Solvent Viscosity Effects on Photochromic Reactions of a Diarylethene Derivative As Revealed by Picosecond Laser Spectroscopy

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Received: March 7, 2002; In Final Form: June 4, 2002

The solvent viscosity effect on photochromic reaction processes such as cyclization and cycloreversion of a diarylethene derivative, 2-bis(2,4,5-trimethyl-3-thienyl)maleic anhydride (TMTMA), was investigated by means of steady-state spectroscopy, picosecond transient absorption, and fluorescence measurements. The cyclization reaction yields from the excited open-ring isomer decreased with an increase in solvent viscosity. Picosecond transient absorption spectroscopy revealed that the cyclization reaction took place via two pathways; very rapid reaction immediately after the excitation in competition with the relaxation to the fluorescent state and the rather slow reaction from the relaxed fluorescent state with the time constant of several hundred picoseconds. The latter slow process was strongly dependent on the solvent viscosity, whereas the former rapid process was almost independent of the viscosity. This viscosity dependence of the reaction from the fluorescent state was attributed to the solvent molecular friction to the rotation of the thienyl moieties leading to the favorable geometry for the cyclization. For the cycloreversion reaction, much smaller solvent viscosity dependence was observed and reaction time constants less than 1−2 ps were estimated by transient absorption spectroscopy. By integrating these experimental results with the potential energy surfaces predicted from theoretical investigation, the mechanism of the photochromic reaction of TMTMA was discussed.

Introduction

Photochromism is a photoinduced reversible isomerization in a chemical species between two forms. The instant property change arising from the chemical-bond reconstruction via photoexcitation has been attracting much attention[1−10] not only from the viewpoint of the fundamental chemical reaction processes but also from the viewpoint of the application to optoelectroinic devices such as rewritable optical memory and switches.

Among various photochromic molecules, diarylethenes with heterocyclic rings have been developed as a new type of thermally stable and fatigue-resistant photochromic compound. Some of these molecules have no thermochromicity even at 150 °C, the colored forms are estimated to be stable for more than 1900 years at 30 °C, and the cyclization and cycloreversion cycles can be repeated more than 10^4 times while adequate photochromic performance is maintained.[3−10] In addition, the photochromic reaction can take place even in the crystalline phase.[5,10] Direct detection of the reaction dynamics[11−17] revealed that most of these photochromic reactions take place in the time region ≤10 ps and the multiphoton-gated reaction pathway was recently found, which may lead to the realization of the nondestructive readout capability.[18]

1,2-Bis(2,4,5-trimethyl-3-thienyl)maleic anhydride (TMTMA) is one of the diarylethene derivatives fulfilling several of these excellent properties. This compound undergoes the following cyclization and cycloreversion photochromic reactions (Scheme 1). The Stokes shift between the absorption and fluorescence of the open-ring isomer of TMTMA is rather large and solvent dependent.[19] These fluorescence properties indicated some conformational rearrangement for the relaxation process in the S_1 potential surface to produce the fluorescent state with a large dipole moment. Because the photocyclization yield was found to decrease with an increase in the solvent polarity,[19] it was suggested that the twisted conformation with the intramolecular CT character was responsible for the fluorescence state, which led to the decreased chance for the cyclization. Our previous investigation by means of picosecond transient measurement,[11] however, revealed that the photocyclization reaction of TMTMA in solutions had a very rapid reaction channel with the time constant of ≤10 ps, which was much shorter than the fluorescence lifetime. To elucidate the contribution of cyclization reaction in the fluorescent state, we have investigated the solvent viscosity effect on the photochromic reaction processes. On the basis of the reaction yields of photochromic processes, picosecond transient absorption, and time-resolved fluorescent measurements, we will discuss the reaction profiles of TMTMA in the following.

Experimental Section

A picosecond laser photolysis system with a repetitive mode-locked Nd^{3+}:YAG laser was used for transient absorption

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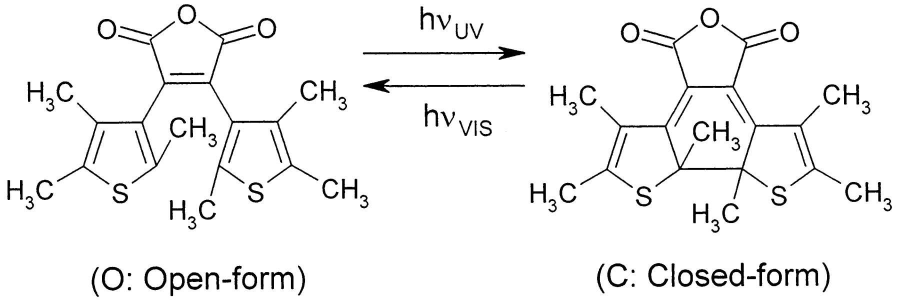
10.1021/jp0206626 CCC: $22.00

SCHEME 1



spectral measurements.[20] The third harmonic pulse (355 nm) or with 15 ps fwhm and 0.5 mJ output power or the second harmonic (532 nm) with 15 ps fwhm and 0.5−1 mJ were used for excitation. The excitation pulse is focused into a spot with a diameter of ca. 0.15 cm. Picosecond white continuum generated by focusing a fundamental pulse into a 10 cm quartz cell containing D_2O and H_2O mixture (3:1) was employed as a monitoring light. A sample cell with 1 cm length was used in the measurement with the excitation at 355 nm, whereas a 0.2 cm cell was employed for the 532 nm excitation. The repetition rate of the laser excitation was kept low (<0.2 Hz), and the solution sample was circulated. Steady-state fluorescence and absorption spectra were respectively recorded by a Hitachi F-4500 fluorometer and a Shimadzu MPS-2000 spectrophotometer.

Fluorescence decay curves were measured by single photon timing spectroscopy.[21] A second harmonics (~360 nm, pulse width ~200 fs) of a hybridly mode-locked, dispersion-compensated femtosecond dye laser (Coherent Satori 774) pumped by a continuous-wave (cw) mode-locked Nd^{3+}:YAG laser (Coherent Antares 76S) was used as an excitation source. A repetition rate of the excitation pulse was reduced to 3.8 MHz with an external pulse picker (Conoptics, Model 360-80, 25D, and 305). A microchannel-plate photomultiplier (Hamamatsu, MCP R2809U) was used as a detector, which gave an instrument response function of ~30 ps (fwhm). The fluorescence decay curves were analyzed by a nonlinear least-squares iterative convolution method based on a Marquardt algorithm.

1,2-Bis(2,4,5-trimethyl-3-thienyl)maleic anhydride (TMTMA) was synthesized and purified as reported previously.[19] Isooctane, cyclohexane, and *n*-hexane (Dotite, Spectrosol) were used as received. *cis*- and *trans*-decalins (Wako Special Guarantee) were purified by passing through a column of silica gel (Wako Wakogel 200). Samples (ca. 10^{-4} M) were deaerated by irrigating with N_2 gas. All the measurements were performed at 22 ± 2 °C.

Results and Discussion

Steady-State Absorption and Fluorescence Spectra. Figure 1a shows ground state absorption spectra of TMTMA in isooctane solution. The solid line is the spectrum of the open-ring isomer of TMTMA. The light exposure at UV light changed the color of the solution from yellow to red. The dotted line corresponds to the spectrum at the photostationary state under the exposure at 396 nm. The broad absorption in the visible region with the absorption maximum at 552 nm was safely ascribed to the closed-ring isomer because the absorption maxima and the spectral band shape were almost the same as those in *n*-hexane solution.[11,19] In addition, the cycloreversion reaction leading to the open-ring isomer took place under the light exposure in the visible region. An absorption change due to the photochromic reactions similar to that shown in Scheme 1 was also observed in other alkane solutions. The spectral band shape and their absorption maxima in these alkane solutions were almost identical with those in *n*-hexane solution, as listed in Table 1.

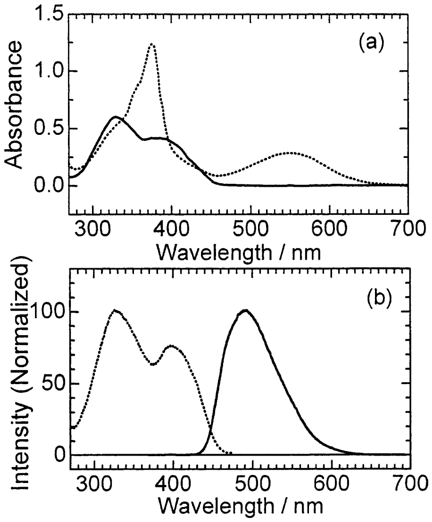


Figure 1. (a) Ground-state absorption spectra of the open-ring isomer (solid line) and the photostationary state under the exposure at 396 nm (dotted line) of TMTMA in isooctane. The closed-ring isomer of TMTMA has absorption maxima at 375 and 552 nm. (b) Fluorescence spectrum of the open-ring isomer of TMTMA in isooctane excited at 355 nm (solid line) and the fluorescence excitation spectrum (dotted line) monitored at 490 nm fluorescence.

TABLE 1: Steady-State Absorption and Fluorescence Maxima in Alkane Solutions

	absorption λ_{max}/nm		fluorescence
solvent	open-isomer	closed-isomer	λ_{max}/nm
n-hexane	331	552	490
isooctane	332	552	490
cyclohexane	333	552	491
trans-decalin	334	554	494
cis-decalin	334	552	494

Figure 1b shows the fluorescence spectrum of the open-ring isomer in isooctane solution (solid line) excited at 355 nm. The fluorescence spectral band shape and its maximum was also independent of alkane solvents, as listed in Table 1, indicating that the structure of the relaxed fluorescent state was similar among these solvents. The excitation spectrum for 490 nm fluorescence (dotted line) was confirmed to be almost the same with the absorption spectrum. No fluorescence from the closed-ring isomer was detected.

Photochromic Reaction Yields. The reaction yields of the cyclization (O to C) and cycloreversion (C to O) were obtained from the time dependence of the spectral change under the steady-state light irradiation. The light at 546 nm was employed

TABLE 2: Photochromic Reaction Yields of TMTMA in Alkane Solution at 22 °C

solvent	viscosity/cP[a]	reaction yield cyclization (O → C)	 cycloreversion (C → O)
n-hexane	0.313	0.13	0.160
isooctane	0.504	0.10	0.153
cyclohexane	0.980	0.086	0.140
trans-decalin	2.128	0.076	0.136
cis-decalin	3.381	0.072	0.131

[a] Solvent viscosity at 20 °C.[22]

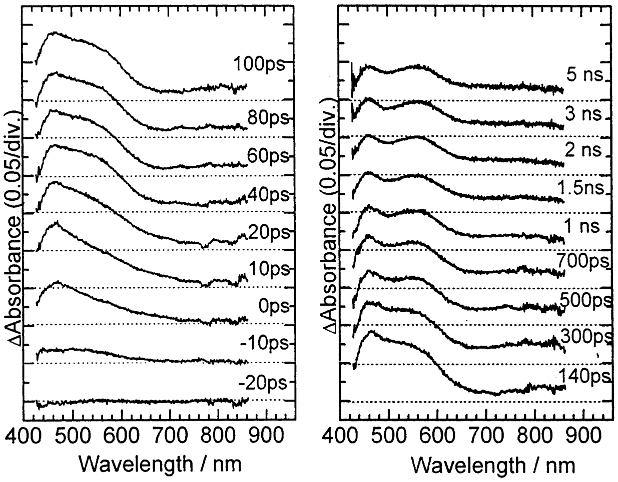


Figure 2. Transient absorption spectra of open-ring isomer TMTMA in *trans*-decalin solution, excited with a picosecond 355 nm laser pulse.

for the cycloreversion process, whereas the light at ca. 396 nm (isosbestic point) was used for the cyclization reaction. In both the measurements, the hexane solution of TMTMA was irradiated under the same condition and used as a reference.[19] The reaction yields were listed together with the solvent viscosity[22] in Table 2. Although both the cyclization and the cycloreversion yields decreased with an increase in the solvent viscosity, the cyclization reaction was more sensitive to the viscosity.

Dynamic Detection of Cyclization Reactions. Figure 2 shows time-resolved transient absorption spectra of the open-ring isomer of TMTMA in *trans*-decalin solution, excited with a picosecond 355 nm laser pulse. The time evolution of the spectra can be divided into three stages. At the first stage (immediately after the excitation), a broad absorption spectrum whose intensity increases toward the blue region appears within the time resolution of the apparatus, followed by the growth of a shoulder around 540−570 nm in the several tens of picoseconds time region. In the second stage in several hundreds of picoseconds after the excitation, the absorbance shorter than ca. 500 nm gradually decreases, together with the appearance of the two absorption peaks at 460 and 560 nm as well as the broad spectrum in the wavelength region longer than 650 nm. In the third stage (on and after ca. 1.5 ns following the excitation), almost no evolution of the spectra was observed. The absorption maximum at 560 nm observed in the time region longer than ca. 1.5 ns can be safely assigned to that of the closed-ring isomer of TMTMA, because the peak position and the spectral band shape are the same as those exhibited in Figure 1a.

First, we concentrate our discussion on the spectral evolution immediately after the excitation. For elucidating the origin of this rapid change, the difference between the spectra at 0 and 40 ps was calculated, as shown in Figure 3. Both of the spectra used for the calculation were normalized at ca. 450 nm. It is evident from Figure 3 that the peak of the difference absorption located around 560 nm and a slight decrease of the absorbance was observed at ca. 650 nm. Because the absorption maximum and the band shape of the difference spectrum in Figure 3 are very close to those of the closed-ring isomer, the rapid spectral evolution in a few tens of picoseconds time region is attributable to the photocyclization to result in the formation of the closed-ring isomer of TMTMA. The rapid appearance of the closed-ring isomer was also observed in other alkane solutions.

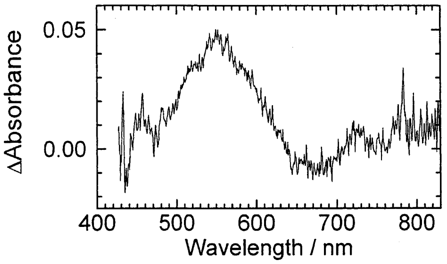


Figure 3. Difference spectrum between the transient absorption at 40 ps and that at 0 ps after the excitation of the open-ring isomer TMTMA in *trans*-decalin solution (see text).

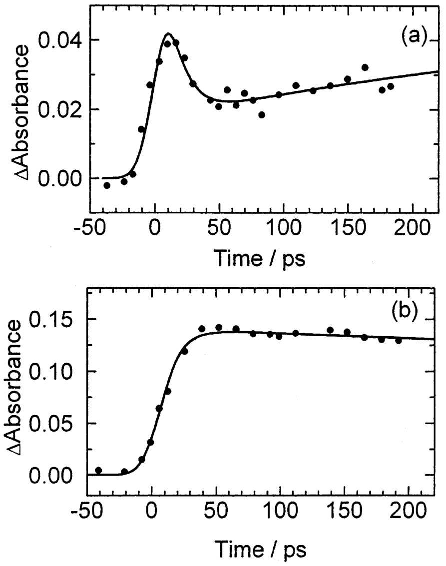


Figure 4. Time profiles of transient absorbance of open-ring isomer TMTMA in *trans*-decalin in the initial 200 ps following the excitation with a picosecond 355 nm laser pulse, monitored (a) at 675 nm and (b) at 560 nm. Solid lines are convolution curves calculated on the basis of laser pulse durations and the time constants (see text).

To estimate the time constant of the rapid photocyclization, we analyzed the time profiles of transient absorbance at 675 and 560 nm (Figure 4). In this figure, solid lines are results calculated by taking into account the durations of the excitation and monitoring laser pulses and time constants of absorbance changes. In this calculation, the time dependence of the transient absorbance was assumed to be biphasic. In the time profile at 675 nm, the instrument-limited rise of the absorbance was followed by the rapid decay, whose time constant was set to be 10 ps in the calculation. After this rapid decay, the slow increase of the absorbance was observed. This slow increase of the transient absorbance will be discussed later. On the other hand, the time profile at 560 nm shows a slower rise than the response function of the apparatus. The time constant of 10 ps was used also for the calculation of this rise behavior. The laser spectroscopy with 15 ps pulse width may make it difficult to discriminate the some relaxation processes such as vibrational cooling from the intrinsic reaction of the closed-ring isomer

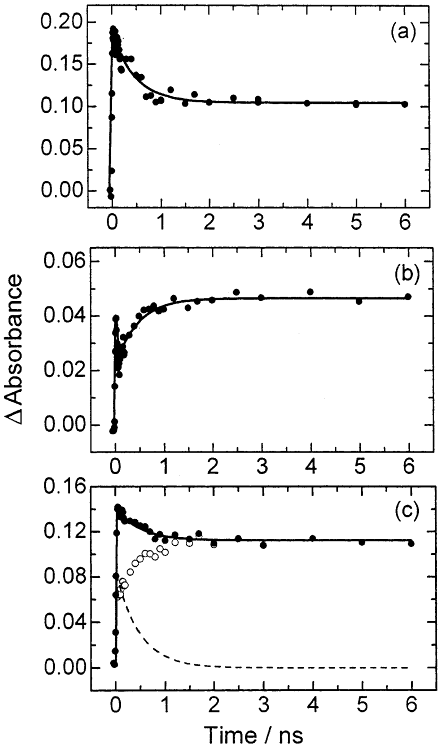


Figure 5. Time profiles of transient absorbance of open-ring isomer TMTMA in *trans*-decalin, excited with a picosecond 355 nm laser pulse, monitored (a) at 475 nm, (b) at 675 nm, and (c) at 560 nm.

formation. This result, however, indicates that there exists a rapid process with the time constant of ≤10 ps in the photocyclization pathways, as was observed in *n*-hexane solution.[11] In other alkane solutions, a similar rapid appearance of the closed-ring isomer was observed with the time constant of ≤10 ps.

Second, we discuss the evolution of the spectra in the nanosecond time region. Figure 5 shows time profiles of the transient absorbance at 475, 675, and 560 nm, respectively. The time profile at 475 nm shows the decrease in the subnanosecond time region with a time constant of 480 ps, followed by a much longer decay. The fluorescence decay profile of the open-ring isomer TMTMA in *trans*-decalin was described by more than one phasic process. On the assumption that the decay profile was biphasic, the time constants and preexponential factors were respectively obtained to be 475 ps (99%) and 3.91 ns (1%). The complex behaviors of the fluorescence decay may be due to the distribution of the conformation of TMTMA in the ground state.[19] Namely, diarylethene derivatives with five-membered heterocyclic rings have at least two conformations with the two rings in mirror symmetry (parallel conformation, **P**) and in C_2 symmetry (antiparallel conformation, **AP**). It is known that the photochemical cyclization can proceed only from the **AP** conformer. As will be shown later, the cyclization reaction takes place also in the fluorescent state. Hence, the longer component might be due to the fluorescence of the **P** conformer, although further investigation is necessary to clearly assign this component. In any event, it is worth noting here that the main component of the fluorescence lifetime agrees with the decay time constant of the transient absorbance at 475 nm within the experimental error. Hence, the absorption spectrum with its maximum around 475 nm was attributed to the fluorescent state of the open-ring isomer TMTMA.

On the other hand, the absorbance at 675 nm shows an increase in intensity with the time constant of 490 ps following the rapid decay around the time origin and reaches the plateau value at ca. 2 ns after the excitation. As was shown in Figure 1a, the closed-ring isomer of TMTMA has little absorption at 675 nm. In addition, such an increase in the absorbance with the same time constant was also observed in longer wavelength region where no absorption due to the closed-ring isomer exists. By integrating the above results with the fact that the time constant of the rise in the absorbance was identical with that of the decay of the fluorescent state, the increase of the absorbance is ascribed to the formation of other species such as the triplet state. Similar temporal behaviors were obtained also in other alkane solutions.

In the time profile at 560 nm, the decrease of the transient absorbance was observed in the subnanosecond time region as shown in Figure 5c. The time profile at 560 nm mainly involves dynamic behaviors of the fluorescent state and the closed-ring isomer. The time profile of the fluorescent state at 560 nm, A^{F}_{560}, is represented as

$$A^{\mathrm{F}}_{560} = \epsilon^{\mathrm{F}}_{560} c^{\mathrm{F}} \exp\left(\frac{-t}{\tau_{\mathrm{f}}}\right) \qquad (1)$$

Here, $\epsilon^{\mathrm{F}}_{560}$, c^{F}, and τ_{F} are respectively the extinction coefficient of the fluorescent state at 560 nm, the initial concentration of the fluorescent state, and the fluorescent lifetime. In this equation, the concentration of the transient species is integrated over the cell length. To analyze the dynamic behaviors of the closed-ring isomer, the contribution of the transient absorbance due to the fluorescent state (broken line) was subtracted on the basis of the initial value of the transient absorbance and the fluorescent lifetime. The initial value of the transient absorbance of the fluorescent state, $\epsilon^{\mathrm{F}}_{560} c^{F}$, was estimated in the following way. As was shown in Figures 2 and 3, the closed-ring isomer was produced immediately after the excitation and the transient absorption spectrum even at 40 ps comprised the contributions from the close-ring isomer and the fluorescent state. From Figure 3, the absorbance due to the closed-ring isomer at 40 ps was estimated to be 0.05. Hence, the rest of the transient absorbance at 560 nm (ca. 0.085) at 40 ps was attributed to the fluorescent state. The lifetime of the fluorescent state (475 ps) was used for the calculation. The dynamic behaviors of the transient absorbance from which the contribution from the fluorescent state was subtracted were shown as open circles in Figure 5c, where the rise of the transient absorbance was observed. In the case that the closed-ring isomer is produced also from the fluorescent state, the time profile of the closed-ring isomer at 560 nm in the subnanosecond to nanosecond time region is given by

$$A^{\mathrm{C}}_{560} = \epsilon^{\mathrm{C}}_{560} c^{\mathrm{F}} \Phi_{\mathrm{F}\rightarrow\mathrm{C}} \left[1 - \exp\left(\frac{-t}{\tau_{\mathrm{f}}}\right)\right] + \epsilon^{\mathrm{C}}_{560} c^{\mathrm{I}} \qquad (2)$$

Here, $\epsilon^{\mathrm{C}}_{560}$ and $\Phi_{\mathrm{F}\rightarrow\mathrm{C}}$ are respectively the extinction coefficient of the closed-ring isomer at 560 nm and the quantum yield of the cyclization reaction in the fluorescent state. The concentration of the closed-ring isomer formed immediately after the excitation is given as c^{I} in eq 2. Because the time profile of transient absorbance at 560 nm is represented by the summation of eqs 1 and 2 in the presence of the slow cyclization reaction channel from the fluorescent state, the decay profile of the transient absorbance can be observed in the case where the $\Phi_{\mathrm{F}\rightarrow\mathrm{C}}$ value was small. On this point, it is worth noting here that neither the rise nor the decay in the subnanosecond to nanosecond time region was observed for the dynamic behaviors of TMTMA in *n*-hexane after the excitation at 355 nm.[11] In addition, the decay behavior at 560 nm was pronounced in

TABLE 3: Fluorescence Lifetimes of the Open-Form TMTMA and Time Constants Obtained by Transient Absorption Spectroscopy

		transient absorbance		
	fluorescence at 490 nm[a] τ_f (A_i)	475 nm (decay)	675 nm (rise)	560 nm (decay)
n-hexane	355 ps (0.993) 5.77 ns (0.007)	330 ps	360 ps	*b*
isooctane	390 ps (0.997) 1.09 ns (0.003)	400 ps	380 ps	390 ps
cyclohexane	425 ps (0.997) 8.75 ns (0.003)	440 ps	400 ps	440 ps
trans-decalin	475 ps (0.990) 3.91 ns (0.01)	480 ps	450 ps	490 ps
cis-decalin	510 ps (0.996) 1.12 ns (0.004)	550 ps	530 ps	500 ps

[a] Double-exponential function, $A_1\exp(-t/\tau_1)+A_2\exp(-t/\tau_2)$, was assumed for the fluorescence decay. The longer time constant was less reliable because the time window of the measurement was not sufficiently wide to resolve it. [b] Neither decay nor rise of the absorbance was detected in *n*-hexane solution (see text).

solution with large viscosity such as *trans*-decalin and *cis*-decalin. These results indicated that the cyclization reaction took place also in the fluorescent state of the open-ring isomer in addition to the rapid process prior to the relaxation to the fluorescent state and the $\Phi_{F\to C}$ value decreased with an increase in the solvent viscosity.

The solvent viscosity effect on reaction profiles of the excited open-ring isomer of TMTMA was summarized in Table 3 where fluorescent lifetimes and the time constants obtained by the transient absorption measurements in alkane solutions were listed. In each of solutions, time constants obtained from the transient absorption spectroscopy were in agreement with the fluorescence. The time constants at 475 and 675 nm were respectively ascribed to the decay of the fluorescent state and the rise of the long-living species such as triplet state. Except for the temporal behavior in *n*-hexane, the decay behavior was observed for the time profile at 560 nm, as mentioned in the above section. Table 3 also shows that the fluorescent lifetimes as well as the time constants in transient absorbance increase with an increase in the solvent viscosity, whereas the cyclization reaction yield decreases with an increasing viscosity of the solvent as was shown in Table 2.

To more precisely elucidate this viscosity dependence, the reciprocal value of the fluorescence lifetime, $1/\tau_f$, was plotted as a function of $1/\eta$ in Figure 6, where the dependence of the cyclization reaction yield on $1/\eta$ is also shown for the comparison. Here, $1/\eta$ is the reciprocal value of the viscosity. Figure 6a shows that $1/\tau_f$ increases almost linearly with an increase in $1/\eta$ value. Such viscosity dependence of the fluorescence lifetime was reported for the excited stilbene,[23] its derivatives,[24] and cyanine dyes,[25] in which systems the isomerization accompanied with large conformational change takes place in the fluorescent state. In relation to the viscosity effect of the molecular diffusive motion and the reaction time constant, it is known that the time constant of the rotational relaxation time of the solute in solution phase scales with the solvent viscosity.[26] The simple Debye–Stokes–Einstein model predicts that the reciprocal value of the rotational relaxation time is in proportion with $k_BT/V\eta$. Here, k_B, T, V, and η are respectively the Boltzmann constant, temperature, molecular volume, and viscosity of the solvent. In analogy with this Debye–Stokes–Einstein model, it has been expected that the rate constant of these isomerization processes with large geometrical change linearly increases with an increase in $1/\eta$ value. For these systems, it was reported that the isomerization reaction rate constants actually increased with decreasing solvent viscosity but the deviation from the complete linear relation was experimentally observed between the rate constant and the $1/\eta$, which was mainly attributed to the difference between the microscopic molecular friction and the macroscopic viscosity.[23,24]

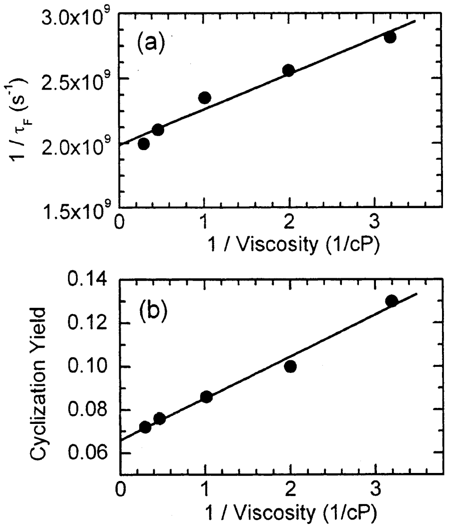


Figure 6. (a) Solvent viscosity dependence of the fluorescent lifetime of the open-ring isomer of TMTMA. (b) Solvent viscosity dependence of the photoinduced cyclization reaction yield of the open-ring isomer of TMTMA.

As briefly mentioned in the introductory section, the open-ring isomer of TMTMA has a rather large Stokes shift and is dependent on the solvent polarity. These fluorescence properties suggested some conformational rearrangement for the relaxation process in the S_1 potential surface to produce the fluorescent state with a large dipole moment. Because the photocyclization yield was found to decrease with an increase in the solvent polarity,[11,19] it was also suggested that the twisted conformation with the intramolecular CT character was responsible for the fluorescence state, which led to the decreased chance for the cyclization. Even in nonpolar alkane solutions, the Stokes shift was estimated to be more than 4800 cm^{-1} from Figure 1b, indicating that large conformational rearrangement also occurs after the excitation, even in nonpolar solution. Hence, the conformational change leading to the rather flat structure of two thienyl moieties in a plane seems a key process for the cyclization reaction in the fluorescent state. The almost linear viscosity dependences of the lifetime of the fluorescent state and the reaction yield indicate that the conformational rearrangement process takes place against the molecular friction, as observed for other photochemical processes such as isomerization with large geometrical change. To summarize the above results and discussion, it is concluded that, not only the rapid reaction channel prior to the fluorescent state formation but also the cyclization reaction takes place in the fluorescent state and the slower cyclization process in the fluorescent state was suppressed with an increase in the solvent viscosity.

To elucidate the solvent effect on this fast cyclization reaction process, transient absorption spectra at 40 ps after the excitation with an 355 nm laser pulse were plotted in Figure 7, where the absorption intensity was normalized at 465 nm. As is clear in this figure, no remarkable differences among these spectra were observed. This result indicates that the fast reaction channel was scarcely dependent on the solvent viscosity. By integrating the above spectra with the results shown in Figure 6, the intercept

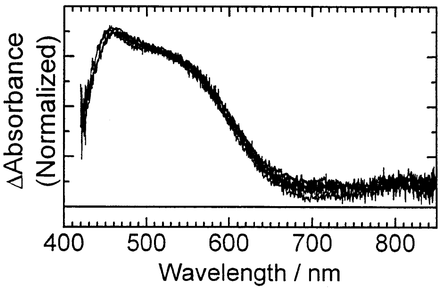


Figure 7. Transient absorption spectra of the open-ring isomer TMTMA in *n*-hexane, isooctane, cyclohexane, *trans*-decalin, and *cis*-decalin, observed at 40 ps following the excitation with a picosecond 355 nm laser pulse. These spectra were normalized at 450 nm.

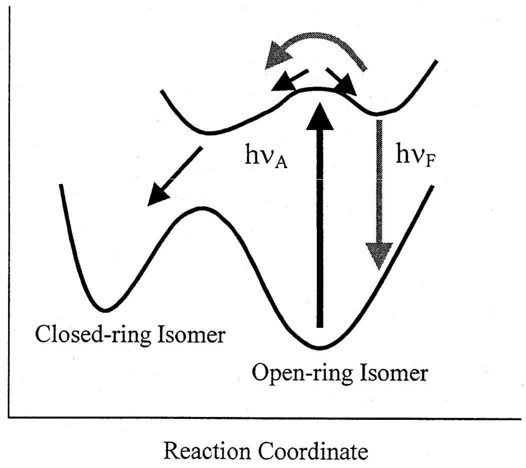


Figure 8. Schematic representation of potential profiles of TMTMA. The reaction coordinate is given as the distance between two carbon atoms that is to be connected via the cyclization reaction.

value in Figure 6b may be attributed to the contribution from the fast reaction channel in the total cyclization reaction.

On the solvent viscosity independent reaction yield in the fast reaction channel, it is worth noting here that the recent theoretical calculation[27] based on ab intio multiconfiguration self-consistent calculation predicts the excited state potential surface of diarylethene derivatives, as shown in Figure 8. In this figure, the reaction coordinate is given as the distance between two carbon atoms that is to be connected via the cyclization reaction. According to this result, the excited state potential surface has a local maximum around the position where the open-ring isomer has the minimum energy in the ground state. In addition, it was predicted that the cyclization reaction yield is strongly dependent on the position of this maximum in the excited state. By analyzing the present results with this theoretical calculation, we propose that the branching toward the cyclization and the twisted conformation on the excited potential surface is determined at the excited Franck−Condon state and this branching ratio does not depend on the solvents examined in the present work. Actually, the solvent independent absorption spectrum in the ground state supports the above idea that the potential surfaces in the ground and excited states are almost the same in these alkane solvents.

As mentioned in the introductory section, the cyclization yield of TMTMA decreased with an increase in solvent polarity.[19] Because the fluorescent state has the charge-transfer character, the energy level at the minimum position of the fluorescent state is stabilized with increasing solvent polarity, leading to a large activation barrier for the cyclization reaction from the bottom of the fluorescent state higher. On the other hand, in nonpolar solution, the energy minimum of the open-ring isomer of TMTMA in the fluorescent state is rather high and, consequently, the energy barrier is smaller than that in polar solution, which opens the cyclization reaction in the fluorescent state.

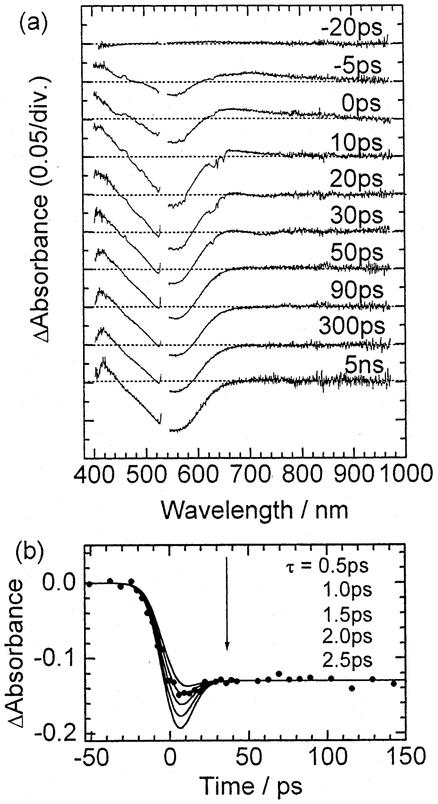


Figure 9. (a) Transient absorption spectra of the closed-ring isomer of TMTMA in *cis*-decalin solution, excited with a picosecond 532 nm laser pulse. (b) Time profile at 550 nm. Solid lines are convolution curves on the basis of the pulse widths of pump and probe pulses and time constants.

Cycloreversion Reaction. Figure 9a shows the time-resolved transient absorption spectra of the closed-ring isomer of TMTMA in *cis*-decalin solution, excited with a picosecond 532 nm laser pulse. Immediately after the excitation, the depletion around 560 nm and positive absorption around 600−750 and 400−450 nm are observed. The former negative absorption can be safely assigned to the bleaching of the closed-ring isomer. The time profile of the absorption signal at 550 nm is exhibited in Figure 9b, indicating that the slight recovery of the bleaching of the closed-ring isomer immediately after the excitation is followed by the constant value. Moreover, the positive signal around 700 nm disappeared within a few tens of picoseconds. Because the decay time constant of this positive signal was estimated to be almost identical with that of the recovery of the negative absorption around 560 nm, this signal might be assigned to the $S_n \leftarrow S_1$ absorption of the closed form. In addition, the contribution from the hot band of the closed-ring isomer in the ground state, which was produced via the internal conversion from the S_1 to S_0 state, might be involved in the positive absorption around 700 nm. By means of the picosecond transient absorption spectroscopy with the pulse duration of 15 ps, we could not quantitatively discriminate these two contributions.

In the time region on and after ca. 40 ps following the excitation, no evolution of the spectra was observed, as shown in Figure 9a. The residual absorption spectra are almost identical with the difference spectrum between the closed-ring and the open-ring isomers, as shown in Figure 1a. Solid lines in Figure 9b are the calculated curves by taking into account the pulse durations of the exciting and the monitoring lights and the quantum yield of the ring-opening reaction as listed in Table 2. The time constants for the recovery of the negative absorption are indicated in the figure. The calculated curves with time constants of $1-2$ ps reproduced the experimental results, indicating that the cycloreversion reaction took place with the time constant $\leq 1-2$ ps. Similar time profiles and ultrafast reaction with the time constant of $\leq 1-2$ ps were also observed other alkane solutions.

As was shown in Table 2, the cycloreversion reaction was also dependent on the solvent viscosity, indicating that the motion of thienyl moieties takes an important role in the cycloreversion reaction as in the cyclization reaction in the fluorescent state of the open isomer. The viscosity dependence of the cycloreversion reaction was, however, much smaller than that of the cyclization in the fluorescent state. This weak dependence of the cycloreversion process may be interpreted along with the recent investigation on the deactivation process of triphenylmethane (TPM) dyes in solution phase,[28] which undergoes ultrafast deactivation depending on the solvent viscosity, and the rotation of phenyl rings take an important role in this deactivation. From the dynamic laser spectroscopy with 30 fs time resolution, it was revealed the solvent viscosity became less effective for the faster deactivation process. This result means that the diffusive friction is less effective for the fast motion and, rather, inertial motion in the first solvation shell becomes dominant. For the present cycloreversion processes, the time constant of the excited state was estimated to be $<1-2$ ps, as shown in Figure 9. Because this time scale is comparable with or slightly shorter than the diffusive motion of the solvent, the cyclization yield was less dependent on the solvent viscosity, as was observed for the deactivation processes of TPM dyes.

Concluding Remarks. The solvent viscosity effect on the cyclization processes revealed the reaction mechanisms of the open-ring isomer of TMTMA in the excited singlet state and discriminated between the fast reaction channel immediately after the excitation and the rather slow reaction pathway in the fluorescent state. Recent theoretical calculation[27] supports the present experimental results. It was deduced that not only the relative geometries of potential surfaces around the conical intersection but also the local maximum position in the S_1 potential surface play important roles in the cyclization process. In the explanation of the fluorescence decay of the open-ring form, we mentioned the parallel (**P**) conformer, which has been reported to have no cyclization channel.[5] As suggested by the biphasic decay of the fluorescence, the **P** isomer might have a longer fluorescence lifetime. On the dynamic behaviors of the **P** isomer, we are now doing the investigation with a wider time window.

For the cycloreversion process, the reaction yield was less dependent on the solvent viscosity than that of the cyclization reaction. This was attributed to the very rapid reaction taking place in the time region shorter than the diffusive motion of the solvent.

Acknowledgment. We appreciate Dr. S. Nakamura in Mitsubishi Chemical Corp. for his valuable discussion. The present work was partly supported by the Grants-in Aid (No. 14340183 and No. 14050061) from the ministry of Education, Science, Sports, and Culture of Japan.

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