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Density Inhomogeneity in Amorphous Chlorobenzene Vapor-Deposited on Cold Substrates

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Light transmission through amorphous chlorobenzene was studied during the vacuum deposition of the vapor onto cold substrates. It was found that samples prepared at 78 K were transparent, but those prepared at 15 K were slightly opaque. Raman and X-ray studies indicated that both kinds of samples were amorphous, but they showed different behavior against annealing. The transparent samples needed some induction period to start crystallization when the temperature was raised for annealing, while the slightly opaque samples underwent crystallization by annealing almost without any induction period. Samples prepared at very-low temperatures are considered to incorporate density inhomogeneity, and the resultant free space around molecular aggregates may allow the samples to start crystallization easily.

Amorphous molecular systems have been extensively studied to determine the thermal behavior related to the glass transition.[1] They have also been explored as functional materials that support the electronic or photonic processes.[2] However, few studies have been made from the viewpoint of structural chemistry.

We have been studying by Raman scattering and X-ray diffraction the structure and structural relaxation in amorphous molecular systems of simple organic compounds.[3–5] The samples were prepared by the vapor deposition onto cold substrates in the form of films with the thickness of about 10 μm. The relaxation behaviors were not affected seriously by the existence of the sample surface or of the interface with the substrate. It has been found that the relaxation takes place over a wide temperature range for compounds with a large degree of intramolecular deformation. Typical examples of such compounds are long-chain aliphatic hydrocarbons.[3] On the other hand, the relaxation takes place in a narrow temperature range for compounds with rigid molecular structures, leading the samples to an abrupt crystallization without showing the glass transition. A typical example is benzene.[4,5] It is noteworthy that the amorphous state of each compound seems to have characteristic temperature range(s) for the structural relaxation.

In this paper, we report the experimental results obtained for the relaxation behavior of amorphous chlorobenzene films prepared at different deposition temperatures. We deal especially with the light-transmission property of samples during the deposition of the vapor. Chlorobenzene gives amorphous samples in a wide range of the deposition temperature. The Raman and X-ray data indicated the initial amorphousness of all the samples. However, the light transmission showed differences among the samples deposited at different temperatures. In addition, by monitoring the relaxation behavior of the samples, it was found that there was a definite difference in the manner of the crystallization among the samples prepared at different temperatures. We discuss these behaviors in relation with the density inhomogeneity in amorphous samples prepared at very low temperatures.

Experimental

Amorphous samples of chlorobenzene were prepared by the vapor deposition in a vacuum chamber with the base pressure below 10^{-7} Pa (Fig. 1). The substrate was a gold-plated copper block which was cooled by a gas-flow-type cold finger (Janis ST-400). This cooling system was surrounded with a doughnut-shaped liquid-nitrogen reservoir attached with a copper sleeve for the radiation shielding. By keeping these parts cold, we could avoid any appreciable deposition of residual gas on the substrate.

The sample vapor was introduced from a room-temperature liquid reservoir through a needle valve. A He–Ne laser beam was introduced to the substrate surface with the angle of 55° from the normal incidence. The reflected light intensity was monitored with a silicon photocell during the sample deposition. From the analysis of the recorded intensity change, we estimated the thickness and optical quality of the sample.

Raman measurements were carried out *in situ* with the above vacuum chamber. The same He–Ne laser for the sample-thickness monitoring was used for the Raman excitation with the power of 12 mW. The spectrum was analyzed with a Triax-550 monochromator (Instrument S. A., Inc.) equipped with a CCD. A holographic notch filter (Kaiser Optical Systems, Inc.) was used to reduce the elastically scattered laser light. X-Ray diffraction was measured using the system reported previously.[4] Temperature of the sample substrates was measured with chromel-gold/iron(0.07%) thermocouples in both the optical and the X-ray experiments.

Results and Discussion

(i) Light-Transmission Property of the Sample during

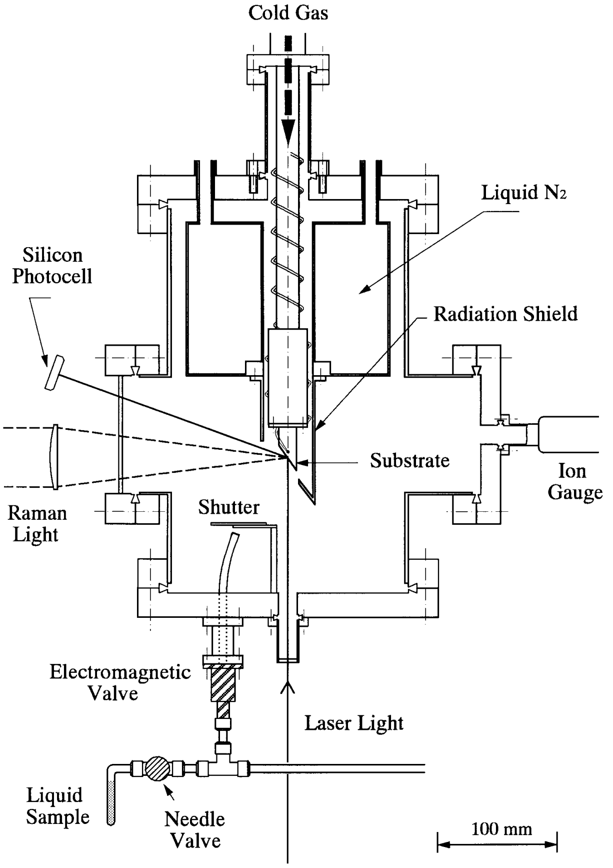

Fig. 1. Cross section of the vacuum-chamber for optical measurements.

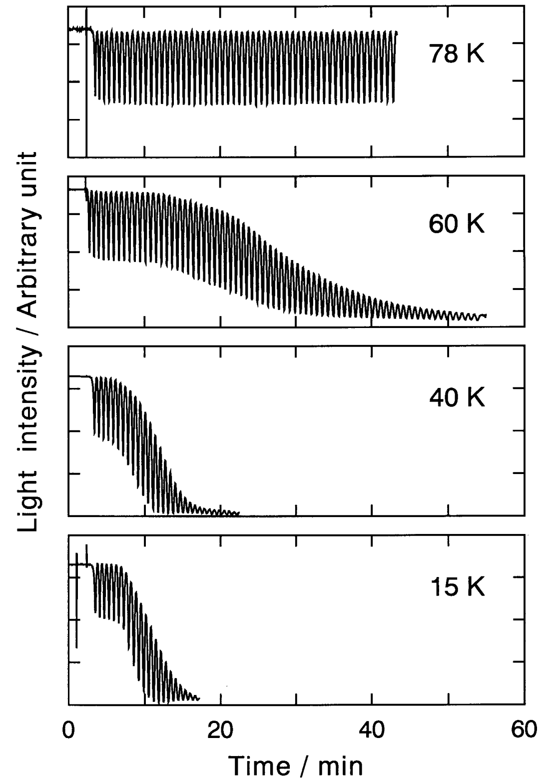

Fig. 2. Change of the light intensity transmitted through the sample film during the vapor deposition onto the substrate at temperatures indicated.

the Vapor Deposition. In our previous studies on amorphous molecular systems, we have found that the appearance of the sample critically depends on the condition of the vapor deposition. However, the sample quality has not been hitherto characterized objectively because the reproducibility of the sample preparation was poor, probably owing to the insufficient vacuum condition. For the present study, we constructed a new vacuum chamber for optical measurements, as described in the experimental section. We confirmed with this chamber that the light-transmission property of the sample systematically depends on the substrate temperature at the vapor deposition.

Figure 2 summarizes the intensity change of the laser light transmitted through the sample film during the deposition of chlorobenzene vapor at different temperatures. We recorded such light intensity every time during the deposition of the sample for the Raman or X-ray measurements. The short-term periodic change is essentially due to the interference among the multiply reflected light beams, and gives the estimation of the film thickness d by

$$d = N\lambda / \left(2\sqrt{n^2 - \sin^2\theta}\right), \tag{1}$$

where N is the number of the dips of the light intensity, λ and θ are the wavelength and incident angle of the laser light, and n is the refractive index of the film. If we assume that $n = 1.52$, namely the same as the liquid chlorobenzene at room temperature,[6] one cycle of the intensity change corresponds to an increment of the film thickness of 0.25 μm.

At 78 K, the curve showed a good periodicity, and almost no long-term decrement was observed. Thus at 78 K, chlorobenzene forms an optically uniform film up to the thickness of at least about 15 μm. At lower temperatures, however, the transmission intensity started to show a long-term decrement after a certain period of the repetition of the interference curve. The rate of the decrement was faster as the temperature was lower.

To examine the shape of the interference curve, we simulated it by assuming multiple reflection of the light in the film (Fig. 3). The total amplitude R of the electric field of the reflected light is given as the sum of the fields of light that undergoes multiple reflections as follows:

$$R = R_0(r_{12} + t_{12}r_{23}t_{21}\xi e^{-i\delta} + t_{12}r_{23}r_{21}r_{23}t_{21}\xi^2 e^{-2i\delta} + \dots). \tag{2}$$

Here, R_0 is the initial amplitude of the incident-light field, and the subscripts 1, 2, and 3 indicate respectively the vacuum space, the film, and the metal substrate. r_{ij} and t_{ij} are respectively the reflection and transmission coefficients at the interface between the media indicated by the subscripts, and are functions of the refractive indices of the corresponding media. δ and ξ are respectively the phase shift and attenuation coefficient of the light field during a forth-and-back unit travel of the light across the film, and are thus the functions of the film thickness d. The intensity of the observed light is given by RR^*. Taking account of the relations, $r_{12} = -r_{21}$ and

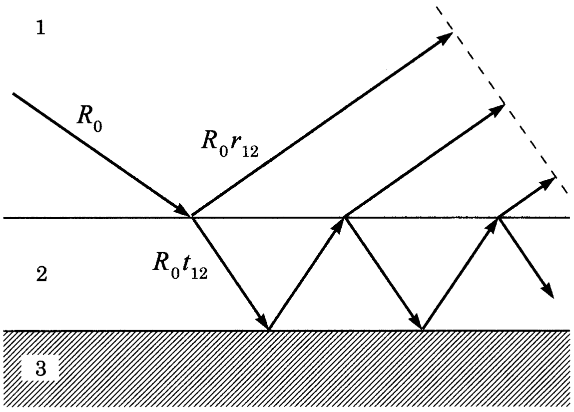

Fig. 3. Schematic representation of the multiple reflection of laser light in the sample film. The numbers 1, 2, and 3 indicate the vacuum space, the chlorobenzene film, and the gold substrate, respectively. See the text for the meaning of the quantities indicated.

$r_{12}^2 + t_{12}t_{21} = 1$,[7] Eq. 2 can be simplified as follows:

$$R = R_0 \frac{r_{12} + r_{23}\xi e^{-i\delta}}{1 + r_{12}r_{23}\xi e^{-i\delta}}. \tag{3}$$

The shape of the interference curve in the initial period before the long-term decrement (Fig. 4, curve a) is not sinusoidal, but is characterized with the round tops and sharp bottoms. This characteristic was confirmed by assuming ξ in Eq. 3 to be unity. Therefore, the film is considered to have a good transparency and a good flatness in the initial period of the sample deposition. Unfortunately, we could not simulate the observed shape quantitatively, since we could not estimate r_{23} on account of the lack of realistic data for the complex refractive index of the gold substrate fabricated by vacuum deposition.

The shape of the interference curve after the long-term decrement of the intensity (Fig. 4, curve b) is almost sinusoidal. This shape is reproduced by assuming R to be the sum only of the first and second terms of Eq. 2. Thus the attenuation of light in the film is considered serious when the sample is deposited to a large thickness at low temperatures. Such attenuation may arise from the scattering of light, since chlorobenzene does not absorb the laser light with the wavelength of 633 nm. It should be noted that the amplitude of the above sinusoidal change was much smaller than that expected from the value of r_{12} inferred from the curve in the initial period. This implies that the flatness of the sample surface is degraded when the thickness of the low-temperature film was increased.

(ii) Initial Amorphousness of Deposited Samples and Their Crystallization by Annealing. The structure of the vapor-deposited chlorobenzene and its crystallization due to annealing have been studied preliminarily with Raman scattering and X-ray diffraction.[5] In short, chlorobenzene films deposited on substrates at 80 K or below do not initially show Raman bands attributed to lattice vibrations, nor do they show X-ray diffraction peaks attributed to the periodic crystalline structure. Thus the films are said to be amorphous initially. These films undergo crystallization in the temperature range around 105 K when the temperature is raised for annealing.

We performed Raman measurements with the new vacuum chamber. Figure 5 shows the evolution of the spectrum for a sample deposited at 15 K. The spectra shown were selected

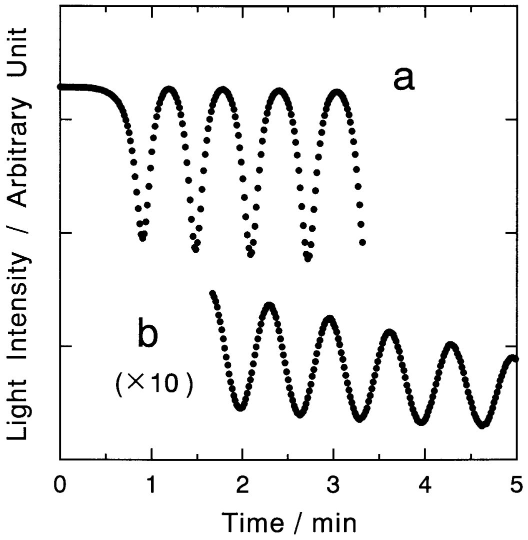

Fig. 4. Enlarged plots of the light intensity transmitted through the sample during the deposition at 40 K. (a) Change in the initial period, (b) change after the long-term decrement of the intensity (multiplied ten times). The abscissa is arbitrarily shifted to compare the shapes of the two curves.

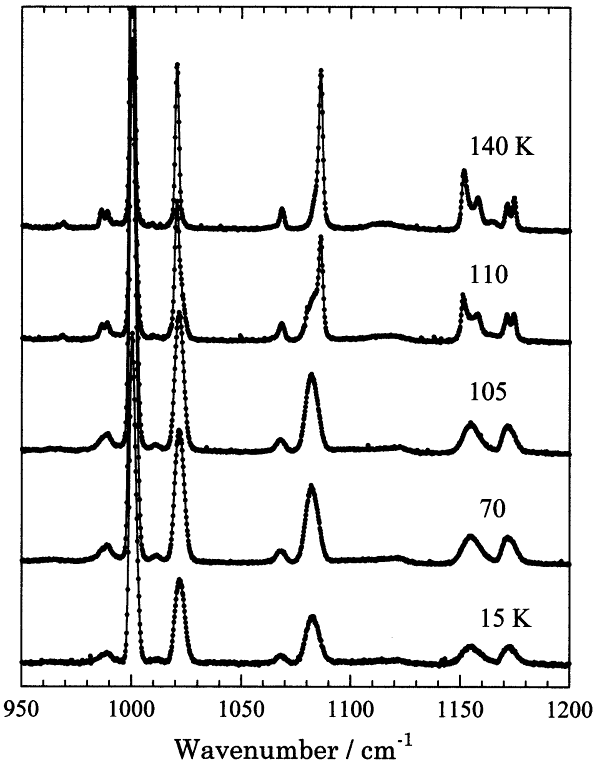

Fig. 5. Evolution of Raman spectrum for the sample deposited at 15 K. The spectra shown were selected from those measured by raising the temperature stepwise.

from those measured by raising the temperature stepwise with the interval of 15 K. The accumulation time for each spectrum was 100 s, and the temperature was raised to the next point within about 10 min. In the temperature region between 100 and 110 K, we inserted extra measurements. As is seen in this figure, a large change took place between the spectra at 105 and 110 K. Since Bragg peaks appear in X-ray diffraction patterns by the annealing in the same temperature region (see Fig. 7 shown later), the above spectral change is considered to indicate the crystallization of the sample.

In Fig. 6, we compare the evolution of the width of the band observed around 1020 cm^{-1} for the samples deposited at 15 and 78 K. The width was estimated by fitting the observed data with a Gauss function, but was not corrected for the spectral slit width of the monochromator of about 1.5 cm^{-1}. Similar plots can be made for many other Raman bands. The deposited samples initially show a large band width, which may be ascribed to the large distribution of the molecular circumstance in the amorphous state. The width shows an irreversible narrowing by the annealing. It is remarkable, however, that the amorphous state of chlorobenzene shows very small changes of the band width until it finally undergoes an abrupt crystallization. This is a characteristic of the amorphous states of simple organic molecules such as benzene or mono-substituted benzenes.[5]

The results shown in Fig. 6 indicate that the amorphous chlorobenzene deposited at 15 K crystallizes around 110 K. This temperature seems slightly higher than that for the sample deposited at 78 K, and the difference will be discussed later in relation with the initial structures of samples deposited at different temperatures. It should be noted here also that both the crystallization temperatures observed for the above two samples were slightly higher than that estimated in the previous study.[5] This is considered to arise from the fact that the overall rate of the temperature elevation in the present study (roughly 10 K in 10 min) was faster than that in the previous study (roughly 10 K in 30 min).

(iii) Crystallization at Constant Temperatures. As has been mentioned above, amorphous chlorobenzene crystallizes when the temperature is raised to the region from 105 to 110 K. We studied this crystallization by monitoring X-ray diffraction at several constant temperatures. Figure 7 summarizes the X-ray diffraction patterns of a chlorobenzene film at several stages of the annealing by the stepwise temperature elevation. It is seen that Bragg peaks attributed to microcrystals appear in the above mentioned temperature region. The Miller indices in the figure were assigned on the basis of the crystal data at 120 K.[8]

Figure 8a presents a plot of the intensity change of the (1 2 1) Bragg peak observed for the samples deposited at 78 K. We raised the temperature of the substrate from 78 K to each annealing temperature indicated within about 5 min. The ordinate of the figure indicates the integral intensity of the peak normalized by the saturating value. It is seen in the figure that the rate of the crystallization increases very much in a narrow temperature region around 105 K. Thus the molecular motion in amorphous chlorobenzene is activated very much in this temperature region, although no glass transition takes place. Detailed analysis of the above crystallization processes will be reported elsewhere.[9] It should be noted that, for the samples deposited at 78 K, the growth of the Bragg peak seems to start after some induction period characteristic to the annealing temperature.

Figure 8b similarly shows the growth of the (1 2 1) Bragg peak during the annealing of the samples deposited at 25 K. It is almost the same as for the samples deposited at 78 K that the growth rate of the Bragg peak increases very much in a narrow temperature region around 105 K. However, it should be noted

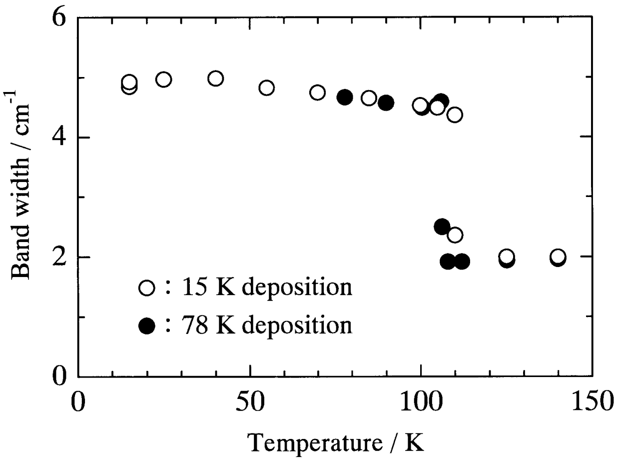

Fig. 6. Evolution of the width of the Raman band around 1020 cm^{-1} observed for the samples deposited at 15 and 78 K. Open circles: 15 K deposition, closed circles: 78 K deposition. The width was not corrected for the spectral slit width of the monochromator of 1.5 cm^{-1}.

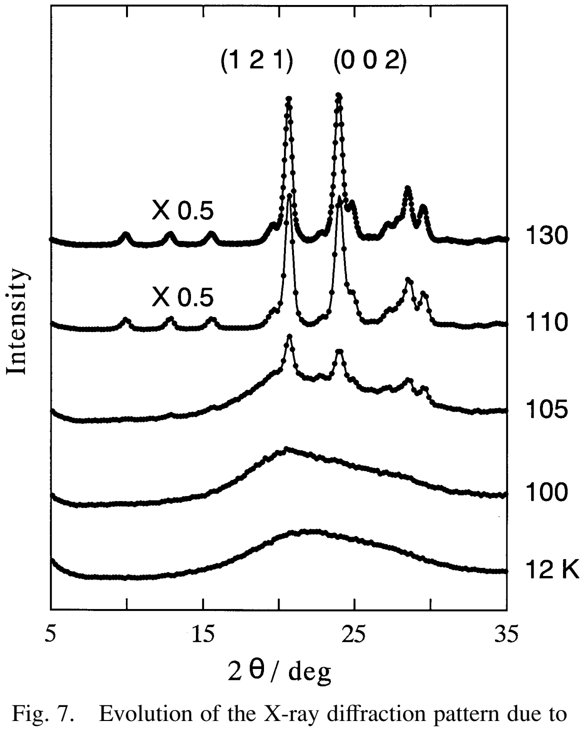

Fig. 7. Evolution of the X-ray diffraction pattern due to the annealing of the sample deposited at 12 K.

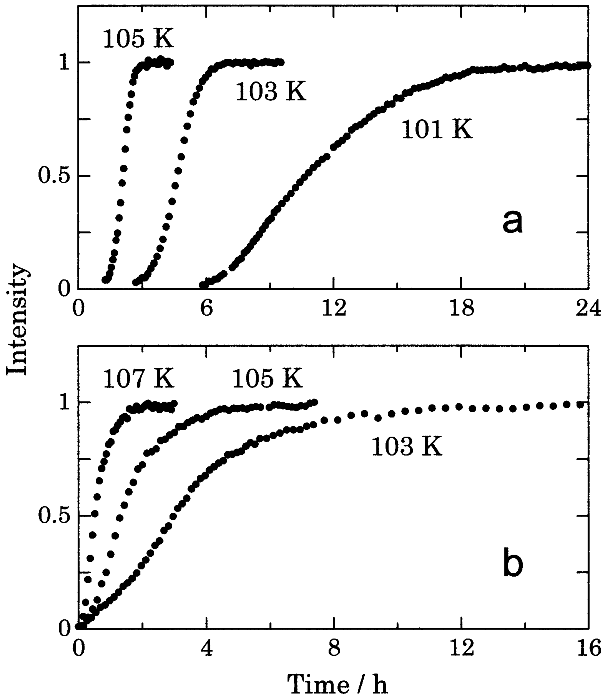

Fig. 8. Increase of the integral intensity of the (1 2 1) peak in the X-ray diffraction patterns during the annealing at a constant temperature indicated. (a) Samples deposited at 78 K, (b) samples deposited at 25 K. The ordinate is the value normalized by the saturating value after a long annealing.

that the Bragg peak started to grow at the time when the temperature was raised to the annealing temperature. Namely, no induction period was needed for the samples deposited at 25 K. Similar difference in the behavior against the annealing was observed in the Raman spectra for the samples deposited at 15 and 78 K.

(iv) Density Inhomogeneity of Samples Prepared at Low Temperatures. We have described so far about the difference between the properties of amorphous chlorobenzene prepared at 78 K and at lower temperatures. For comparing their properties, we made the thickness of all the films to be about 10 μm. The samples prepared at 78 K were transparent, while those prepared at temperatures as low as 15 or 25 K were slightly opaque. The former transparent samples needed some induction period before starting the crystallization, whereas the latter opaque samples did not need such an induction period.

Let us recall that light scattering occurs in a medium that has spatial inhomogeneity of polarizability. As the cause of the polarizability inhomogeneity in molecular solids, there are two possibilities. One is the disorder in the orientational distribution of microcrystals with an anisotropic polarizability. The other is the inhomogeneity in the molecular density. Since our samples were amorphous from preparation, the inhomogeneity in the polarizability is not due to the orientational disorder of microcrystals. As is sometimes pointed out, amorphous materials might include very-small-size microcrystals which are not detectable by the methods such as Raman scattering or X-ray diffraction. However, light scattering arising from such a cause is not considered serious in our present case, even if there is a distribution of such microcrystals in the sample. This is because the anisotropy of the refractive index of the chlorobenzene crystal is inferred to be small,[10] and the polarizability inhomogeneity arising from the above cause would be small.

Thus the polarizability inhomogeneity responsible for the observed light scattering is considered to arise from the inhomogeneity in the molecular density in the amorphous samples. It is likely that molecules deposited on the sample surface at very low temperatures are frozen rapidly at the positions of local potential minima, even if the potential energies of their conformations are much higher than those of the relaxed conformation. By repeating such depositions, microscopic spaces may be left among the molecular aggregates, producing as a result non-negligible inhomogeneity of the refractive index as large as 0.5, that is, the difference between the indices of liquid chlorobenzene and vacuum. This inhomogeneity in the refractive index is fairly large compared with the inhomogeneity that might arise from the orientation distribution of anisotropic microcrystals,[10] and may cause the light scattering in the sample deposited at very-low temperatures.

The same density inhomogeneity as considered above may have made the relaxation behavior of the opaque samples different from that of the transparent samples. Namely, the molecular conformation in the amorphous sample frozen at 25 K may have been far apart from that of the crystal. Thus to promote the crystallization, higher annealing temperatures were needed compared with those for the samples prepared at 78 K. However, the free space left around the molecular aggregates allowed the molecular diffusion to some extent, making the initiation of the crystallization easier. This is in contrast with the behavior of the transparent and dense samples, in which cooperative molecular motions and long induction periods were needed to start the crystallization.

The above mentioned difference among amorphous chlorobenzene samples prepared at different deposition temperatures may be related to the difference in the enthalpy of the samples. It has been known that the vapor-deposited glassy states have higher enthalpies in general than the states obtained by the mild conditions such as the quenching of liquids, and that the enthalpy of the vapor-deposited glassy state is higher as the deposition temperature is lower.[11,12] The high-enthalpy glassy states show prolonged relaxation phenomena below the glass-transition temperature, and seem to approach the states of the liquid-quenched glasses. In our study, however, we have not obtained any structural information related to the difference between the transparent and opaque amorphous states of chlorobenzene. Raman scattering has revealed itself insensitive against the small structural difference in the amorphous state. By X-ray diffraction, on the other hand, we have obtained an indication that the diffraction pattern changes slightly by the annealing. Detailed analyses are now undertaken in our laboratory, and will be published elsewhere.[13]

Finally, we would like to touch on the importance of monitoring the light transmission through the sample in the study of amorphous or glassy molecular systems. By this method, we can obtain some information on the optical quality of the sample, as it has been shown in this paper. In addition, we recently found that the light interference in the transparent samples is sensitive to a slight change of the refractive index, and this gives the information on the relaxation in the sample by the annealing.[14]

X-ray measurements were performed with the aid by S. Ohta and I. Onozuka. The contribution by M. Murai in the analysis of the Raman data is also appreciated.

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10 So far as we know, there is no experimental datum of the refractive-index anisotropy of the chlorobenzene crystal. However, the magnitude of this anisotropy is inferred to be about 0.2 or smaller, since the corresponding anisotropy is from 0.3 to 0.4 even for fairly anisotropic crystals such as naphthalene or anthracene. For these crystals, the refractive-index anisotropy is estimated by the Maxwell's relation from the dielectric constant anisotropy. See for the dielectric constant anisotropy of these crystal; R. W. Munn and D. F. Williams, *J. Chem. Phys.*, **59**, 1742 (1973), N. Karl, H. Rohrbacher, and D. Siebert, *Phys. Status Solidi A*, **4**, 105 (1971).

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