Structural Relaxation in Amorphous 1,2-Dichloroethane Studied by Transformation between Conformation Isomers

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Structural relaxation in amorphous 1,2-dichloroethane (DCE) samples prepared by vapor deposition on cold substrates were studied by Raman scattering. The gauche and trans molecules of DCE were found to coexist in amorphous states immediately after the deposition, and structural relaxation occurred with temperature elevation before crystallization. Mole fraction of the gauche isomer increased during this relaxation process, although trans is the stable isomer in gaseous and crystalline states. At the final amorphous stage immediately before crystallization, the gauche mole fraction was close to the mole fraction of the supercooled liquid state. It was also found that trans molecules located at positions with lower density were more easily transformed into the gauche conformation, while the distribution of the local structure around the resultant gauche molecules remained almost unchanged during the structural relaxation. Such behaviors of amorphous DCE are discussed from the viewpoint of the characteristic molecular structure of DCE.

1. Introduction

Amorphous or glassy materials are important because of their merits in various stages of applications.[1] The term "amorphous" is used to describe materials having a noncrystalline structure, while the thermodynamic term "glassy" implies that the solid material has undergone glass transition. In this paper, we use the term "amorphous" in reference to materials in either category. This is because the compound investigated in this study, 1,2-dichloroethane (DCE), does not undergo glass transition, and because there are critical cases for which the nature of a material cannot be characterized only by glass transition, as in the case of DCE.

Today's amorphous organic materials are expected to enable new functions in the fields of optics and electronics.[1] From the viewpoint of basic science, amorphous materials are in non-equilibrium states, and thus necessarily undergo structural relaxation toward stable states. However, the structure and structural relaxation of amorphous systems made of organic molecules are not yet well understood.

We have been studying the properties of vapor-deposited amorphous samples of simple organic compounds by vibrational spectroscopy,[2−6] X-ray diffraction,[4−7] and light interference.[8,9] Recent studies on neat[8] and binary[9] systems of monosubstituted benzenes have revealed the following facts about the nature of vapor-deposited amorphous molecular systems. The volume of an amorphous sample immediately after deposition is higher than that estimated for a supercooled liquid at the same temperature. As the sample temperature is raised, first, the sample volume increases as a result of thermal expansion. Next, one of two structural changes occurs: a direct crystallization from the amorphous state or a gradual structural change (so-called structural relaxation) followed by glass transition. The former is seen in compounds with rigid molecular structures, while the latter is seen in compounds with flexible molecular structures.

Suga and co-workers studied the thermal properties of vapor-deposited butyronitrile[10] and 1-pentene[11] by calorimetry. They showed that vapor-deposited amorphous samples have larger enthalpies than liquid-quenched amorphous samples, and that an enthalpy relaxation occurs before the glass transition when the sample temperature is raised. Our results on the structures of vapor-deposited amorphous molecular systems are consistent with their results obtained by the thermal method.

In the present study, we selected DCE as a model compound to obtain information on the molecular environment in amorphous systems. DCE is a typical compound with conformation isomers of the molecule. DCE molecules take on "trans" or "gauche" conformations, whose electric properties are nonpolar and polar, respectively (Figure 1).[12] Many studies have been conducted on this compound in relation to its conformational equilibrium.[13] The trans isomer is more stable than the gauche isomer in the isolated state. The two isomers coexist in the gas and liquid phases in thermal equilibrium, but only the trans is present in the crystal of the known structure.[14,15] Gauche molecules are stabilized in the liquid state owing to the electrostatic interaction between their dipole moments.[16] Therefore, the gauche mole fraction x_g is larger in the liquid phase than in the vapor phase at the same temperature. Thus, the populations of DCE isomers are sensitive to the phase. We used this property of DCE as the probe of molecular environment in amorphous systems.

Amorphous DCE may be in nonequilibrium states with respect to both the intra- and intermolecular freedoms of conformation. Thus, we expect to be able to see the structural relaxation of amorphous samples through the change in the populations of conformational isomers. It is well known that vibrational spectroscopy is a powerful tool in the study of DCE, and relevant data have been accumulated.[17] Thus, we employed Raman scattering to study amorphous DCE. In this paper, we report the Raman results on amorphous DCE, and discuss the structure and structural relaxation due to the temperature elevation in comparison with the behavior of other amorphous molecular systems.

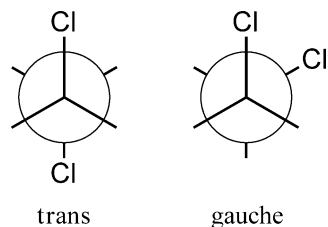* To whom correspondence should be addressed. E-mail: kiku.ishii@gakushuin.ac.jp.

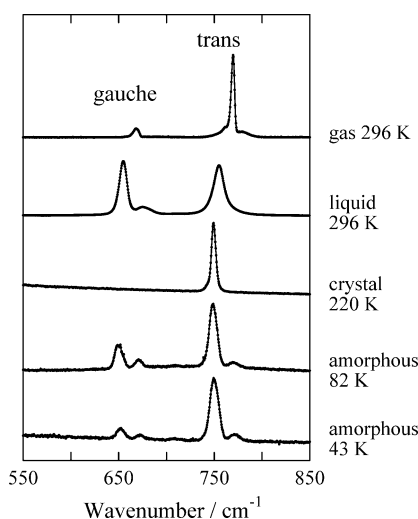**Figure 1.** Two conformational isomers of 1,2-dichloroethane (DCE).

Figure 2. Raman spectra in different phases; C−Cl stretching vibrational region. The two bands around 650 and 670 cm^{-1} are assigned to symmetric and antisymmetric stretching vibrations of gauche molecules, respectively, while that around 750 cm^{-1} is attributed to trans. See section 3.1 for the small band around 770 cm^{-1} in the spectra of the amorphous samples.

2. Experimental Section

Commercial DCE (Tokyo Kasei Kogyo) was used after distillation and fractional crystallization. The amorphous samples were prepared by vapor deposition on a cold substrate in a vacuum chamber described previously[8] at a base pressure below 10^{-7} Pa. The substrate was a gold-plated copper block cooled by cold helium gas using a flow-type cold finger. The sample thickness was made to be about 10 μm in each run by monitoring the interference fringe of reflected laser light. To study the structural relaxation in the sample, the sample was heated at a constant rate of 0.28 K min^{-1}.

Raman spectra were measured with a Triax 550 monochromator (Jobin Yvon-Spex) equipped with a CCD detector cooled with liquid nitrogen. The scale of the Raman shift was calibrated with atomic emissions from a neon lamp. An Ar$^+$ ion laser operated at 514.5 nm was used for the Raman excitation with a power of 40 mW in front of the vacuum chamber. The spectral slit width of the monochromator was about 1.6 cm^{-1}. The band wavenumber, width, and integrated intensity of each Raman band were determined by fitting the band shape to a Gaussian function.

3. Results and Discussion

3.1. Raman Spectra of DCE in Different States. Figure 2 shows the C−Cl stretching region of the Raman spectra of DCE in different phases. Spectra of gas, liquid, and crystal phases of DCE have been studied extensively.[17] The bands around 650 and 670 cm^{-1} are attributed to gauche, and the band around 750 cm^{-1} is attributed to trans. The results in Figure 2 indicate that the two isomers coexist in the gas and liquid states, while
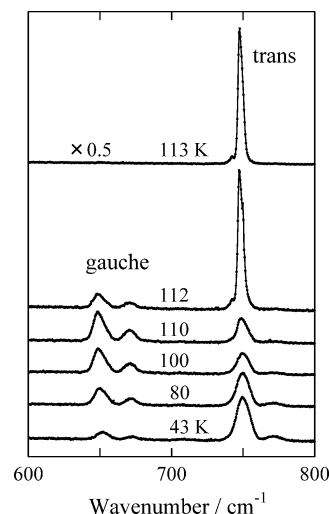

Figure 3. Evolution of Raman spectra of a sample deposited at 43 K during the continuous temperature elevation. Spectra showing typical features were selected.

only the trans isomer is present in the crystal. For the amorphous samples deposited at 43 and 82 K, both the gauche and trans bands are observed. Similar results were obtained for the samples deposited at other temperatures below 82 K. X-ray diffraction confirmed that all samples vacuum-deposited under such conditions were amorphous. This revealed that the two isomers coexisted in the amorphous state. The intensity ratios of the gauche and trans bands depended on the deposition temperature. This will be described in detail in section 3.3.

Figure 3 shows the evolution of the Raman spectra during heating of the sample deposited at 43 K. The intensity of the gauche bands around 650 and 670 cm^{-1} increased with temperature, while that of the trans band around 750 cm^{-1} decreased. When the temperature reached around 112 K, an abrupt spectral change occurred: the spectrum began to resemble that of the crystal. These changes suggest that the gauche mole fraction x_g increased in the amorphous state before crystallization. To obtain x_g from the intensity ratios of the bands around 650 and 750 cm^{-1}, we had to estimate the ratio of Raman-scattering cross sections of these bands. The estimation procedure will be described in the next section.

It should be noted that a small hump is seen around 770 cm^{-1} in the spectra of amorphous samples. This is attributed to the CH$_2$-rocking vibration that is Raman-forbidden for symmetrical trans molecules[17] but is Raman-active for deformed trans molecules. The appearance of this band suggests the asymmetric molecular environment around the trans molecules in the amorphous state. We will discuss this in detail elsewhere.[18]

3.2. Estimation of the Ratio of Raman Scattering Cross Sections of Gauche and Trans Bands in the Liquid State. The intensities of gauche and trans Raman bands, I_g and I_t, are assumed to be proportional to their respective amounts, n_g and n_t. Thus, the ratio of these band intensities can be represented as

$$\frac{I_g}{I_t} = \frac{\sigma_g}{\sigma_t} \cdot \frac{n_g}{n_t} \qquad (1)$$

where σ_g and σ_t are the cross sections of the gauche and trans bands, respectively. Thus, if we know σ_g/σ_t, n_g/n_t can be estimated from the intensity ratio of the Raman bands. Mizushima and co-workers[19,20] have reported analysis data that yield $\sigma_g/\sigma_t = 0.43$ for the gauche and trans bands observed
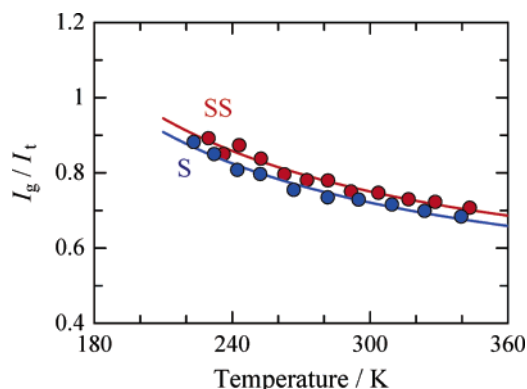
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Figure 4. Raman-intensity ratio of the 650 cm^{-1} gauche band to the 750 cm^{-1} trans band of liquid DCE as a function of temperature. Data were obtained by Raman spectroscopy under ss and s polarizations (see section 3.2).

around 650 and 750 cm^{-1} for gaseous DCE. However, the corresponding value for condensed phases has not yet been reported. We measured Raman spectra of liquid DCE over a wide temperature range including the supercooled region, and estimated the σ_g/σ_t for liquid as described below. Figure 4 plots the ratio of the integrated intensities of the gauche and trans bands around 650 and 750 cm^{-1}, respectively,[21] measured by Raman spectroscopy under two different polarization conditions: (i) s polarization for both incident and scattered light, and (ii) s polarization for the incident light and no polarization for the scattered light. Data under the latter polarization condition were needed to match those obtained by experiments on the amorphous samples.

For a system under thermodynamic equilibrium, n_g/n_t is given by

$$\frac{n_g}{n_t} = 2 \exp\left(-\frac{\Delta G}{RT}\right) = 2 \exp\left(-\frac{\Delta H - T\Delta S}{RT}\right), \quad (2)$$

where $\Delta G = G_g - G_t$, $\Delta H = H_g - H_t$, and $\Delta S = S_g - S_t$ are, respectively, the differences in free energy, enthalpy, and entropy between the gauche and trans isomers, R is the gas constant, and T is temperature. The factor 2 in eq 2 accounts for the two kinds of optical isomers having the gauche conformation.

Using eq 2, eq 1 is rewritten as

$$\frac{I_g}{I_t} = \frac{\sigma_g}{\sigma_t} \cdot 2 \exp\left(\frac{\Delta S}{R}\right) \exp\left(-\frac{\Delta H}{RT}\right) \quad (3)$$

ΔH and ΔS include the contribution of the intermolecular term in addition to the intramolecular term. The intermolecular term in ΔS is thought to be negligible since the principal factor determining the intermolecular entropy is the mass of the molecule, which is the same for the trans and gauche conformations. Thus, we adopted the ΔS for the gas phase as being equal to that of the liquid. According to Tanabe,[22] $2 \exp(\Delta S/R) = 1.85$ for the gas. We used this value for the corresponding factor in eq 3.

In the case of ΔH, however, we must take into account the contribution of the intermolecular interaction. It has been known that gauche molecules owe their stability to their electrostatic interaction with the surrounding medium. Watanabe et al.[19] estimated ΔH on the basis of the Onsager equation, and showed that ΔH depends almost linearly on temperature. By using their results, we first attempted to fit the observed I_g/I_t in Figure 4 via eq 3. However, there seemed to be a systematical difference

between the fitting function and observed data. Presumably, the constant molecular volume used in the Onsager equation was inadequate over the wide temperature range. Thus, we assumed a linear dependence of ΔH on temperature as indicated in eq 4, where a and b are the fitting parameters.

$$\frac{I_g}{I_t} = \frac{\sigma_g}{\sigma_t} \cdot 1.85 \exp\left(-\frac{aT + b}{RT}\right) \quad (4)$$

By fitting this equation to the observed data in Figure 4, we obtained the solid curves and the values of the factors $(\sigma_g/\sigma_t)\exp(-a/R)$ and b.

It has been known that $\Delta H = 0.0$ kJ mol^{-1} for liquid DCE at room temperature.[22] By using this condition, we finally obtained $\sigma_g/\sigma_t = 0.41$ for the ss polarization and 0.39 for the s polarization. These are slightly lower than the value reported for the gas phase (0.43). The temperature dependence of ΔH can be expressed as follows. That is, gauche is slightly more stable than trans in liquid below room temperature.

$$\Delta H = (4.5 \text{ J mol}^{-1} \text{ K}^{-1})T - 1.34 \text{ kJ mol}^{-1} \quad (5)$$

3.3. Populations of Trans and Gauche Isomers in Vapor-Deposited Samples. The structure and thermal states of film samples immediately after vapor deposition onto cold substrates have been important issues in our studies. We have found that optical transparency diminishes as the sample thickness is increased at very low substrate temperatures.[6] This is related to the density inhomogeneity of the sample, and thus to the dynamics of molecules at the top surface of the sample during vapor deposition. That is, molecules supplied from the vapor have kinetic energies corresponding to room temperature. After the deposition on the sample surface, the molecules lose their thermal energy rapidly through interaction with the surrounding cold molecules. During this freezing process, each molecule may find its intra- and intermolecular conformations at a local minimum of the potential energy. In the present study, we examined such processes through the behavior of the conformational isomers.

Figure 5a shows x_g measured for samples with a thickness of about 10 μm just after vapor deposition. Clearly, the x_g of the sample deposited at 30 K almost coincided with that of the room-temperature vapor (0.22), and x_g was larger for samples deposited at higher temperatures. These observations suggest that DCE molecules are frozen very rapidly at the substrate temperature of 30 K and that they can change their conformation for some time at higher substrate temperatures. The reason for the increase in x_g at higher temperatures will be discussed in the next section.

Figure 5b shows the record of x_g during the vapor deposition of each sample in Figure 5a. These data show that the x_g of each sample was almost constant or increased slightly as the sample thickness was increased. Since the local x_g of the sample may reflect the local temperature, the data in Figure 5b imply that the increase in the effective temperature at the top surface of the sample during deposition was almost negligible, as small as a few degrees Kelvin at most.

3.4. Relaxation of Amorphous DCE by Temperature Elevation. Figure 6 shows the evolution of x_g of amorphous DCE samples deposited at different temperatures. The temperature dependence of x_g calculated by using eq 2 for a hypothetical supercooled liquid is shown by a dashed line for comparison. We found that the x_g of all samples clearly increased toward the value of the supercooled liquid as the temperature was raised, except the sample deposited at 82 K.
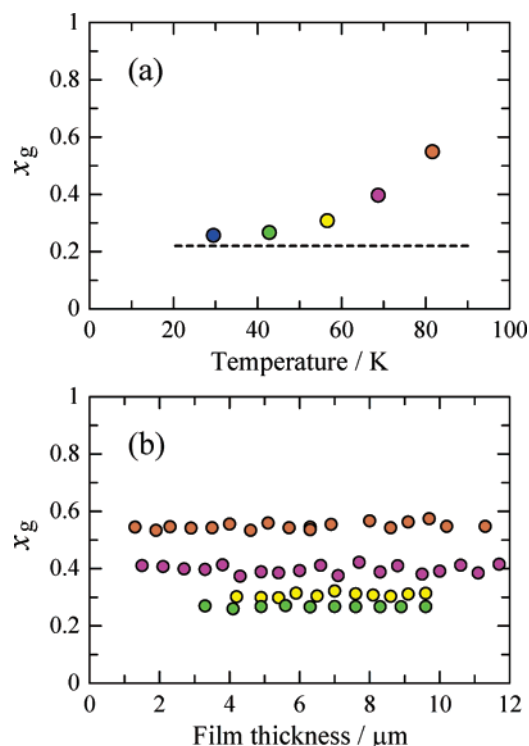
Figure 5. Gauche mole fraction x_g of amorphous samples vapor-deposited at different temperatures. (a) x_g immediately after the deposition to a thickness of 10 μm. (b) Record of x_g of four samples in (a) during the deposition at 43, 56, 69, and 82 K.
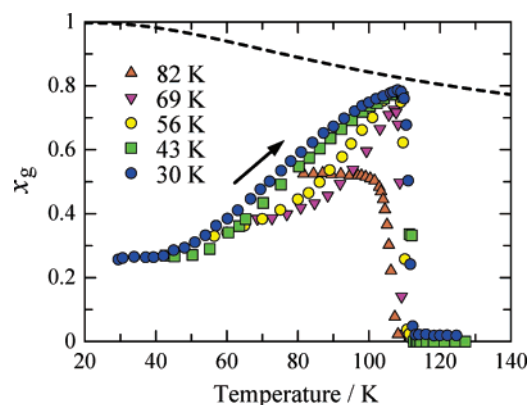

Figure 6. Irreversible change of x_g of samples deposited at different temperatures due to the temperature elevation at a constant rate. Dashed line indicates x_g in hypothetical supercooled liquid estimated using the thermodynamic data of eq 5. Abrupt decreases of x_g around 110 K are due to the crystallization of the samples.

When the temperature was raised to around 110 K, the x_g of all samples abruptly dropped to zero. This was due to the crystallization of the amorphous sample because Bragg peaks appeared in the X-ray diffraction pattern around this temperature for samples prepared under similar conditions.[23]

The increase in x_g of the above samples with increasing temperature is unexpected for amorphous systems since the structural relaxation in such systems usually occurs toward the crystal structure. We examined the behavior of a sample deposited at 43 K by stopping the heating at 100 K, and cooled it again before it underwent crystallization. The result indicated that the value of x_g at 100 K was preserved. Thus, the increase in x_g of the amorphous samples was due to the irreversible structural relaxation. It is worth studying why amorphous DCE relaxes toward the liquid structure.
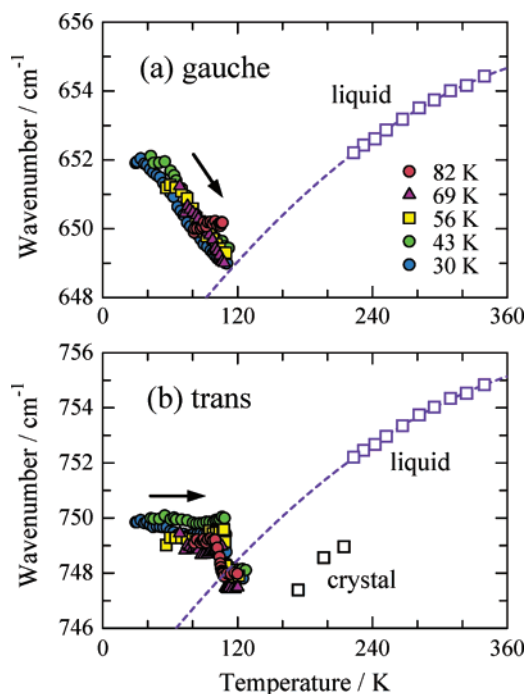

Figure 7. Irreversible change of the wavenumber of gauche and trans bands for samples deposited at different temperatures. Corresponding data measured for supercooled liquid on cooling are shown for comparison. The dashed lines are a guide for the eye. For the trans band, similar data for the crystalline samples that emerged from the supercooled liquid are also plotted.

It is seen in Figure 6 that the evolution of x_g is different for samples deposited at different temperatures. This implies that the relaxation processes occur through different paths. It is noted that all data for samples deposited at different temperatures show a slow increase rate of x_g at the initial process of the temperature elevation. This is thought to reflect the lack of low potential barriers around the deposited molecules depending on the deposition temperature.[23] The most remarkable example is that of the sample deposited at 82 K. The x_g of this sample almost remained at its initial value until the sample finally underwent an abrupt crystallization. We attribute this to the stable local packing of molecules formed during deposition at mild temperature conditions.[6]

Figure 7 shows the evolution of the wavenumber of the gauche and trans bands around 650 and 750 cm^{-1} during heating. The temperature dependence of the wavenumber of the corresponding bands of the supercooled liquid is also shown for comparison. First, we examine the data on the gauche isomer in Figure 7a. It is found that the gauche band wavenumber of the initial sample on deposition was smaller as the substrate temperature was higher. On the other hand, the corresponding wavenumber of the liquid shifted to smaller wavenumber with lowering temperature. Since the density of liquid increases as the temperature is lowered, this implies that the band wavenumber decreased with increasing sample density. Thus, it is thought that the local density around the gauche molecules in the initial samples was larger as the substrate temperature was higher. In addition, the evolution of the band wavenumber of all samples except the sample deposited at 82 K suggests that the local density increased as the temperature was raised. The band wavenumber of all samples, except the sample deposited at 82 K, approached the value of the supercooled liquid with increasing temperature. This suggests more directly than the results of x_g in Figure 6 that the molecular environment
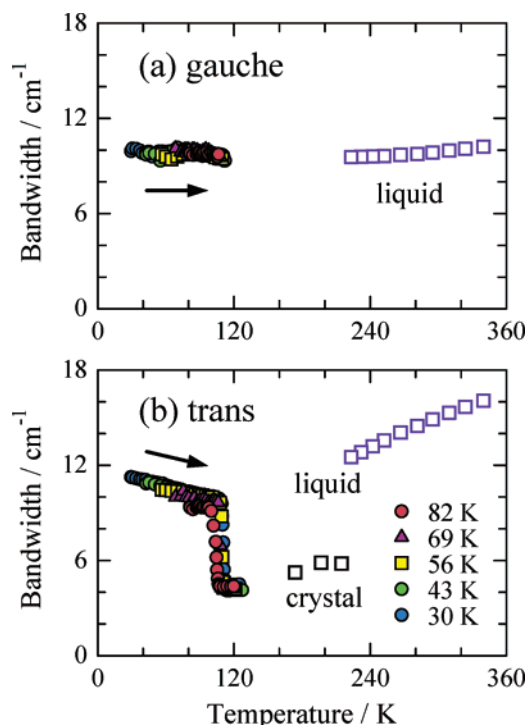
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Figure 8. Irreversible changes of the width at half-maximum of the gauche (650 cm^{-1}) and trans (750 cm^{-1}) bands for samples deposited at different temperatures. Corresponding data measured for the super-cooled liquid on cooling are shown for comparison. For the trans band, similar data for the crystalline samples that emerged from the supercooled liquid are plotted as well.

Figure 9. (a) Evolution of the shape of the trans band around 750 cm^{-1} observed for the sample deposited at 30 K during the temperature elevation. Intensity was normalized at the peak of each spectrum. (b) Density dependence of the band wavenumber of the corresponding band of the liquid. The density data were collected from ref 19.

of gauche molecules approached that in the liquid before crystallization.

Next, we examine the data of trans in Figure 7b. The relation between the initial band wavenumber and substrate temperature is similar to that of the gauche band. On the basis of the same consideration as for the gauche band, the local density of trans molecules in the initial sample increased slightly with the substrate temperature. In contrast to the behavior of the gauche band, however, suppressed changes were observed for the evolution of the trans band wavenumber for all the samples regardless of deposition temperature. This suggests that mo-lecular environment of the trans molecules remained almost unchanged despite the temperature increase.

The width of a vibration band includes information on the distribution of molecular configuration while the band wave-number represents the average molecular configuration. Figure 8 shows the temperature evolution of the widths of gauche and trans bands at around 650 and 750 cm^{-1}, respectively, for samples deposited at different temperatures. The corresponding bandwidths of the liquid and crystal phases are also plotted in Figure 8. For the gauche band (Figure 8a), nearly the same bandwidth was observed irrespective of deposition temperature, and no remarkable change was observed upon temperature elevation. These results indicate that the distribution of molecular configuration of gauche molecules was not influenced by the deposition temperature and did not change appreciably during the temperature elevation. Note that the gauche band disappears immediately after the spectral change around 110 K due to the crystallization.

Figure 8b shows that the trans bandwidth decreased abruptly around 110 K. This is attributed to the crystallization. Before the crystallization, a slight but continuous decrease in bandwidth was observed for all the samples except the sample deposited at 82 K. These decreases in width suggest that the distribution
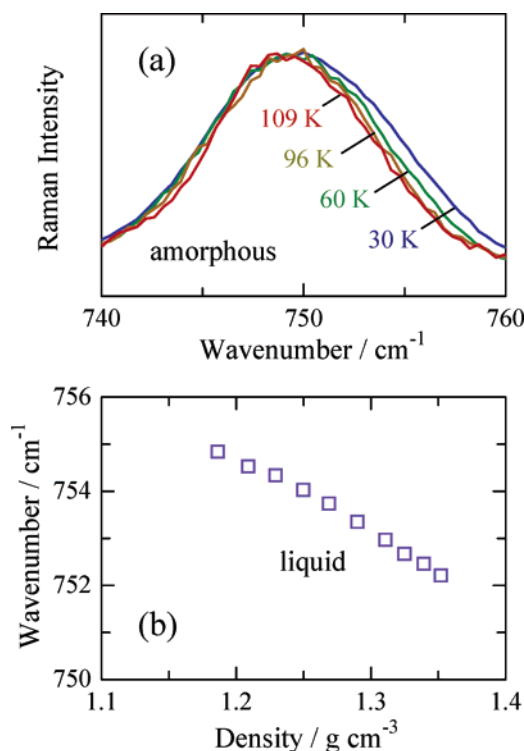
of molecular configuration of trans molecules became narrower as a result of the temperature elevation.

To understand the cause of the above decrease in the trans bandwidth, we focused on the change in the band profile. Figure 9a shows the evolution of the trans band profile of the sample deposited at 30 K. The intensity of each band was normalized by the peak intensity. We see that the higher-wavenumber component diminished with increasing temperature. Similar results were observed for the other samples except that deposited at 82 K. Since the trans band of the liquid shifts to higher wavenumbers with decreasing sample density (Figure 9b), the observed change in trans band profile indicates that trans molecules located at positions with lower density in the sample transform more easily into the gauche conformation.

3.5. Comparison with Relaxation Processes in Other Amorphous Molecular Systems. The experimental results obtained so far for vapor-deposited amorphous DCE samples suggest that their relaxation mechanism is as follows. The initial sample consists of gauche and trans molecules in a nonequi-librium state. The structural relaxation that is accompanied by the conformational change from trans to gauche occurs gradually when the sample temperature is raised. Although the molecular environment of gauche molecules approaches those in the supercooled liquid state, the sample crystallizes at the final stage of the structural relaxation without undergoing glass transition.

This structural relaxation in amorphous DCE is fairly distinct from those of the amorphous benzene derivatives that we have studied previously.[3−9] The structural relaxation in amorphous DCE takes place over a very wide temperature range, while those in amorphous benzene derivatives occur in narrow temperature ranges of less than 10 K. We believe that this difference is caused by the soft molecular structure of DCE that can be easily transformed between the trans and gauche conformations, and also by the unique molecular shape of trans
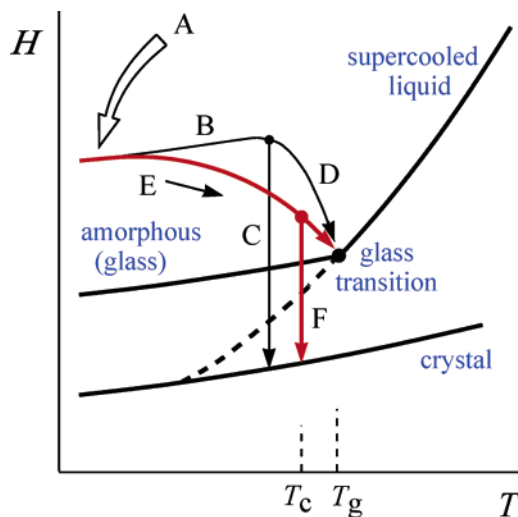
Figure 10. Schematic diagram illustrating the temperature dependence of the enthalpy of the system in different phases related to the glass transition. The symbols from A through F denote the following processes: A, vapor deposition; B, thermal expansion of amorphous solids comprising benzene derivatives; C, direct crystallization seen in rigid benzene derivatives; D, structural relaxation seen in flexible benzene derivatives; E, structural relaxation observed in amorphous DCE; and F, direct crystallization of DCE. T_g and T_c denote the glass transition temperature and crystallization temperature, respectively.

DCE that easily permits the rotation of the molecule around the axis connecting the two chlorine atoms.[14,15]

We depicted the characteristics of structural relaxation in amorphous DCE in Figure 10 that schematizes the enthalpy of the system as a function of temperature. Process A is the initial vapor deposition onto a cold substrate. This process yields an amorphous sample with a high enthalpy, in which the distribution of molecular configuration depends on the substrate temperature. The sample deposited at medium temperature is transparent and has a relatively dense structure, while that deposited at a fairly low temperature is opaque and has a less dense structure.[6]

Processes B and E are observed during heating of the deposited samples. The amorphous benzene derivatives studied previously follow path B, whereby the sample undergoes thermal expansion while almost retaining its initial amorphous structure. This is thought to reflect the high-energy barrier against the reorientation of substituted benzene molecules in solid states. The subsequent processes (C and D) are the direct crystallization and structural relaxation, respectively. The sample compound follows one of these paths depending on the flexibility of the molecule.[3,9]

In contrast to benzene derivatives, amorphous DCE follows path E when the sample temperature is raised. That is, the sample gradually releases enthalpy, which is accompanied by the structural transformation from trans to gauche despite the dense molecular environment in the solid amorphous state. Amorphous DCE is able to take path E because of the above-mentioned adaptability of the molecular structure of DCE. Thus, amorphous DCE undergoes a structural relaxation that spans a wide temperature range. However, the small molecular size of DCE is thought to cause the amorphous samples to undergo direct crystallization (path F) just before reaching the point of glass transition.

4. Conclusions

We have studied the structure and structural relaxation in amorphous DCE focusing on the ratio of the gauche to trans

isomers. The basic data for the estimation of this ratio came from our derivation of the ratio of the Raman scattering cross sections, σ_g/σ_t, of the bands around 650 and 750 cm^{-1} due to these isomers from the spectral data of liquid DCE over a wide temperature range.

The amorphous DCE samples were fabricated by vapor deposition on cold metal substrates. The initial gauche mole fraction x_g of the film sample having a thickness of about 10 μm was almost the same as the x_g of the room-temperature vapor when the substrate temperature was 30 K. However, the initial x_g was larger as the substrate temperature during deposition was higher. In addition, x_g increased irreversibly toward the value of the liquid as the samples were annealed by temperature elevation. The evolution of the gauche band wavenumber supports this interpretation. These results suggest that DCE molecules undergo structural relaxation, somehow attaining dielectric stabilization through the surrounding molecules as in liquid state. It should be noted that the gauche bandwidth showed almost no change during annealing. This indicates that the newly appearing gauche molecules see similar molecular environment.

In contrast to the behavior of the gauche band, the trans band wavenumber roughly retained its initial value during annealing, while its bandwidth became narrower on the higher wavenumber side. These results suggest that trans molecules located in regions of lower density in the sample have larger probabilities to transform into the gauche structure.

It was noted that structural relaxation in amorphous DCE occurs over a wide temperature range in contrast to the glass states of benzene derivatives. This behavior of amorphous DCE is attributed to the characteristic molecular structure of DCE owing to which the gauche–trans transformation is possible without causing much displacement of the chlorine atoms at both ends of the molecule. Such a structural relaxation is expected to occur in many amorphous molecular systems if the molecule has a skeletal component that allows conformational transformation with a small activation energy.

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