime of $^1X^*$. Therefore the rate constant k_6 is larger than $k_4 + k_5$ in toluene. On the other hand, the time constant for formation MC in polystyrene is ca. 10 times as slow as that in toluene. Also, the short-lived species X with a lifetime of 1.1 ns was observed. These facts indicate the rate constant k_6 is smaller than $k_4 + k_5$ in polystyrene, and the reaction from X to MC is the rate-determining process. This is because process 6 is a structural change from the cisoid open-ring species X to the trans form MC; therefore the microviscosity of the polymer film has a strong effect on process 6. These results show the effectiveness of the photochromic molecule as a probe to obtain information on the molecular environments.

The decay time measured at 440 nm corresponds to $(k_7 + k_8)^{-1}$. Process 7 was accelerated by oxygen. In the absence of oxygen in toluene, the main process of the decay of $^3X^*$ was process 8. In the case of polystyrene, the sample preparation and absorbance measurements were performed in air. However, the oxygen contained in polystyrene was below one-fiftieth of oxygen-saturated toluene, and the collision probability of SP with oxygen was low because of the low diffusivity of oxygen in polystyrene. Therefore process 7 was also suppressed. Both the decay time at 440 nm and the slow rise time component at 640 nm in polystyrene were equal to those in degassed toluene.

The kinetic parameters obtained in the present study are different from those reported by Lenoble and Becker.[10] This discrepancy may be caused by the difference in the resolution time and the time range observed. There may exist both subnanosecond and 10–20-ns phenomena.

Conclusion

Having studied the photoisomerization of SP in polystyrene film and having compared the results with those in toluene solution, we obtained the following interesting results on the photochemistry of SP: The fast isomerization process within 300 ps occurred via the excited singlet state in the cisoid open-ring species $^1X^*$ both in polystyrene and in toluene, whereas the slow isomerization via the cisoid species in the excited triplet state $^3X^*$ in polystyrene was similar to that in argon-degassed toluene. Moreover, the peculiar feature of isomerization in polystyrene was found in the conversion process from X to MC due to the restriction of molecular motion. Molecular conformational change was significantly influenced by the molecular environments.

Thus we were able to determine the complicated photochromism of SP in a polymer film. The resemblance and differences of the photochromism of SP in polystyrene and in toluene were clarified. Finally, on the basis of these conclusions, it is evident that photochromic molecules are suitable probes to detect the molecular environments.

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