Bull. Chem. Soc. Jpn., ***69***, *2831—2838 (1996)*

Amorphous State of Vacuum-Deposited Benzene and Its Crystallization

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(Received May 21, 1996)

The structure of benzene films that were vacuum-deposited on cold-metal substrates to be 5—20 μm in thickness was studied with Raman spectroscopy and X-ray diffraction. Films deposited below 30 K were amorphous. They crystallized when the temperature was raised to about 60 K. If the substrate temperature at sample deposition was set above 45 K, films including crystalline particles were obtained. Structural relaxation in the amorphous state did not take place in an appreciable manner before the crystallization. Only an increase in intramolecular Raman-band intensities was observed during the relaxation in the amorphous state. Such behavior of amorphous benzene is compared with that of amorphous states of other simple organic compounds. The above crystallization temperature is discussed in relation to the previously estimated glass-transition temperature of benzene by referring to NMR data.

Amorphous states of simple organic compounds have long attracted the attention of people who are interested in properties of solid molecular systems.[1—3] We have studied the structure and structural relaxation of amorphous molecular systems by using Raman and infrared spectroscopies.[4—11] Three types of organic molecules, namely polyacenes, polyphenyls, and long-chain normal hydrocarbons, have been studied. In these studies, amorphous samples were prepared as films with the thickness of 5—20 μm by the vacuum-deposition of molecules onto cold substrates. Study of amorphous benzene has been desired, since benzene is the common origin of the polyacene and polyphenyl groups and also is one of the most important organic compounds. However, it has been considered that the amorphous state of benzene might be difficult to make because of its simple molecular shape. We thus tried to prepare amorphous benzene and studied its Raman spectra. We also studied, by monitoring the Raman-spectral evolution, the relaxation in amorphous benzene that is finally transformed into the crystalline state.

Raman spectroscopy has shown its ability for studying amorphous molecular systems.[4—11] However, some other methods have been desired for inquiring into the complementary and more direct information on the structure, since the absence of definite Raman bands in the lattice-vibration region does not exclude the existence of short-range order much smaller than the wavelength of the excitation light. Electron diffraction has been applied to the study of amorphous naphthacene and pentacene films prepared by vacuum-deposition on cold substrates.[1] However, it is difficult to apply this method to the study of amorphous films of a variety of organic compounds, since special substrates such as a thin carbon film supported by copper mesh are needed.[1] It should be noted also that the real temperature is difficult to determine for the sample on such a thin low-temperature substrate in a vacuum. Therefore, electron diffraction is not appropriate for the study of amorphous films made of small molecules.

X-Ray diffraction has been attempted to analyze the structure of amorphous water[12] and toluene,[13] and seems more informative than electron diffraction. However, the previous studies have been done on amorphous samples as thick as 1 mm. We needed the data on much thinner samples for comparing with the Raman results. To use thin samples is considered important also to avoid the generation of a temperature gradient in the sample during the sample preparation at low temperatures. We thus designed and constructed a cryostat for the in situ X-ray measurement of vacuum-deposited thin films. By using this cryostat, we tried to obtain diffraction data for analyzing the structure of amorphous benzene, and also tried to study its relaxation process.

The glass formation of simple organic compounds has been explored by studies on binary mixtures[14] or by the microemulsion technique.[15] The glass-transition temperature (T_g) of benzene has been estimated to fall in the range 120—130 K.[14,15] We observed, in this study, that the vacuum-deposited amorphous benzene crystallizes around 60 K. We will discuss the relationship between these characteristic temperatures. We would like to emphasize that this paper is the first report on the amorphous-state formation of benzene in the neat state.

In this paper, we display first Raman spectra of benzene films vacuum-deposited at low temperatures, and then their spectral evolution during the annealing by the stepwise elevation of temperature. We next report the results of X-ray diffraction of similarly-prepared benzene films. It is shown that amorphous benzene is prepared by the vacuum deposition below 30 K, and crystallizes around 60 K. We discuss these results for benzene in comparison with those for other compounds studied previously. Finally, we discuss the crystallization temperature (T_c) observed for amorphous benzene in relation to previously estimated T_g by referring to the NMR data.[16]

Experimental

(i) Raman Scattering Measurements. In situ Raman measurements were done by using a cryostat that was designed and constructed by us for the vacuum deposition of samples that are liquid at room temperature. A turbomolecular pump with a liquid-nitrogen-trap was used for the evacuation. The base pressure of the vacuum chamber was of the order 10^{-5} Pa. A gas-flow-type cold finger (Janis Research Co., Supertran-B) was used for cooling the substrate as in our previous studies.[8] The substrate was a copper block the surface of which was coated with gold. The substrate temperature was controlled with a temperature controller (Lake Shore, 805), and was measured with a chromel–gold/iron(0.07%) thermocouple. An electromagnetic valve (General Valve, 9-vvv-900) was attached at the bottom of the vacuum chamber for introducing the sample vapor. A sample tube containing liquid benzene was connected to the valve. Reagent-grade benzene (Wako Pure Chemical Industries) was used after distilling and degassing. For estimating the thickness of the deposited film, the interference of the reflected laser light was monitored. The deposition rate was controlled to the order 0.2 μm min^{-1}.

The optical system for the Raman measurements was almost the same as in the previous studies.[6,8] The 514.5 nm radiation from an Ar$^+$-ion laser was used for the excitation with a power of 40 mW. The line-focussing condition of the laser light was used for diminishing the sample heating by the light. The excitation light was introduced with the s-polarization at an incidence angle of 60°. The scattered light was collected at the right angle and introduced into a double monochromator (Spex Industries, 1403). No polarization analyzer was used in the optics collecting the scattered light. All the spectra were measured with a spectral slit width of about 3 cm^{-1}.

(ii) X-Ray Diffraction Measurements. In situ X-ray diffraction measurements of vacuum-deposited films were made by using a cryostat that was designed and constructed also by us. The same evacuation system as in the Raman experiment was used. The base pressure of the vacuum chamber was of the order 10^{-5} Pa. A cross-sectional view of the cryostat is displayed in Fig. 1. In short, it is equipped with a closed-cycle helium refrigerator (Daikin, V204SCL), an electromagnetic valve the same as in the Raman experiment, and two 0.3-mm thick curved beryllium windows for the X-ray measurements. It is also equipped with a diode laser and a photodiode for monitoring the sample thickness by recording the interference of light. The substrate for the sample deposition was gold-coated copper. The temperature of the cold finger cooled with the above refrigerator was controlled with a temperature controller (Scientific Instruments, 9650). The substrate temperature was measured with the same thermocouple as in the Raman measurements.

A powder X-ray diffractometer (Mac Science, MXP3H) was used for the measurement along with the above cryostat. The two arms of this diffractometer, one for the X-ray source and the other for the detector, can both be driven. Cu or Mo X-ray sources were used at the condition of 40 kV and 20 mA. Diffracted X-rays were detected with a scintillation counter after they were monochromatized with a graphite monochromator. One of the two types of the scanning condition, namely the synchronized θ–2θ scanning and the 2θ scanning with the fixed incidence angle at 2°, was chosen taking account of the sample thickness and/or of the target range of the scattering parameter. Because of geometrical restriction by the beryllium windows, the allowed diffraction angle 2θ was limited below 103° in the case of the θ–2θ scanning, and below 56° in the 2θ scanning.

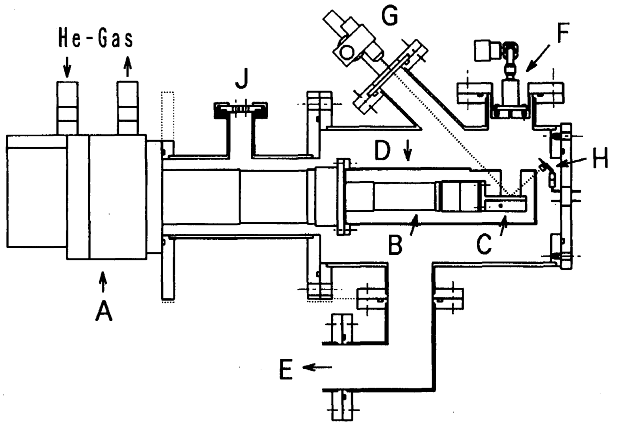

Fig. 1. A cross-sectional view of the cryostat for the in situ X-ray measurement on vacuum-deposited thin films. A: body of helium refrigerator, B: cold finger, C: substrate, D: radiation shield, E: port for evacuation, F: electromagnetic value for sample introduction, G: diode laser, H: photodiode, J: feed-through for heater and thermocouple. X-Ray is introduced and detected in the plane including the central axis of the electromagnetic valve (F) and perpendicular to this cross-sectional plane. Therefore, the curved beryllium windows, which are soldered on the outside of the cylindrical body of the chamber, are not depicted in this figure.

Results and Discussion

(i) Raman Spectra of Benzene Films Deposited at Low Temperatures. In Fig. 2, low-frequency Raman spectra of benzene in various state are compared. The intensity of each spectrum is normalized by that of the 990 cm^{-1} band which will be discussed later. Short horizontal lines at the left-hand-side in the figure indicate the base line for each spectrum. The spectrum of the crystalline powder at 6 K was measured for a benzene sample which was put in a glass tube and slowly cooled in a cryostat (Oxford Instruments, MD5). The sharp Raman bands of the crystal below 140 cm^{-1} are attributed to the rotational lattice vibrations split by the intermolecular interaction.[17] In contrast with this spectrum, the spectrum of the molten liquid at 281 K does not show definite bands, indicating that there is no long-range structural order in the liquid.

Spectra of the films deposited on the substrate at various temperatures are shown in the same figure. The spectra of the films deposited at 17 and 30 K are structureless as that of the liquid is, while the films deposited at 45 and 78 K show weak bands which apparently correspond to those of the crystalline sample. The spectra at 17 and 30 K indicate that the molecules deposited at these temperatures were frozen rapidly on deposition. In other words, the molecules were trapped at positions of local minima of potential energy, forming disordered amorphous states without long-range structural order. The spectra at 45 and 78 K indicate, on the other hand, that the molecules deposited at these temperatures maintained the kinetic energy for moving around on the surface and made fairly ordered structures like in the crystal. Note that the bands appearing in the spectrum at 45

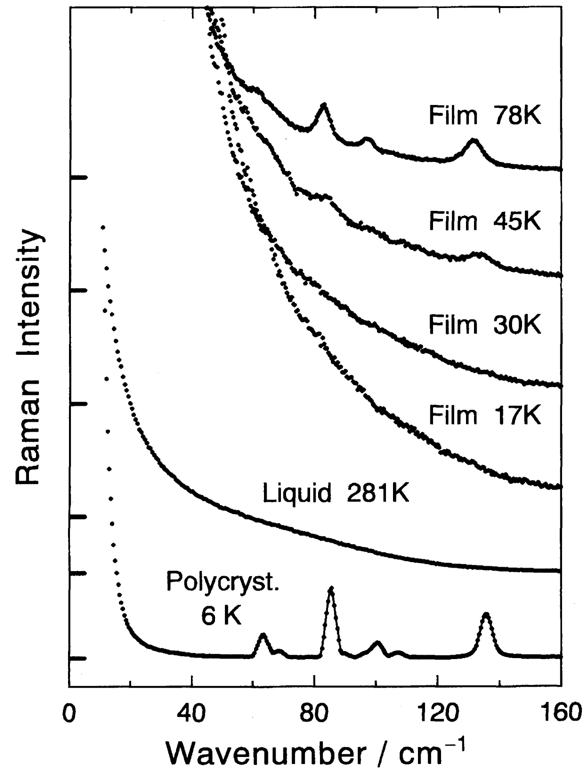

Fig. 2. Low-frequency Raman spectra of benzene in various states. The spectra of the films were recorded just after the deposition on the substrate at the temperatures indicated. The intensity of each spectrum is normalized by that of the 990 cm^{-1} intramolecular vibration band.

K are broad and weak compared with those in the spectrum at 78 K. This suggests that the crystalline ordering was not sufficient in the film formed at 45 K.

The amorphousness of the films deposited at low-temperatures is also shown by the spectral features of intramolecular Raman bands. In Figs. 3a and 3b, the totally-symmetric breathing band around 990 cm^{-1} and the in-plane C–H deformation-band(s) around 1160—1190 cm^{-1} are compared respectively for the film deposited at 17 K, crystalline sample at 6 K, and liquid at 283 K. The intensity of each spectrum in these figures is adjusted arbitrarily for comparing the band shapes. The 990 cm^{-1} band (Fig. 3a) of the amorphous film has a peak frequency almost the same as that of the crystal, but its band width is much larger than that of the crystal, even larger than that of liquid.[18] This indicates a large distribution of molecular circumstances in the amorphous film.

A similar situation is also seen in the spectral region around 1160—1190 cm^{-1} displayed in Fig. 3b. Thus the amorphous film shows a broad band as the liquid does, while the crystal shows four distinguishable bands which are considered to be split on account of the intermolecular interaction in the crystal.[19] To be noted is that the band shape of the amorphous film seems to reflect the relative intensities of four peaks of the crystal. This forms a contrast to the fact that the broad band of the liquid has a broad Lorentzian-type shape indicating the short relaxation time of the vibrationally-excited state in the liquid. The band shape of the amorphus film might suggest not only a wide distribution of the molecular circumstance in the amorphous film, but also the existence of precursors of intermolecular interactions like in the crystal.

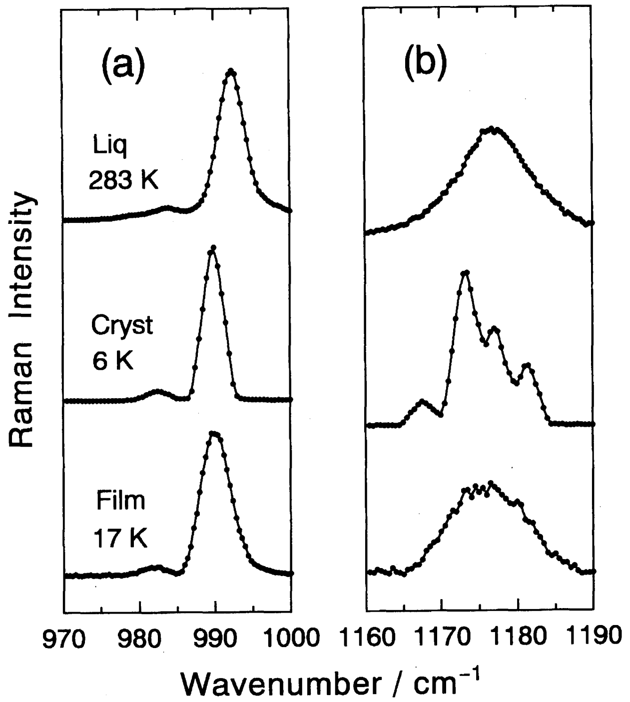

Fig. 3. Raman band in the intramolecular vibration region of benzene in various states; from top to bottom, molten liquid at 283 K, polycrystals at 6 K, and film vacuum-deposited at 17 K. The intensity of each spectrum is adjusted arbitrarily for comparing the band shapes.

(ii) Evolution of Raman Spectra during Annealing. Figure 4 shows the evolution of the low-frequency Raman spectra of the film deposited at 17 K during the annealing by the stepwise temperature rise. It took about an hour to record several spectra at a constant temperature. The time interval between the measurements at different temperatures was from 10 to 20 min. As in the case of previous studies,[8] no conspicuous difference was found in the results even if we changed the experimental conditions to some extent. The ordinate of Fig. 4 indicates the Raman intensity divided by $n(\omega)+1$ to make a correction for the thermal excitation of the vibration in the low-frequency region,[20] where ω is the angular frequency of the vibration, and $n(\omega)=\{\exp(\hbar\omega/kT)-1\}^{-1}$. The original intensity of each spectrum was normalized by that of the 990 cm^{-1} band. As it is seen in the figure, the spectrum was structureless up to 49 K. At 58 K, an abrupt spectral change took place, giving new bands essentially the same as that of the crystal. Thus the film made by the deposition at 17 K was initially amorphous, and it crystallized at 58 K by the annealing.

It is not clear what was the cause of the large intensity rise at the low-frequency region of each spectrum. Since the initial film was slightly opaque on deposition, the elastically-scattered laser light might have been detected as stray light in the monochromator. However, this rise diminished a little after the crystallization, on which the elastic light

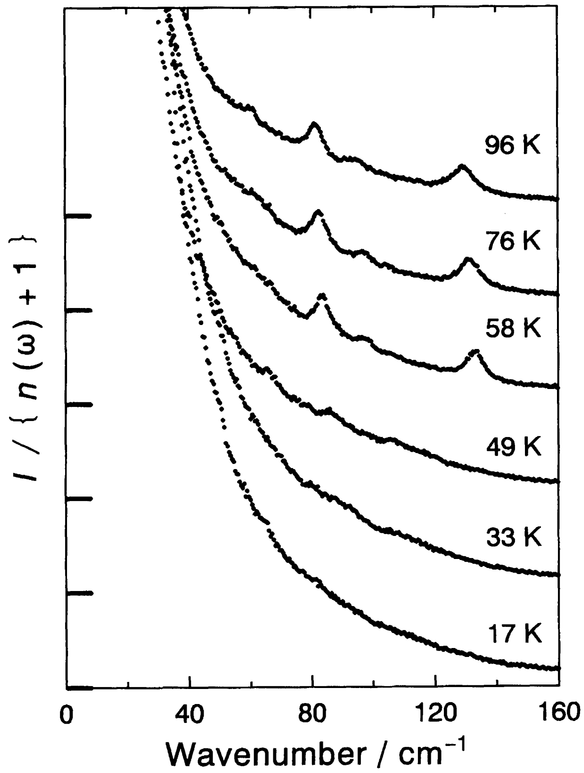

Fig. 4. Evolution of low-frequency Raman spectra during the stepwise annealing of the benzene film deposited at 17 K. The ordinate is the spectral intensity corrected for the thermal excitation of vibrational modes (see the text).

scattering increased, apparently because of the appearance of crystalline grain. Since crystalline samples with macroscopic grain size do not give so strong underlying scattering intensity above 20 cm^{-1} (see the bottom spectrum in Fig. 2), the large intensity shown by the amorphous film in the low-frequency region might arise from Raman scattering allowed by the disorder in the sample. There remained an unnegligible rise even at 96 K. Therefore, the sample might still have included some degree of disorder even at this temperature.

Spectral evolutions due to the annealing were also seen in the intramolecular vibration region. Figure 5 shows the evolutions in the same spectral regions as shown in Fig. 3. The sample was the same as that of Fig. 4. The band around 990 cm^{-1} showed changes in the peak frequency and width in the same temperature region where the lattice spectrum changed (Fig. 4). The band width was broad below 49 K and became narrow above 58 K (see Fig. 6 and the related discussion for the band-width data similarly recorded). The spectral region around 1160—1190 cm^{-1} also showed a corresponding change. In this case, the fine structure arising from the factor-group splitting appeared on crystallization, taking the place of the initially-observed broad band.

To specify the temperature region where the crystallization takes place, we examined the spectral evolution for five samples deposited below 30 K. It was found that the crystallization takes place at almost the same temperature, from 55 to 60 K, irrespective of the initial temperature at deposition and of the deposition rate. Figure 6 shows an example of the change of the width of the 990 cm^{-1} band. In this measurement, we raised the temperature by 2 K steps in the crystallization region, and stayed more than 10 min at a constant temperature. The band-width change occurred in a narrow temperature region around 60 K. Thus this may be roughly considered to be the characteristic temperature T_c

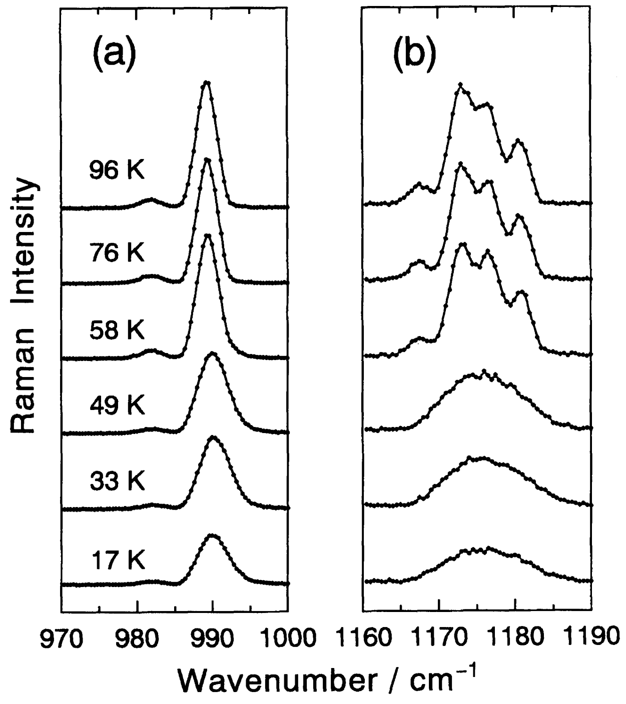

Fig. 5. Evolution of intramolecular-region Raman spectra during the stepwise annealing of the benzene film deposited at 17 K. The ordinates of figures (a) and (b) are mutually shifted to show the correspondence of the bands observed at the same temperature.

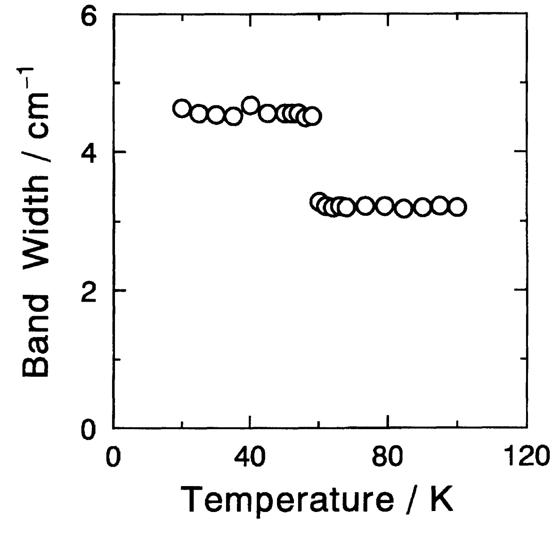

Fig. 6. Change of the width of the 990 cm^{-1} Raman band observed for the benzene film deposited at 20 K. The width is not corrected for the spectral slit width of the monochromator of about 3 cm^{-1}. An abrupt change was observed between the measurements at 58 and 60 K.

for the crystallization of amorphous benzene.

Before the above crystallization took place, almost no indication of substantial change was seen in the width of the 990 cm^{-1} band below T_c (Fig. 6). However, the intensity of this band showed a gradual increase as the annealing progressed. Figure 7 shows the change of the integrated intensity of the 990 cm^{-1}band of three samples prepared at different temperatures. These samples had almost the same thickness, about 10 μm. All the samples showed an increase in the intensity before the crystallization took place around 60 K. A similar increase in the intensity was seen for all the Raman bands measured. Such a behavior of amorphous benzene has a strong resemblance to that of amorphous naphthalene,[10] although T_c of amorphous benzene (ca. 60 K) is much lower than that of naphthalene (ca. 105 K). We have previously discussed[10] the possible cause of the increase of the Raman intensity during the annealing of the amorphous molecular systems. Interestingly, the band intensity of the three samples shown in Fig. 7 traces almost the same change irrespective of the deposition temperature. This suggests that the structure of amorphous benzene does not depend strongly on the deposition temperature. We have previously observed that the relaxation behavior of amorphous anthracene depends on the deposition temperature.[9] Therefore, the above behavior of amorphous benzene may reveal the characteristics of the relaxation in amorphous states of compounds with small and simple molecular shapes.

(iii) X-Ray Diffraction by Amorphous Film. Raman spectroscopy has proved of great use in studying the states of amorphous molecular systems. However, as it has been mentioned previously, we cannot exclude the possibility of existence of short-range order in the sample only on the basis of the Raman spectra. Spectroscopy does not bring us direct information of the sample structure either. For these reasons, we did X-ray diffraction measurements on molecular films vacuum-deposited on cold substrates.

Figure 8a shows the X-ray diffraction pattern of a benzene film deposited on a metal substrate at 13 K. For this sample, the deposition rate was about 0.2 μm min^{-1}, and the final film thickness was 9 μm. The abscissa of the figure is the scattering parameter $s=(4\pi/\lambda)\sin\theta$, where λ is the X-ray wavelength and θ is the half-scattering-angle. This diffraction was measured with the 2θ scanning condition with the X-ray source (Cu $K\alpha$) fixed at an incidence angle of 2°. This condition was chosen to reduce the X-ray intensity coming from the diffraction by the substrate. The pattern shown in Fig. 8a was corrected by subtracting the underlying contribution from the substrate (see the slope underlying the broad peak in the similarly-measured original pattern shown in Fig. 9). In Fig. 8b, the diffraction pattern of liquid benzene at 293 K is also shown for comparison. This pattern was measured with the θ–2θ scanning condition with the same X-ray source. This result for the liquid is essentially the same as the previously reported one.[21]

The broad peak observed for the film at 13 K resembles that of the liquid in shape. This indicates that this film was in an amorphus state even from the view point of X-ray diffraction. It is easily verified that the so-called Laue function, which has the form $\sin^2(\pi Mm)/\sin^2(\pi m)$ for a linear periodic lattice and

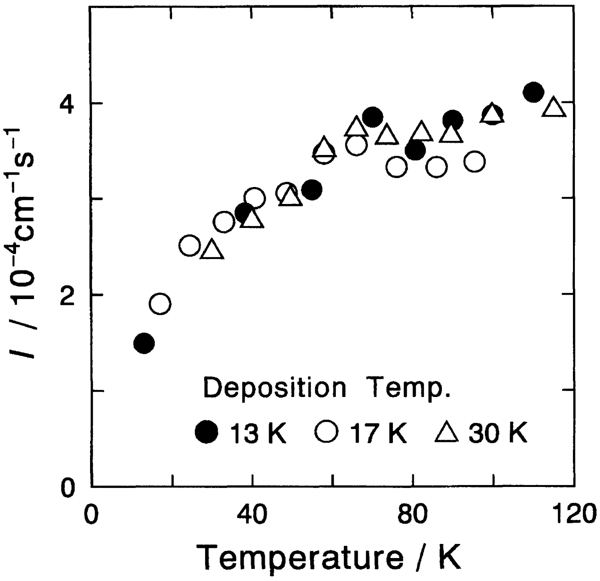

Fig. 7. Increase of the integrated intensity of the 990 cm^{-1} band of the benzene films during the annealing. Data for the three independent samples deposited at different temperatures are plotted. Thickness of all these samples was about 10 μm.

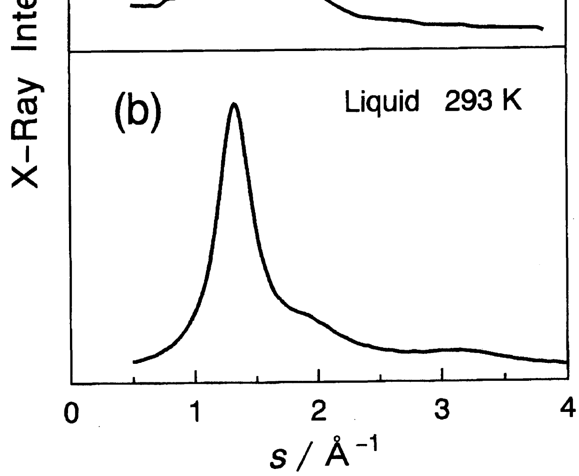

Fig. 8. X-Ray diffraction patterns of the amorphous benzene film at 13 K and molten benzene liquid at 293 K. The abscissa is the scattering parameter s (see the text). For the film, the diffraction intensity coming from the substrate has been subtracted.

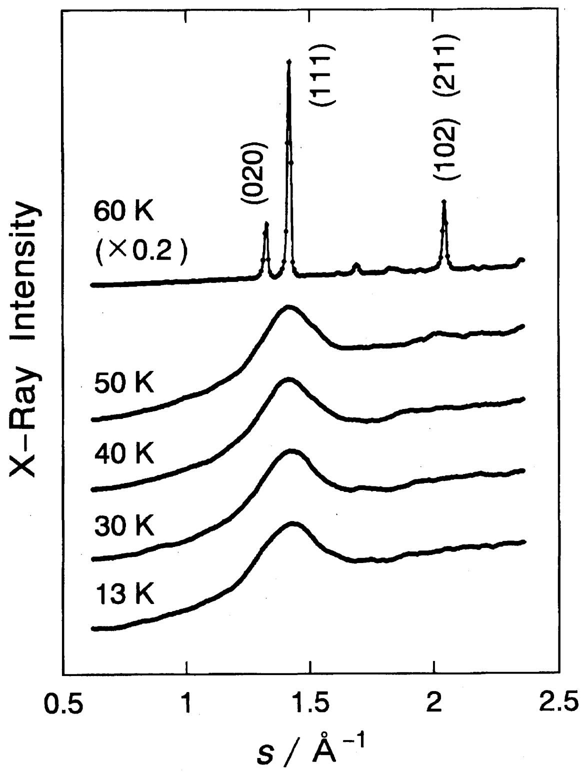

Fig. 9. Evolution of the X-ray diffraction pattern during the stepwise annealing of the benzene film deposited at 13 K. No correction was made for the diffraction intensity coming from the substrate. The ordinate scale for the pattern at 60 K is changed five times to reduce the peak height in the figure. Miller indices of the benzene crystal are indicated for some of the Bragg-diffraction peaks which appeared after the crystallization at 60 K.

is the base of the sharp diffraction observed for crystalline materials, gives a definite peak of m-th order diffraction when the number M of the incorporated periodic-lattice units is as large as twenty. Therefore, the blurred diffraction pattern observed for the amorphous film indicates that there was no structural periodicity which extended to the size as large as tens of the lattice parameters. This is a new and important view of the microstructure of amorphous molecular systems. If one takes a close look at Fig. 8, the peak position of the film is found at a slightly larger scattering parameter that the liquid. This may indicate that the distribution of the interatomic distances in the low-temperature amorphous film is slightly shifted to the shorter side compared with that of the room-temperature liquid.

For the analysis of the microscopic structure of the amorphous film, we need diffraction data in a wide range of the scattering parameter s. In addition, the intensity data must be reliable enough to bear up against various numerical corrections and transformations throughout the analysis. We tried the measurement with a Mo$K\alpha$ X-ray source of the s value up to 16, and calculated the electron radial-distribution-function. However, the diffraction from the substrate was so strong that we have not yet obtained reliable results.

(iv) Evolution of X-Ray Diffraction during Annealing. Similarly to the case of the Raman measurements, we monitored the evolution of the X-ray diffraction pattern of the deposited films during the annealing by the stepwise temperature elevation. In Fig. 9, we display the result obtained for a film deposited at 13 K. The diffraction pattern was almost unchanged up to 50 K. This is in harmony with the Raman results that no significant change in the spectral features was observed before the crystallization took place. An abrupt change was observed when the temperature was raised to 60 K, where many sharp diffraction peaks appeared in place of the broad peak. All the new peaks can be assigned to the diffraction from the benzene crystal of known structure,[22] if we make allowance for thermal shrinkage of the lattice at the low temperature. The relative intensities of these diffraction peaks showed a small sample dependence, suggesting the occurrence of a weak preferential orientation of microcrystals in each sample. However, such a behavior was not so strong as to manifest the effect of the substrate.

The above X-ray observations were reproducible for many films prepared in similar conditions. The crystallization took place in almost the same temperature range as monitored with Raman spectra. On the basis of the Laue function described above, the size of the crystalline particles of benzene detectable by X-ray diffraction is estimated to be the order of 100 Å. On the other hand, the crystalline particles that show definite Raman bands of lattice vibrations may be on the order 1000 Å or larger, since the structural coherence comparable to the light wavelength is required in this case. Thus the above Raman and X-ray results indicate that the growth of crystalline particles in amorphous benzene proceeds rapidly from the sub-hundred to the thousand-ångstrom region in a narrow temperature range around 60 K. In other words, the rate of the diffusion motion of benzene molecules changes largely in this temperature region. It should be noted that the present Raman and X-ray results do not exclude the possible existence of small nuclei of the crystals in the initial amorphous films. A slight indication of such structures was seen in Raman spectra in the intramolecular-vibration region (see the discussion in the last part of Section (i)).

(v) Glass Transition and Crystallization of Amorphous Benzene. Since amorphous molecular films prepared by the vacuum deposition on cold substrates are considered to be in non-equilibrium states, their relaxation behavior may depend on the thermal history of each sample. However, as has been mentioned,[6,10] amorphous molecular systems sometimes undergo crystallization in a narrow temperature region which is characteristic for each compound and almost insensitive to their thermal history. Such behavior is considered to reflect the large increase of the molecular mobility in the corresponding temperature region, and resembles the grass-transition phenomenon that is observed around a temperature characteristic for each glassy substance.

Angell et al.[14] studied the glass transition in many kinds of binary mixtures of simple organic liquids with differential thermal analysis. They inferred T_g of neat benzene to be 131 K by extrapolating the data, although they thought that this particular extrapolation was not reliable because of the restriction of the data in the region of low concentrations of benzene. Dubochet et al.[15)] studied with similar thermal measurements the glass transition in pseudoternary microemulsions made with an organic liquid and an aqueous phase (propylene glycol–water mixture). They estimated by this technique the T_g of benzene to be about 120 K. These results might seem not incompatible with the well-known NMR results[16)] that the reorientation of benzene molecules about their hexad axes starts to take place in the crystal lattice around 90 K.

In contrast to these findings, the crystallization in vacuum-deposited amorphous benzene takes place around 60 K. This temperature (T_c) seems reasonable as compared with crystallization temperatures of amorphous naphthalene (ca. 105 K)[10)] and amorphous anthracene (ca. 200 K).[9)] However, if one took a simple model that the crystallization in glassy materials must occur above T_g, and if he stuck to the previous results on T_g, he might throw some doubt on our results. To reply to such a question, we would like to point out two issues as follows.

The first issue concerns the effect of a small amount of the coexisting ingredient on the glass-forming behavior of molecular substances. We accidentally found that butyronitrile (C_3H_7CN) elevates the crystallization temperature of amorphous benzene to above 80 K, sometimes as high as 120 K. We encountered this phenomenon both in our Raman and X-ray experiments. A small amount of butyronitrile which had swelled the synthesized-rubber O-rings used for the vacuum seal in the preceding experiments in our laboratory was considered to have contaminated the benzene sample. We confirmed the crystallization of amorphous benzene around 60 K by avoiding the use of such old O-rings in the later experiments. Thus T_g estimated by the previous thermal studies cannot be regarded as the true T_g of neat benzene, since the coexistence of foreign compounds could not be avoided in these studies.

The second issue is that, even if the true T_g of benzene fell in the temperature region around 120 K, it may not contradict the T_c of amorphous benzene around 60 K. Amorphous states of simple organic molecules, for which the rigid-body approximation seems to be appropriate, sometimes undergo crystallization without showing an apparent glass transition.[10)] This is considered to reflect the less-complicated structure of the potential-energy surfaces of the amorphous states of these molecules. Because of this, the glass-forming behavior of molecules such as benzene may form a clear contrast to that of molecules such as butyronitrile[23)] or *o*-terphenyl[24)] which have been known to make glass states easily. These latter molecules have freedom for molecular deformation and tend to have asymmetric molecular shapes in amorphous states. Such structural characteristics may stabilize the glass state even at temperatures where the short-range diffusion motion of molecules are allowed. However, in the amorphous states of compounds with simple molecular shapes, the crystallization is considered to precede the glass transition, since the local rearrangement of the intermolecular conformation can take place only with small thermal energies.

Returning to the NMR data, we can roughly estimate the correlation time τ of the reorientation of benzene molecules in the crystal at low temperatures. By extrapolating the line in Fig. 4 of Ref. 16, τ around 60 K is estimated to fall in the range from 10^0 to 10^2 s. These values agree well with the time scale of the crystallization phenomena observed by our Raman and X-ray experiments. Note that the previously-found characteristic temperature 90 K,[16)] which has been related to the onset of the reorientation of benzene molecules, is referred to the time scale of the NMR frequency of the order 10^7 Hz. The crystallization of amorphous benzene observed in our experiments is thus considered to be triggered by microscopic molecular motions which take place in the system much less frequently.

Conclusion

We studied with Raman spectroscopy and X-ray diffraction the structure of the benzene films which were vacuum-deposited on cold metal substrates. The initial state of the films prepared at temperatures below 30 K is amorphous from the view points both of Raman spectroscopy and of X-ray diffraction. This gives us a new aspect that amorphous states made of simple organic molecules can have disordered structures even in the scale as small as tens of the lattice size. The amorphous benzene undergoes crystallization around 60 K. This was observed both in the Raman and X-ray experiments, indicating the rapid growth of the crystalline particles in a narrow region around this temperature. This crystallization temperature T_c would pose a paradox, if we made much of the previously estimated glass-transition temperature T_g of benzene as high as 120 K. The relation between T_c and T_g of amorphous molecular systems was discussed. It was pointed out that the previously estimated T_g of benzene might have been affected by some coexisting ingredient, and also that T_c of amorphous systems made of simple molecules can be lower than the hypothetical T_g which would be observed if the crystallization did not take place. It was further pointed out that the T_c of amorphous benzene around 60 K is reasonable as compared with the T_c of other compounds, and in harmony with the correlation time of the reorientation motion of benzene molecules estimated by extrapolating the NMR data to the same temperature region.

The financial support given by Iketani Science and Technology Foundation during this study is greatly appreciated.

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