Energy Releasing and Conformational Dynamics of Stilbene Dendrimers upon Photoisomerization

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The energy-releasing process and the conformational dynamics of stilbene dendrimers (tetramethoxystilbene (generation (G) 0, G1, G2, and G4) upon photoexcitation are studied by the time-resolved transient grating method. For all dendrimers, the excited triplet (T_1) state formation was observed. From the time-resolved studies on energy and the molecular volumes changes, it is found that the conformational change completes with the decay of the T_1 state for G0−G2. However, the dynamics is slightly slower for G4, which is attributed to the conformational change of the dendron part. The molecular volume change due to the conformational rearrangement of the dendron upon the trans to cis isomerization is slightly positive (molecular expansion). The expansion is explained in terms of the creation of the void volume surrounded by the dendron side chains. Although the diffusion coefficient (D) of the trans and cis forms of G0 is almost the same, the difference becomes larger with increasing generation. This is clear evidence for the large conformational change upon isomerization. The larger D of the trans form compared with that of the cis form is explained in terms of the surface roughness of the dendrimers.

1. Introduction

Dendrimers are highly branched, monodisperse macromolecules constructed by a central core and reiterative sequences (dendron). The generation number of the dendrimer is defined by the number of branching points between the periphery and the core. The photophysics as well as photochemistry of the dendrimers have attracted considerable attention in recent years.[1−19] In particular, when a chemical reaction system was incorporated in the dendrimer system, the effect of bulky and highly congested dendron to the energetic flow and reaction scheme could be unique and the research on the effect would be motivated.

For example, dendrimers having azobenzene as a core have been synthesized and studied.[8−15] The *trans*-azobenzene dendrimers undergo an isomerization reaction upon photoexcitation. Jiang and Aida reported that the infrared photon energy absorbed as the vibrational energy in the dendron part is accumulated about five photons at the azobenzene core and enhances the cis−trans isomerization.[14] Wakabayashi et al. measured the energy-releasing process from the photoexcited state of fourth generation *para*-aryl ether dendrimers by using the fluorescence detection and thermal lens techniques and reported that about 50% of the excitation energy was not released from the para-isomer for on the order of more than a 100 ms.[16] They suggested a long-term internal energy storage in the dendron. This observation may be related with the anomalous five-photon process of the azobenzene dendrimer, which must be explained by a combination of sequential absorption and intramolecular energy storage. However, such a long-term energy storage in the dendron is very difficult to understand on the basis of conventional theories as well as accumulated experimental results in the condensed phase studied so far. The energy-releasing process and the conformational dynamics of dendrimers should be further investigated.

Recently Mizutani et al. reported the first synthesis of stilbene dendrimers: a stilbene core with a benzyl ether-type dendron (Figure 1).[17] These stilbene dendrimers exhibit rather strong fluorescence. Interestingly, the lifetime of the first (G1), second (G2), third (G3), and fourth (G4) generations of the dendrimers was almost constant ca. 9.3−9.7 ns at 23 °C.[17−19] It is now well-accepted that *trans*-stilbene without a dendron undergoes the isomerization through the excited singlet state.[20−22] The isomerization reaction of stilbene proceeds by the transition around the C═C double bond to give the perpendicular excited singlet state followed by the deactivation to the ground state to yield the cis and trans isomers in the ground state. If the trans to cis isomerization of stilbene dendrimers also takes place in the excited singlet state by the same reaction scheme as stilbene, the isomerization occurs with rotation of the bulky group within a lifetime of 10 ns, regardless of the size of the dendron. Such isomerization by C═C double-bond twisting is expected to need a large volume change. If a large volume change occurs, the isomerization rate is expected to be viscosity dependent. Contrary to this expectation, the fluorescence lifetime is reported not to depend on the viscosity.[19] This observation may suggest that the photoisomerization of the stilbene dendrimers proceeds by a volume-conserving mechanism rather than conventional 180° rotation around the C═C double bond.[17−19] However, there has been no experimental investigation on the conformational change of dendrimers upon such isomerization reaction.

In this paper, we studied the energy-releasing process and the volume change upon the photoexcitation of stilbene dendrimers in a time domain by the transient-grating (TG) technique. The TG method has a prominent character to detect

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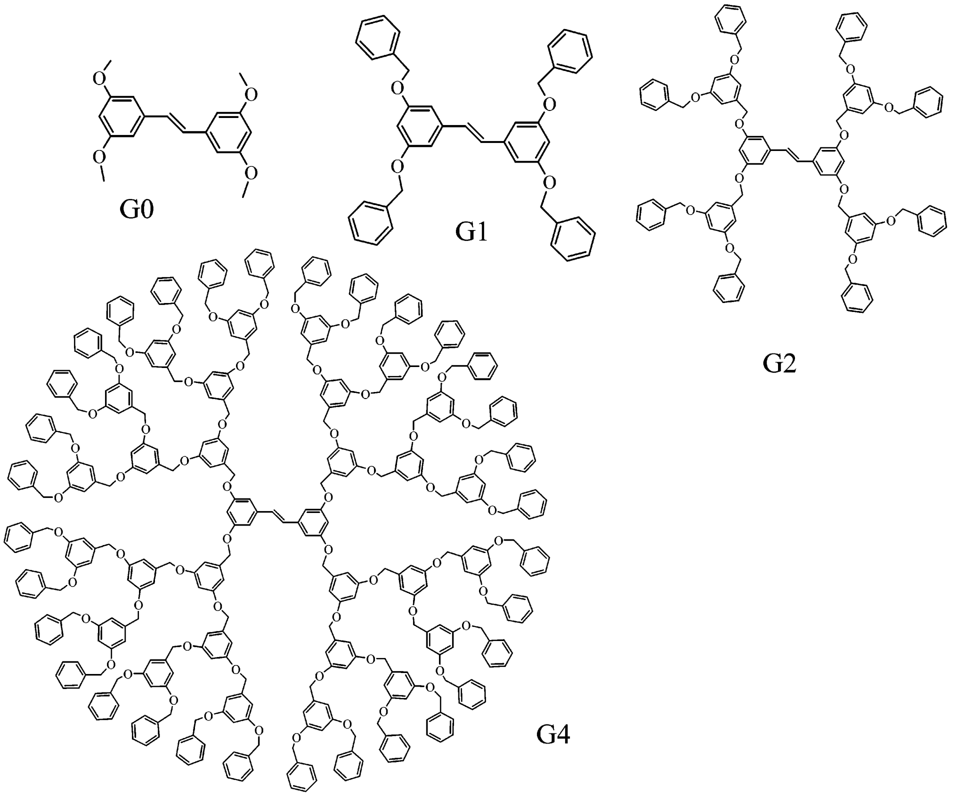


Figure 1. Molecular structures of the stilbene dendrimers we studied.

thermal energy, molecule volume change, and a molecular diffusion process with high sensitivity, and this characteristic feature enables us to study various photophysical and photochemical processes from viewpoints of the nonradiative transition, the conformational change, or molecular dynamics.[23−35] This unique character together with a high sensitivity and a high time resolution makes the TG method a very powerful tool for studying chemical reactions.[26,27] We have recently applied this technique to protein reaction dynamics and observed conformational change without accompanying absorption change.[28−35] The photoisomerization group (chromophore) attached to a bulky group of the dendrimers can be a model of photosensitive biological proteins such as the rohodopsin. We applied this TG technique to the stilbene dendrimers and focused our attention mostly on the energy and conformation change of the bulky dendron upon the isomerization reaction. Previously, it has been already reported that all compounds exhibit similar absorption spectra at 300−360 nm with the absorption maximum at 310 nm due to the stilbene core. The absorption of the benzyl ether group of the dendron at 280 nm is almost the same between cis and trans isomers and does not influence the electronic properties of the stilbene core. All compounds also exhibit a very similar fluorescence spectral peak at 380 nm. Therefore, we can study the effect of the dendron by comparing the properties of G4 with the other smaller generations (G0, G1, and G2). We found a slow dynamics with about 50 ns lifetime, and this dynamics is attributed to the relaxation from the lowest excited triplet (T_1) state to the ground state. For G4, we observed a slightly slower dynamics, which may be attributed to the conformational change of the dendron part after the trans−cis isomerization of the stilbene core. The conformational change of the dendron induces the molecular volume expansion, although the volume change is very small compared with the molecular volume. We also conclude that an internal energy storage and an energy storage due to the steric hindrance of the bulky dendron group are not large. Interestingly, a large conformational change in G4 is suggested by the large difference in D between the trans and cis forms.

2. Experimental Section

The experimental setup for the TG experiment was similar to that reported previously.[28−35] Briefly, a beam of an excimar laser (308 nm, XeCl) was split into two beams and crossed again at the sample cell to make the optical interference pattern. A He−Ne laser beam (633 nm) was used as a probe beam. The diffracted probe beam (TG signal) was isolated from the excitation laser beam with a glass filter (Toshiba R-60) and a pinhole. The TG signal was detected by a photomultiplier tube (Hamamatsu R-928) and fed into a digital oscilloscope (Tetronix TDS-520). The TG signal was averaged by a microcomputer to improve a signal-to-noise (S/N) ratio. Photoacoustic signals were detected by a piezoelectric transducer (PZT). The signal was directly detected by the digital oscilloscope.[28−35]

The energy entering the sample was adjusted below 2 μJ/pulse. The sample solution was changed to a fresh one after every 200 shots of the excitation laser pulses. The repetition rate of the excitation laser was less than 1 Hz. The size of the excitation beam at the sample position was ca. 1 mm ϕ. The irradiated volume is small (typically ca. 4×10^{-3} mL) compared with the entire volume of the sample solution (0.5 mL). All measurements were carried out at 21 °C. The value of the grating wavenumber q was determined from the decay rate of the thermal grating signal of a calorimeter reference sample, nitrobenzene, which gives rise to only the thermal grating signal due to the nonradiative transition within the pulse width of the excitation laser.[28−35]

The dendrimers were synthesized as reported previously.[17−35] The sample solutions were prepared just before the measurement in a dark room.

3. Method

The transient grating (TG) is created in the sample solution by crossing two coherent beams. The TG intensity under the experimental condition is proportional to the sum of squares of the refractive index (δn, phase grating) and the absorbance (δk, amplitude grating) changes, which are induced by the spatially modulated light intensity. Since absorption of any chemical species in this reaction is negligible at the probe wavelength (633 nm), the TG signal comes from the refractive index change upon photoexcitation. The refractive index change mainly comes from the thermal energy releasing (thermal grating) and created (or depleted) chemical species by the photoreaction (species grating). There are mainly two contributions in the species grating: the population grating term due to the absorption spectrum change and the volume grating term due to the molecular volume change. The TG signal intensity (I_{TG}) can be simply represented as follows

$$I_{\mathrm{TG}}(t) = \alpha[\delta n_{\mathrm{th}}(t) + \delta n_{\mathrm{p}}(t) - \delta n_{\mathrm{r}}(t)]^2 \tag{1}$$

where α is a constant and δn_{th}, δn_{p}, and δn_{r} are the refractive index changes of the thermal grating, product, and reactant, respectively. The minus sign for the term δn_{r} reflects the depletion of the reactant by the photoirradiation. If the energy is released as the thermal energy quickly, the temporal profile of the thermal grating is given by

$$\delta n_{\mathrm{th}}(t) = \delta n_{\mathrm{th}}{}^0 \exp(-D_{\mathrm{th}} q^2 t) \tag{2}$$

where D_{th} is the thermal diffusivity of the solution and q is the grating wavenumber. The magnitude of $\delta n_{\mathrm{th}}{}^0$ is expressed by

$$\delta n_{\mathrm{th}}{}^0 = \frac{\mathrm{d}n}{\mathrm{d}T}\frac{h\nu\phi W}{\rho C_p}\Delta N \tag{3}$$

where $dn/\mathrm{d}T$ is the temperature dependence of the refractive index, $h\upsilon$ is the photon energy of the excitation energy (389 kJ/mol), ρ is the density, C_p is the heat capacity at a constant pressure, and W is the molecular weight. Furthermore, ϕ is the quantum yield of the nonradiative transition and is given by

$$\phi = (h\nu - \Phi\Delta H - \Phi_{\mathrm{f}} E_{\mathrm{f}})/h\nu \tag{4}$$

where ΔH is defined by the enthalpy change from the reactant to the product, Φ is the quantum yield of the chemical reaction, Φ_{f} is the quantum yield of fluorescence, and E_{f} is the average photon energy of the fluorescence.

For determining the enthalpy change (ΔH), we quantitatively measured the refractive index change due to the thermal grating ($\delta n_{\mathrm{th}}{}^0$) under a weak laser power region, in which the species grating signal intensity is linear to the square of the excitation laser power. By taking the ratio of δn_{th} of the sample [δn_{th}(sample)] to δn_{th} of the calorimetric reference [δn_{th}(reference)], $\Phi\Delta H$ can be determined from eq 4.

The time evolution of the species grating intensity depends on the diffusion process of the species and the concentration change due to a chemical reaction. In this stilbene dendrimer case, since the back thermal reaction (cis to trans) is sufficiently slower than the observation time (<10 ms), the temporal profile is expressed by a molecular diffusion equation and given by

$$\delta n_{\mathrm{spe}}(t) = \delta n_{\mathrm{spe}}{}^0 \exp(-Dq^2 t) \tag{5}$$

where D is the diffusion coefficient.

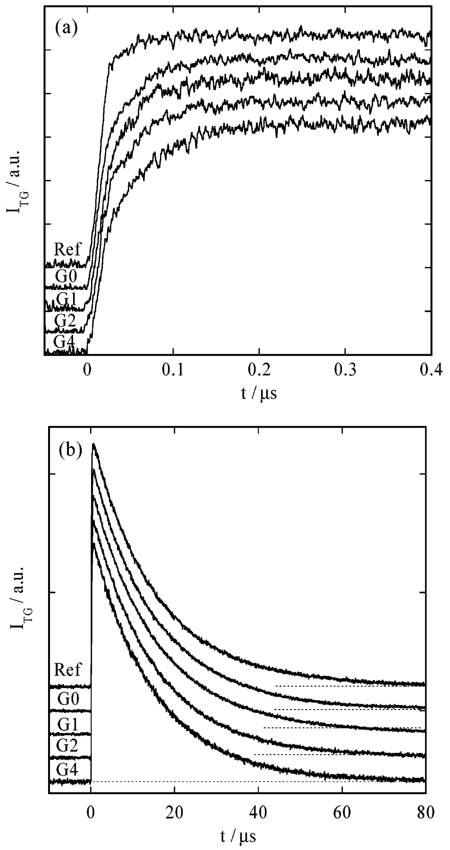


Figure 2. Observed TG signals after photoexcitation of the calorimetric reference sample, G0, G1, G2, and G4 in THF under the air-saturated solution (a) in a submicrosecond and (b) in a 100 ms time region. The signals are shifted vertically to avoid the overlap. The dotted lines in part b denote the baseline for these signals. The sample is indicated in the figure. Ref denotes the calorimetric reference sample.

The reaction volume, $\Phi\Delta V$ can be measured from the PA intensity and ΔH determined from the TG experiment by the method previously reported.[28−35] Briefly, if the chemical reaction is completed within the instrumental response time, the PA signal intensity (I_{PA}) is expressed as follows

$$I_{\mathrm{PA}} = \alpha'(h\nu\phi\alpha_{\mathrm{th}} W/\rho C_p + \Phi\Delta V) \tag{6}$$

where α' is a proportional constant that includes the sensitivity of the apparatus and α_{th} is the thermal expansion coefficient. Thus, the molecular volume change can be determined from the ratio of the PA signal intensity of the sample to that of the calorimetric molecule and ϕ from the TG experiment.

4. Results and Discussion

4−1. Photoisomerization Reaction and Conformational Change. The TG signals after photoexcitation of G0 (tetramethoxystilbene), G1, G2, and G4 in THF under the air-saturated solution were measured. Figure 2 shows the observed TG signals a few microseconds after the excitation. The signals for all samples rise fast with the time response of our system and then rise slowly. The signals decay to almost the baseline in the microsecond time region but not completely (*vide infra*). The TG signal of a calorimetric reference sample (nitrobenzene), which releases the energy of the excited state quickly under the same condition, is also depicted in Figure 2. The calorimetric reference signal rises with a time response of our system and decays to the baseline completely with the rate constant of $D_{\mathrm{th}}q^2$. This characteristic decay rate constant is a clear indicator to

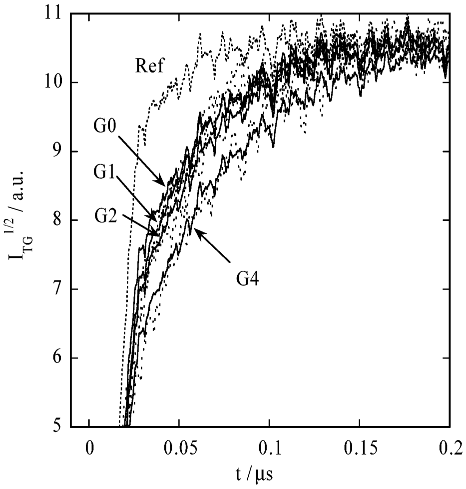


Figure 3. TG signal intensities of G0, G1, G2, and G4 in Figure 2 are normalized and the signals' rising parts are amplified (dotted lines) to show the rising components clearly. The solid lines indicates the best fitted curve by eq 7 convoluted with the response curve (denoted by Ref).

TABLE 1: Properties of Stilbene Dendrimers (G0, G1, G2, and G4) in Tetrahydrofuran

solute	G0	G1	G2	G4
Φ_f[a]	0.43	0.43	0.43	0.43
Φ_f[b]	0.33	0.36	0.38	0.40
Φ[c]	0.32	0.32	0.29	0.24
τ_s/ns[d]	49	47	54	79
$\delta n^s/\delta n^{tot}$	0.16	0.22	0.20	0.30
Φ_{isc}[e]	0.20	0.28	0.25	0.38[f]
$\Phi\Delta H$/kJ mol^{-1}	22 ± 10	24 ± 10	22 ± 10	21 ± 10
$(\delta n_c - \delta n_t)/\Phi\delta n_{th}^0$/%	18 ± 3	18 ± 3	22 ± 3	26 ± 3

[a] Fluorescence quantum yield under argon-purged conditions.[19] [b] Fluorescence quantum yield under air-saturated conditions.[19] [c] Photoisomerization quantum yield under air-saturated conditions.[19] [d] Lifetimes of the slow-rising component of the TG signal. [e] Quantum yield of the triplet formation under air-saturated conditions with an assumption that the slow rising of the thermal grating signal comes from the thermal energy. [f] Dynamics of possible conformational change of the dendron part is neglected.

show that the origin of the signal is the thermal grating. Since the decay rate constant of the dendrimers agrees well with $D_{th}q^2$, the main part of the signal component in this time range should be attributed to the thermal grating signal, which is produced by the thermal energy coming from the nonradiative transition and the enthalpy change of the reaction.

The rise part in the submicrosecond time range was fitted by a convolution of the response curve taken by the calorimetric reference sample with the function

$$\delta n(t) = \delta n^{tot} - \delta n^{s} \exp(-t/\tau_s) \qquad (7)$$

where δn^{tot} and δn^s are the total refractive index change and the slow component, respectively, and τ_s is the lifetime of the slow-rising component. The profile can be fitted rather well for all dendrimers (Figure 3). The lifetime of the slow component (τ_s) was ca. 50 ns for G0−G2 and 80 ns for G4 (Table 1).

Since this lifetime is close to that of the lowest excited triplet (T_1) state of stilbene (60 ns),[36] we attribute the slow-rising dynamics to the decay of the T_1 state, that is, the slow dynamics is originated by the thermal energy associated with the relaxation from the T_1 state. To further confirm this assignment, we saturated the solution with O_2 and found that the rate of the slow-rising component becomes much faster. This enhanced rate is consistent with the quenching of the triplet state by the oxygen molecule dissolved in the solution.

If we assume that the slow-rising signal comes only from the thermal grating signal, the quantum yield of the $S_1 \rightarrow T_1$ intersystem crossing (Φ_{isc}) of the dendrimers can be calculated from an energy balance relation of[26,27]

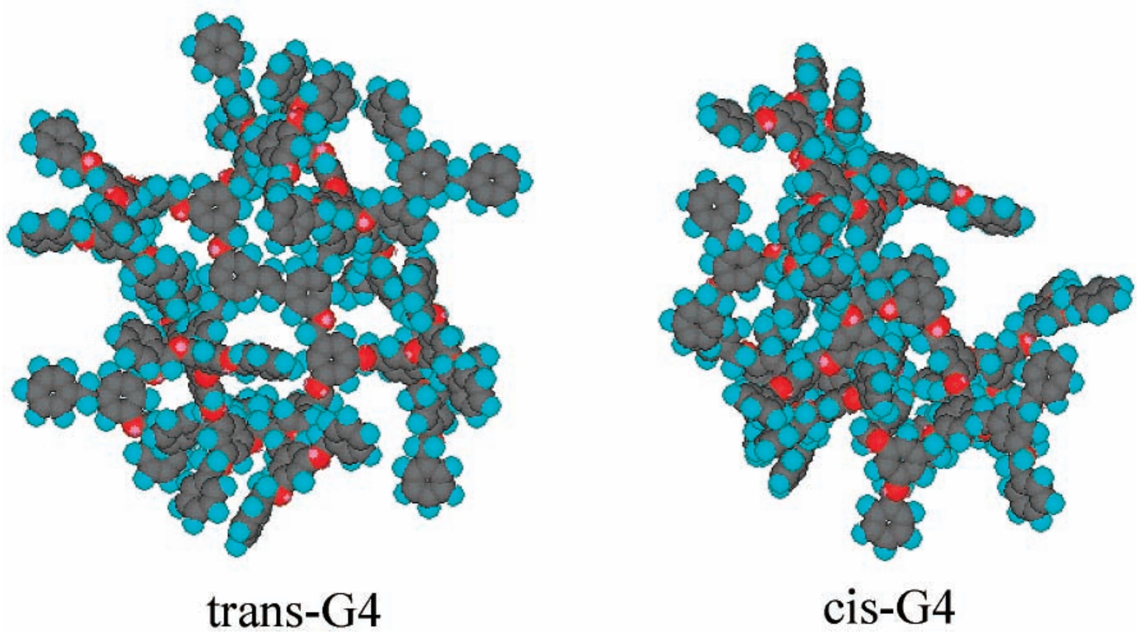
$$\Phi_{isc} = \phi h\nu(\delta n^s/\delta n^{tot})/E_T \qquad (8)$$

where E_T is the energy of the T_1 state. With an assumption of $E_T = 206$ kJ/mol,[36] the observed Φ_{isc} values for the dendrimers are calculated and listed in Table 1. Although the species grating signal may contribute to a part of the rising component, the nonnegligible amplitude of δn^s clearly indicates the significant triplet formation of these dendrimers after the photoexcitation. This is in contrast to the very small Φ_{isc} of stilbene. The nonnegligible triplet formation may result from the relatively long lifetime of the S_1 state of the dendrimers (10 ns for G0−G4) compared with that of stilbene (10 ps).[20−22]

Interestingly, we found that the slow-rising component is larger and slower for G4 compared with that for G0−G2 (Figure 3 and Table 1). This difference in the slow dynamics cannot be due to the different quenching efficiency of O_2, because we can observe the same difference even under the nitrogen-purged condition, under which the triplet quenching is negligible. Therefore, the difference may be explained by either the different character of the triplet state (i.e., larger Φ_{isc} and longer triplet lifetime) or dynamics besides the triplet decay, such as the conformational change that is superimposed on the triplet relaxation dynamics. We believe that this slow dynamic represents the conformational change of G4 in the ground state, because it is unlikely that Φ_{isc} is larger and the triplet lifetime is longer only for G4, although the other excited-state characters (lifetime of the fluorescence, absorption spectrum, quantum yield of reaction, etc.) are very similar. On the basis of these considerations, we attribute this slow dynamics to the slow volume change of the dendron part after the isomerization of the stilbene core. However, a quantitative measurement of the volume change from this rising component is difficult, because of the superimposed triplet dynamics in this time range.

It is interesting to examine what is the time scale of the conformational dynamics of the bulky dendron. We carefully analyzed the TG signal after the slow-rising part. The thermal grating signal can be fitted by $D_{th}q^2$ very well after this slow process. Furthermore, any conformational change and energy releasing was not observed in a longer time region. These facts suggest that the conformational change completes within 80 ns.

Using the TG technique, the thermal contribution can be separated from the other contributions by the signal fitting with the characteristic time constant of the thermal diffusion ($D_{th}q^2$).[28−35,37] This is a unique advantage of the TG method compared with the photoacoustic (PA) method, in which the thermal contribution is always mixed with the volume contribution and these two contributions should be separated with the temperature dependence or the solvent dependence method to vary the thermodynamic properties of the solution. However, using the thermal grating signal, we can measure the enthalpy change without changing any properties of the solution. The thermal grating intensities of the dendrimers are compared with that of the calorimetric reference sample and $\Phi\Delta H$ is determined as listed in Table 1. Since the absolute value of ΔH is sensitive to the accuracy of the reported Φ_f, it may not be appropriate to discuss these values here. However, we can compare the relative values among the dendrimers. It is interesting to note that there is no notable generation dependence on ΔH. This fact indicates


trans-G4

cis-G4

Figure 4. Possible conformations of the trans and cis forms of G4.

that the energetic destabilization due to the steric hindrance of the bulky dendron is minor. On the basis of the negligible generation dependence of the released thermal energy together with the fact that there is no slow heat-releasing process in our observation time range, we concluded that there is no long-term internal energy storage in these dendrimers.

The thermal grating signal of the calorimetric reference sample completely decays to the baseline, whereas those of dendrimers do not (not clearly shown in Figure 2 because of the very weak intensity). The signals of the dendrimers after the complete decay of the thermal grating signal correspond to the difference in the species grating signals between the trans and cis forms (eq 1). Writing the refractive index change of the created cis form and the depleted trans form as δn_c and δn_t, respectively, one may find that the intensity represents $\delta n_c - \delta n_t$. As mentioned in section 3, this signal consists of the population grating and volume grating terms. Since the contribution of the population grating is expected not to depend on the generation number, as explained in the next section, the difference in $\delta n_c - \delta n_t$ for different generation dendrimers should represent the generation dependence of ΔV. The $(\delta n_c - \delta n_t)/\Phi \delta n_{th}^0$ values can be determined very accurately and are listed in Table 1. It shows that this value is almost constant for G0, G1, and G2, which supports the above consideration. From these values, the volume change caused by the rearrangement of the dendron side chains can be determined by $\Phi\Delta\Delta V = (\Phi\Delta V(\mathrm{G4}) - \Phi\Delta V(\mathrm{G2}))$, where $\Delta V(\mathrm{G4})$ and $\Delta V(\mathrm{G2})$ are the volume change due to the isomerization of G4 and G2, respectively. It was calculated to be about 1.4 mL/mol. Since Φ of G4 is reported to be 0.24, $\Delta\Delta V$ is 6 mL/mol. This result indicates that the volume change due to the bulky and congested dendron is very small compared with the total molecular volume (0.17%) and it is a positive value, i.e., volume expansion by the isomerization.

We tried to measure the absolute values of the volume change by using the PA method. However, the volume change was so small that ΔV could not be determined accurately. We only determined that $\Phi\Delta V$ is 10 ± 8 mL/mol for all dendrimers. The positive volume change and the small value is consistent with the results from the TG signals.

It may be interesting to speculate on the cause of this volume expansion for G4. Possible conformations of trans and cis forms of G4 are shown in Figure 4. The conformation of the trans form is symmetric and there are many spaces that allow the solvent molecules enter, whereas the conformation of the cis form is rather compactly crowded. These molecular models suggest that the larger partial molar volume of the cis form versus the trans form may result from cavities that cannot be accessible for the solvent molecules in the cis form.

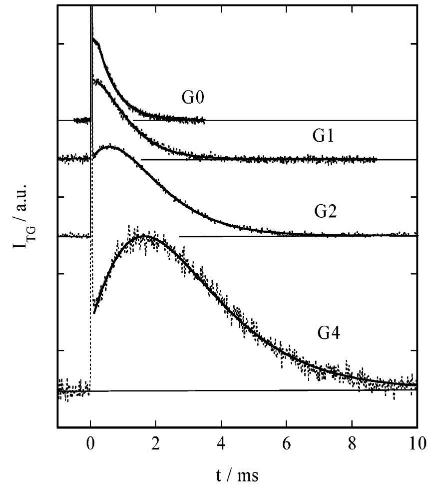


Figure 5. TG signals of G0, G1, G2, and G4 in THF under the air-saturated solution in the millisecond time region. The solid lines indicates the best fitted curve by eq 9.

4−2. Molecular Diffusion. The TG signals after photoexcitation of the dendrimers in THF under the air-saturated solution in a longer time region (after the decay of the thermal grating signal) are depicted in Figure 5. These signals consist of the species grating component. Considering the observation time range and the negligible slow thermal back reaction from the cis to trans form, one may attribute the dynamics to the molecular diffusion process.

It is found that the TG signal of G4 can be reproduced well by a biexponential function,

$$\delta n_{spe}(t) = \delta n_f \exp(-D_f q^2 t) + \delta n_s \exp(-D_s q^2 t) \qquad (9)$$

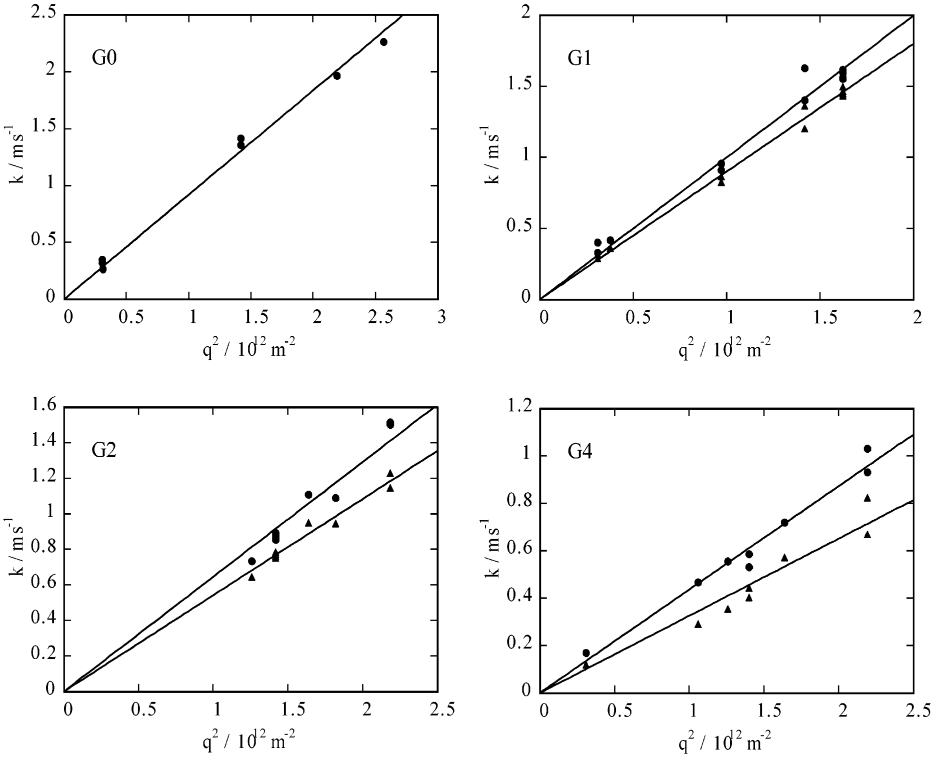


Figure 6. The q^2 plot of the decay rate constants (k) of the species grating signals of G0, G1, G2, and G4. The closed circles and closed triangles denote cis and trans isomers, respectively. The linear lines represent the best fitted ones by $k = Dq^2$. The slopes of the plots represent the diffusion coefficients.

where D_f and D_s are the diffusion coefficients of the fast and slow components, respectively and $|\delta n_f| < |\delta n_s|$. The sign of δn can be determined by using the fact that there is no interference dip between the thermal grating and species grating signal. Since the refractive index change due to the thermal grating is negative, one can conclude that the sign of δn_f should be negative and δn_s should be positive. From these signs of the preexponential factors and eq 1, δn_f should be attributed to the refractive index of a molecule that is produced by the reaction (the cis form), and δn_s is due to a molecule that is depleted by the reaction (the trans form). On the basis of this assignment, D_f and D_s should correspond to the diffusion coefficient of the cis form (D_c) and the trans form (D_t), respectively. The clear biexponential profile indicates that D of the trans and cis forms are clearly different.

On the other hand, the species grating signal of G0 is well fitted by a single-exponential function. This fact means that D of the trans and cis forms are very close (i.e., $D_f = D_s$ in eq 9) for G0. Although the single-exponential function cannot reproduce the TG signal well for G1 and G2, the amplitude of the rising component is weak and it was rather difficult to fit the data by a biexponential function uniquely. Hence, we made the following assumption to analyze the curve. As described in the Method section, the species grating consists of the population grating and the volume grating. Since the volume grating contribution is small, as shown in the previous section, the relative amplitude of δn_f and δn_s is mainly determined by the change of the absorption spectrum. It was reported that G1−G4 exhibit similar absorption spectra with the absorption maximum at 310 nm due to the stilbene core. The absorption of the benzyl ether group of the dendron appears at 280 nm, and this absorption spectrum is almost the same between cis and trans isomers, which indicates that the absorption spectrum is not sensitive to the conformational change of the dendron. Considering the very similar change in the absorption spectrum for G1−G4 upon the isomerization, we can satisfactorily assume that the ratio of δn_f to δn_s is almost constant for G1−G4. On the basis of this consideration, we used the ratio of δn_f to δn_s determined from the analysis of G4 to analyze the species grating signal of G1 and G2. The obtained decay rates are plotted against q^2 in Figure 6. From the slopes of the plots, D values are calculated and listed in Table 2. The assignment of D for the trans and cis forms is based on the same consideration as that of G4. One may notice that the difference between D_t and D_c increases with increasing generation number.

TABLE 2: Diffusion Coefficients (D/10^{-10} m^2/s) of the *trans*-(D_t) and *cis*-Dendrimers (D_c) in THF at 21 °C and Calculated Partial Molar Volume (V/mL mol^{-1}) by the Atom Increment Method[a]

solute	G0	G1	G2	G4
D_t	0.92	0.90	0.54	0.32
D_c	0.92	1.00	0.65	0.43
V	163	330	776	3454
D_{SE}	1.11	0.88	0.66	0.40

[a] D_{SE} denotes the D calculated with the Stokes−Einstein relationship.

Frequently, a diffusion coefficient of a molecule in liquid solution has been compared with a theoretically calculated one based on the Stokes−Einstein equation,[38]

$$D_{SE} = k_B T / 6\pi\eta r \qquad (10)$$

where k_B is the Boltzmann constant, T is temperature, η is viscosity, and r is the radius of a spherical molecule. The D values calculated using this equation are listed in Table 2. The radii of the dendrimers were calculated from the van der Waals volume obtained from the atomic increment method.[39] Naturally, since the van der Waals volume does not depend on the conformation of the dendrimers, the Stokes−Einstein equation predicts that D_t should be the same as D_c. This prediction agrees with the observation for G0.

An interesting point here is that D_t is different from D_c for the other dendrimers and the difference increases with increasing generation. This change cannot be due to the volume difference between the trans and cis isomers, because the volume change upon the photoisomerization reaction is shown to be very small compared with the total volume, only 0.17% of the total volume for G4. Furthermore, the larger D of the cis form seems to be inconsistent with the larger volume of this form. Therefore, the effect of the volume change to D should not be a main factor.

The Stokes−Einstein equation has been derived for a spherical molecule in a continuum medium. When the shape of the molecule is different from spherical, a correction for the shape is necessary. For example, the Perrin's theory has been frequently used.[38] This Perrin's correction for a ellipsoidal shape predicts that D becomes smaller upon increasing the difference in the major and minor axes of the ellipsoid. However, although the *trans*-dendrimer is more spherical than the cis form, the trans form has smaller D compared with the cis form. This is in contrast to the prediction from Perrin's formula. Hence, apparently, the observed difference in D between the trans and cis forms cannot be explained by the different shape.

We think that the difference in D is explained in terms of the molecular conformations as follows. The diffusion coefficient is determined by not only the molecular size but also surface corrugation and roughness. A theoretical study showed that the larger the surface roughness is, the smaller the diffusion coefficient is.[40] On the basis of this idea, the smaller D_t may reflect the rough surface of the trans form and it seems to agree with the molecular model depicted in Figure 4. Therefore, the different D_t and D_c is a clear indication that the molecular conformation is significantly altered upon the trans-to-cis isomerization. It is important to stress that the observed molecular volume change between the trans and cis forms is small, despite the large conformational change.

Conclusion

The energy releasing and conformational change upon photoisomerization of stilbene dendrimers of generation 0, 1, 2, and 4 were studied by the time-resolved TG method. For all generations, we observed a slow dynamics of about 50 ns lifetime and this dynamics is attributed to the relaxation from the lowest excited triplet (T_1) state to the ground state. For G0, G1, and G2, the conformational change is complete within this lifetime. For G4, the dynamics is slightly slower, which may be attributed to the conformational change of the dendron part after the trans−cis isomerization of the stilbene core. The difference of the diffusion coefficients between the trans and cis forms become larger upon increasing the size of the dendron group. A large conformational change in the fourth generation is suggested by the large difference in D between trans and cis forms. The conformational change of the dendron induces the molecular volume expansion, although the volume change is very small compared with the total molecular volume (0.17%). The volume expansion accompanied with the trans−cis isomerization is explained in terms of the creation of cavities surrounded by the dendrons. The energy storage due to the steric hindrance of the bulky dendron group is not large.

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