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Infrared and Raman Studies of Structural Relaxation in Amorphous Tetracosane, n-$C_{24}H_{50}$

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Structural relaxation in amorphous tetracosane n-$C_{24}H_{50}$ was studied by infrared and Raman spectroscopies. Samples were prepared by vacuum deposition onto cold substrates and the spectral changes were monitored as the temperature was raised stepwise. Several distinguishable relaxation processes were found to take place similarly to the case of amorphous states of other hydrocarbons. However, in contrast to the previous study, we arrived at a conclusion that the initial relaxation of the disordered molecules does not take place in a single step. In the later part of the relaxation, metastable orthorhombic-type subcells were found to appear. They disappear finally when the adjustment of the mutual position of extended molecules occurs to attain the lateral molecular packing of the stable triclinic crystal. The intermolecular interactions along the chain direction are also discussed.

The relation between the vibrational spectra and molecular conformation of normal hydrocarbons has well been studied in crystalline and liquid states.[1,2] Hagemann et al.[3] applied infrared spectroscopy to the study of the relaxation in amorphous states of henicosane n-$C_{21}H_{44}$ (hereafter C21), hexatriacontane n-$C_{36}H_{74}$ (hereafter C36), and a low-molecular-weight polyethylene. They observed the spectral changes as the samples were annealed stepwise with the temperature rise.

We have been studying by Raman spectroscopy the relaxation processes of amorphous systems made with simple organic molecules.[4—9] Raman spectroscopy plays a complementary role to infrared spectroscopy, and is superior for these kinds of studies in the following sense. Namely, the conventional infrared absorption spectroscopy is performed on the samples deposited on transparent substrates such as KBr, and sometimes suffers serious heating effects from the probe light and/or the radiation from the surroundings. Raman measurements, on the other hand, can be performed on samples prepared on metal substrates whose temperature can be determined well. As a Raman study of the relaxation in amorphous long-chain hydrocarbons, we have briefly reported the results on amorphous C36.[4]

In this paper, we report the results of infrared and Raman spectroscopies on the relaxation in amorphous tetracosane n-$C_{24}H_{50}$ (hereafter C24). The samples were prepared on cold substrates, and the spectral changes were studied as the sample temperature was raised stepwise. The crystal of C24 is triclinic[10] at room temperature in contrast to the previously studied C21 (orthorhombic[11]) and C36 (monoclinic[12] or orthorhombic[13]). The main features of the infrared spectral changes observed for C21 and C36 by Hagemann et al.[3] were essentially confirmed for C24. Thus amorphous C24 is also considered to undergo relaxation through several steps turning finally into the structure of the stable crystal. However, with the aid of Raman spectra, we arrived at a conclusion a little different from that of Hagemann et al.[3] as to the initial relaxation of the disordered molecules. We also obtained some new indications that a change of intermolecular interaction along the molecular-chain direction takes place in the final stage of the relaxation.

The appearance of both the triclinic- and orthorhombic-type molecular packings in the lateral direction, which has been observed for C21 and a low-molecular-weight polyethylene in the intermediate step of the relaxation process,[3] was similarly observed for C24. Thus, it is inferred that the energies of the lateral packings of these two types are very similar, and both the packings appear during the relaxation process of amorphous long-chain hydrocarbons irrespective of the type of the packing in their stable crystals.

It is emphasized in conclusion that the relaxation in amorphous long-chain hydrocarbons can be analyzed in detail by applying both the infrared and Raman spectroscopies. The general issues of the relaxation in amorphous molecular systems are also discussed in connection with the observations on amorphous systems of other types of compounds so far studied.

Experimental

Tetracosane was purchased from Tokyo Kasei Kogyo Co. It was purified first by recrystallization from benzene, and then by zone refining. In both the infrared and Raman experiments, the vacuum deposition of the sample was carried out at the substrate temperatures of 18 and 80 K. No significant difference was observed between the results for the samples prepared at these temperatures.

Infrared spectra were measured with a DA3.16 Fourier-transform spectrophotometer (Bomem Inc.) with a spectral resolution of 1 cm^{-1}. The sample chamber was modified to be equipped with a Supertran B cold finger (Janis Research Co.) which can be cooled either with cold helium or nitrogen gases. An 805 temperature controller (Lake Shore Co.) was used for controlling the cold-finger temperature. The sample was evaporated in a small glass furnace, and was deposited onto a cooled KBr plate whose temperature was monitored by an alumel–chromel thermocouple. The sample deposition was carried out under the vacuum of about 10^{-4} Pa. The sample thickness was estimated to be about 10 μm from the absorbance of the vibrational bands. The deposition rate was about 30 Å s^{-1}.

Raman spectra were measured with the cryostat as reported previously.[7] The same cold finger and temperature controller mentioned above were used. The sample was prepared similarly to the infrared experiment, but in the Raman experiments, the substrate was a cold copper block whose surface was coated with gold. The sample thickness was estimated by using a thickness monitor of the quartz-oscillator type. The thickness was about several tens of micrometers and the deposition rate was about 15 Å s^{-1}. The optical system for the Raman measurement was the same as the previous studies.[6] The 514.5 nm radiation from an Ar$^+$ ion laser was used for the excitation with a power of 40 mW. A cylindrical lens was used for the laser-light focussing to diminish the sample heating.

Results and Discussion

(i) Structure of Films Deposited at Low Temperatures. Molecules of long-chain normal hydrocarbons have been known to take the extended chain structure in the crystal, the carbon atoms being arranged in a planar zigzag form.[14] In this so-called *all-trans* conformation, the conformations around all the C–C bonds (except the terminal C–C) are *trans.* On the contrary, in the liquid or gaseous states, the molecules are inferred to have disordered twisted structures in which the conformation around many of the C–C bonds are *gauche.*[2] The room-temperature crystals have three different crystal systems depending on the carbon atom number of the molecule.[10,14] The room temperature crystal of C24 is triclinic with $Z=1$.[10]

In Fig. 1, infrared spectra of C24 films vacuum-deposited on the substrate at 80 K are compared with that of the crystalline powder at 80 K. The small bands indicated by an arrow around 1350 cm^{-1} of the deposited sample are those which have been attributed to the CH_2 wagging vibrations at the molecular portion with *gauche* conformations.[2] Raman spectra of similarly prepared films showed the features of disordered twisted molecular conformations as in the liquid state. Among the Raman features, it should be noted that the deposited samples do not show the band of the longitudinal acoustic mode (LAM)[15] which is an indication of the extended chain structure. See Ref. 4 in which Raman spectra of amorphous C36 have been reported; the spectra of amorphous C24 are almost the same as these. Taking account of all the above spectral features, the C24 films deposited at low temperatures are inferred to have an amorphous structure in which the molecules are disordered and twisted as in the liquid state.

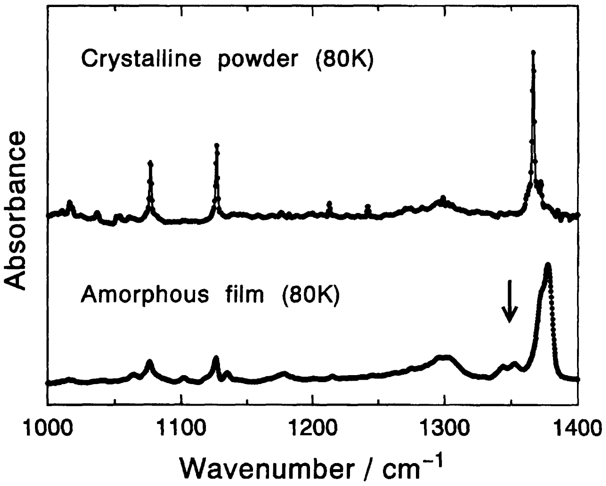

Fig. 1. Infrared spectra of tetracosane n-$C_{24}H_{50}$; (a) polycrystalline sample at 80 K and (b) amorphous sample vacuum-deposited at 80 K.

(ii) Change of Molecular Conformation during Annealing Process. When the deposited films are annealed by raising the temperature stepwise, they show spectral evolutions which indicate that the film structure changes through several stages from the low-temperature amorphous state to the room-temperature triclinic crystal. In the initial stage, spectral evolutions mainly attributable to the intramolecular conformation changes are observed. In the later stages, on the other hand, spectral evolutions attributable to the changes in the intermolecular packing are observed. These structural changes are irreversible, reflecting the fact that the amorphous states prepared by the present method are not thermodynamically equilibrium states.

In Fig. 2, the evolution of infrared spectra of the film deposited at 80 K is shown. The weak bands seen at 1214 and 1244 cm^{-1} in Fig. 2a are the so-called *band progression*[16] of the wagging vibration with the *all-trans* conformation,[17] while the bands seen at 1343 and 1353 cm^{-1} in Fig. 2b are attributed to the wagging vibration of the molecules with *gauche* conformations.[2] Figure 3 shows the relative changes of the integrated intensity of these infrared bands. Figure 3a indicates that the *gauche* conformations made at low temperatures remain frozen in until the temperature is raised

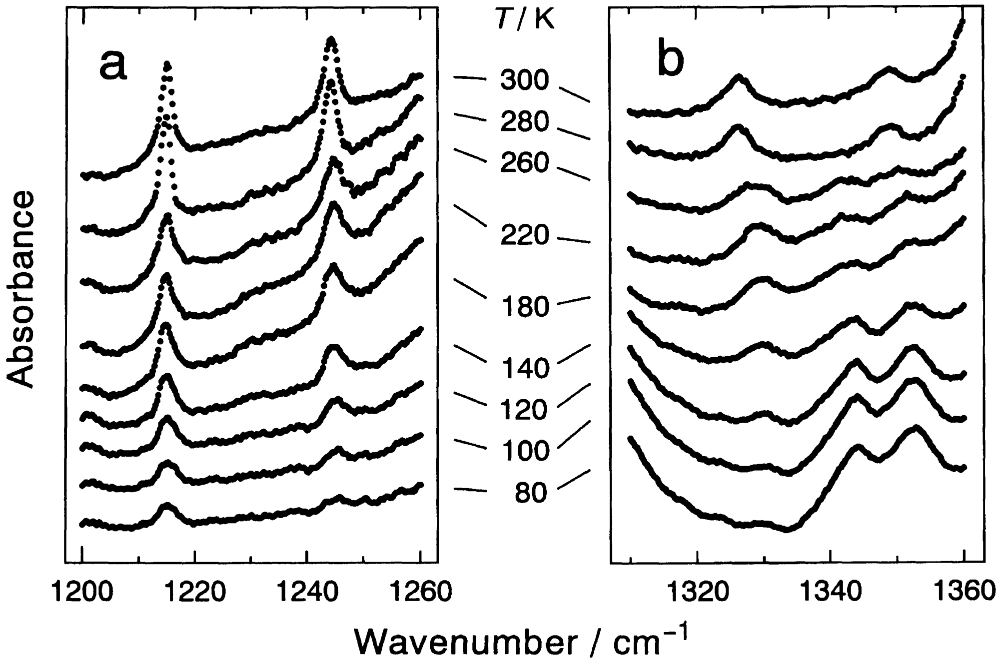

Fig. 2. Evolution of infrared spectra of tetracosane deposited at 80 K. Spectra were recorded raising the temperature stepwise; (a) Band-progression region of the CH_2-wagging vibration of the *all-trans* molecule, (b) wagging bands (1343 and 1352 cm^{-1}) of the molecules with *gauche* conformations.

as high as 80 K. Then they start to relax, and such structural changes continue until about 180 K. The decrease in the concentration of the *gauche* conformation gives rise to the increase in the concentration of the *trans* conformation as seen in Fig. 3b. These observations are essentially in harmony with the previous infrared and Raman studies on amorphous normal hydrocarbons.[3,4] Most of the C–C bonds become *trans* at 180 K. However, it should be noted that a few percent of these remain *gauche* at this temperature (Fig. 3a). For C24, this fact implies that there remain many molecules which are still not *all-trans* at 180 K. To be noted also is the fact that the progression bands show broad widths in the same temperature region (Fig. 2a). Therefore, even the molecules which have attained a nearly *all-trans* conformation still seem to suffer some stress. Thus the transformation of disordered twisted molecules into the *all-trans* conformation have not been completed at 180 K.

The above inferences are confirmed by the LAM band intensity in the Raman spectrum. Figure 4a shows the intensity change of the LAM band. The LAM band was not observed for the initial samples deposited at temperatures below 100 K. It appeared weakly when the temperature was raised to about 150 K, and then gradually increased in intensity until it seemed to be saturated around 250 K. Therefore, the transformation of the disordered molecules with many *gauche* conformations into the *all-trans* conformation is completed through at least several conformational rearrangements rather than a single structural evolution claimed previously.[3]

Now, most of the molecules are considered to become *all-trans* around 250 K. However, as indicated in Fig. 4b, the frequency of the LAM band is not the same as that of the stable crystal at this temperature.[7] This implies that the molecular packing along the chain direction has not yet reached that of the stable crystal at this annealing state. This point will be discussed in Section iv.

(iii) Change in Intermolecular Packing in Later Stage of Annealing—Lateral Direction. Vibrational spectra of molecular systems reflect not only the conformation of the molecules themselves but also the intermolecular interactions. In the later part of the spectral evolution of amorphous C24, we observed some features which reflect the change in the intermolecular packing.

Figure 5 shows the evolution of infrared spectra of the film deposited at 80 K. The bands seen in this figure are attributed to the rocking modes of CH_2 groups.[17] The initial spectrum at 80 K shows a broad band peaked at 721 cm^{-1} which is considered to reflect the disordered conformations of the molecules. The final spectrum at 300 K shows a single sharp band at 717 cm^{-1}. This is attributed to the rocking vibration of the *all-trans* methylene chain in which adjacent CH_2 groups vibrate in the phase opposite to each other. The interesting observation to be noted is that two weak bands (one the shoulder around 720 cm^{-1} and the other the band around 735 cm^{-1}) appeared above 120 K and disappeared finally above 280 K. Apparently, these bands correspond to those observed for normal hydrocarbons with monoclinic or orthorhombic crystal systems.[18] In

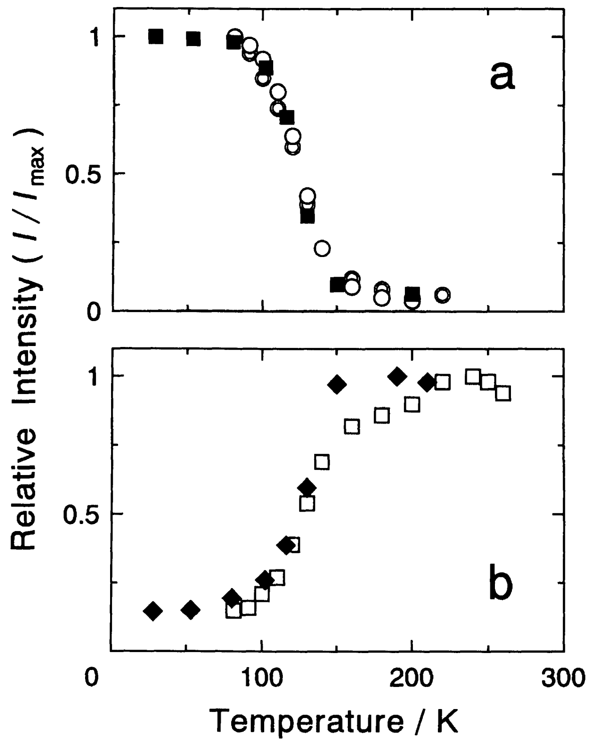

Fig. 3. Intensity changes of the infrared bands by the annealing. Intensities are indicated by the relative value normalized by the maximum value of the same band in each experiment. (a) The intensity decrease which indicates the decrease of the *gauche* conformations; ○ 1343 cm^{-1} band of the sample deposited at 80 K, ○ 1352 cm^{-1} band of the sample deposited at 80 K, and ■ 1343 cm^{-1} band of the sample deposited at 18 K. (b) The intensity increase of 1244 cm^{-1} band which indicates the increase of the *all-trans* conformation; □ sample deposited at 80 K and ◆ sample deposited at 18 K.

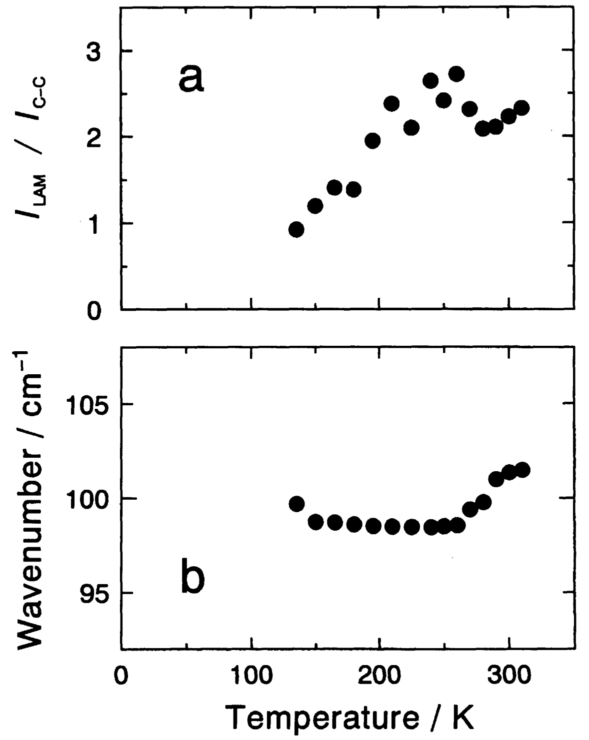

Fig. 4. Intensity (a) and wavenumber (b) changes of the LAM band in the Raman spectra of the sample deposited at 80 K. The LAM intensity shown in (a) is that normalized at each temperature by the intensity of the C–C stretching Raman band at 1062 cm^{-1}.

these crystal systems, two molecules are contained in the unit cell and the vibrational bands undergo factor-group splitting due to lateral interactions. On the other hand, since the C24 crystal at room temperature is triclinic with only one molecule in the unit cell, the rocking band observed in this frequency region should have a single peak. The spectra of the C24 films observed above 280 K agree with this inference.

In describing lateral arrangements of normal hydrocarbon molecules, the notion of the local assembly of CH_2 groups called subcell is sometimes employed.[19] We call hereafter the subcell of the type seen in triclinic crystals the triclinic subcell and that of the type seen in monoclinic or orthorhombic crystals the orthorhombic subcell. Such lateral arrangements of CH_2 groups can be considered even if the molecules with disordered conformations are interacting each other without the close contact along the whole molecular chains. Thus, the extra two bands observed in the temperature range between 120 and 270 K are considered to arise from the part of the sample where orthorhombic subcells appeared locally during the annealing. This is a metastable structure of C24 samples which would finally have triclinic subcells when the relaxation of the whole system is completed at room temperature.

A similar spectral feature which indicates the appearance of the metastable intermolecular arrangement in the lateral direction was observed in the Raman spectrum. Figure 6 shows the evolution of the Raman spectrum in the CH_2 scissors-vibration region. The two bands seen around 1440 and 1470 cm^{-1} are the scissors bands split by the Fermi resonance with the overtone of the rocking vibration around 720 cm^{-1}.[20] In addition to these, an extra band (indicated by an arrow) was observed at 1416 cm^{-1} in the later stage of the annealing process and disappeared at 300 K. Apparently, this band corresponds to that observed for the normal hydrocarbon crystals with orthorhombic subcells, and can be attributed to one of the initial pair of bands being split by the factor-group interaction.[21]

In Fig. 7, we compare the intensity change of the 731 cm^{-1} infrared band appearing in Fig. 5 (closed circles) with that of the 1416 cm^{-1} Raman band appearing in Fig. 6 (open circles). The correspondence of these changes is quite good. Thus, the appearance of the orthorhombic subcells has been confirmed by both the infrared and Raman spectra.

Judging from the intensity ratio of the infrared bands in Fig. 5, about one half of the CH_2 groups are consid-

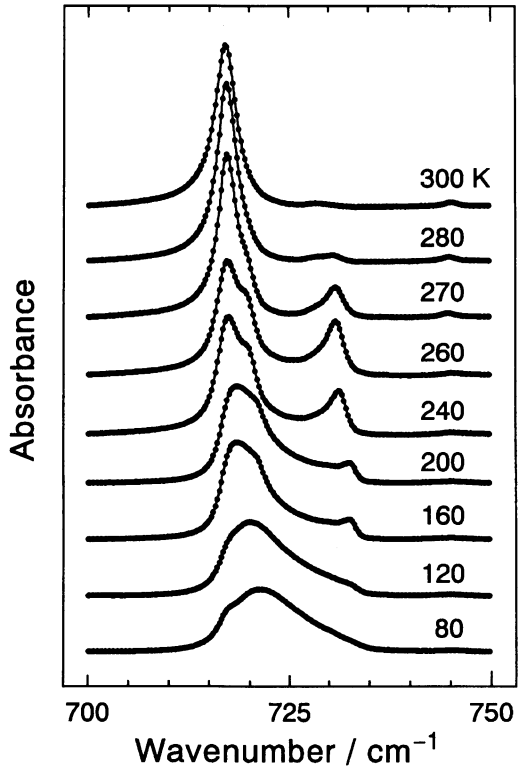

Fig. 5. Evolution of infrared spectra of the sample deposited at 80 K. The wavenumber region of the rocking vibration of CH_2 groups is displayed. The 720 cm^{-1} shoulder and the 735 cm^{-1} band observed at the annealing stages below 270 K are attributed to the factor-group split bands arising from the sample region with metastable orthorhombic subcells.

ered to belong to orthorhombic subcells at 260 K. The corresponding spectrum[3)] of amorphous C21 at 240 K is almost the same. This indicates that around these temperatures the probabilities of the appearance of the triclinic and orthorhombic subcells in amorphous normal hydrocarbons is almost the same, and also implies that the energies for the formation of these subcells are almost the same although the orthorhombic arrangement has been inferred to be slightly more stable than the triclinic arrangement.[14)]

As shown in Fig. 7, the orthorhombic subcells which appeared in the later stage of the annealing process of amorphous C24 diminish in a narrow temperature range around 280 K. This structural change has a close connection to the rearrangement of the molecular positions along the chain direction. This will be discussed next.

(iv) Change in Intermolecular Packing in Later Part of Annealing—Chain Direction. Figure 8 shows the evolution of infrared spectra of the film deposited at 80 K in the C–H stretching vibration region. The bands observed in the highest frequency region around 2960 cm^{-1} are attributed to the two asymmetric stretching modes of the terminal CH_3 groups.[22)] In the initial stage at 80 K, a broad band with a very weak shoulder on its high-frequency side was observed. At 250 K, the existence of the shoulder become obvious. At 270 K, the shoulder suddenly grew into a definite band, and a pair of bands were observed above this temperature.

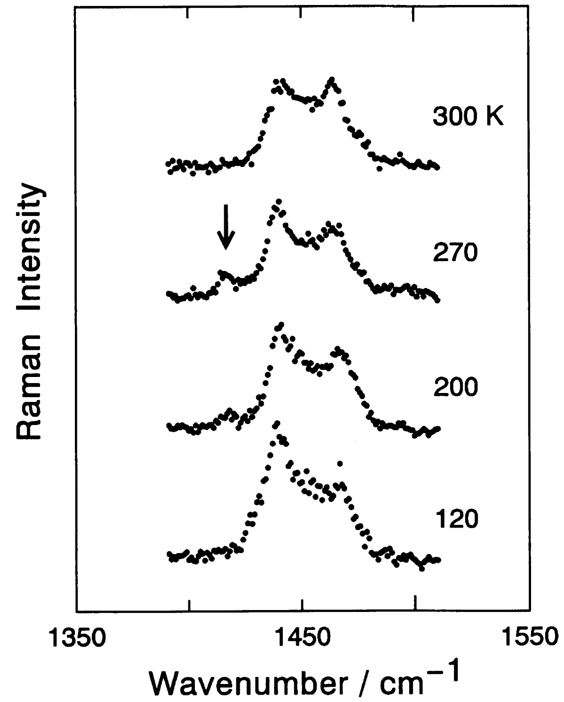

Fig. 6. Evolution of Raman spectra of the sample deposited at 18 K. The wavenumber region of the scissors vibration of CH_2 groups is displayed. The weak band at 1416 cm^{-1} (indicated by an arrow) is attributed to one of the factor-group split bands arising from the sample region with metastable orthorhombic subcells.

The above spectral changes are interpreted as follows with the aid of the LAM-frequency change shown in Fig. 4b and the spectral changes shown in Figs. 5 and 6. First, the CH_3 groups are placed under various circumstances in the initial amorphous state. Thus the asymmetric CH_3 vibrations give a single broad band (Fig. 8). In the temperature region around 200 K where most of the C–C bonds have become *trans*, the CH_3 groups are considered to be surrounded by the adjacent columnar methylene chains. Under this situation, the asymmetric CH_3 vibration bands show splitting as in the crystal. However, the contact between the CH_3 groups of the neighboring molecules along the chain direction may not be tight. This is inferred from the fact that the LAM frequency at this annealing stage around 200 K is smaller than that of the room-temperature crystal as illustrated in Fig. 4b. It has been discussed that increasing intermolecular interaction causes the LAM frequency to increase.[23)] The low-frequency shift in the amorphous samples are as large as 5% for C36 and 3% for C24.[7)] Thus, it is inferred that there was some space between the molecules adjacent along the chain direction, making the LAM frequency small.

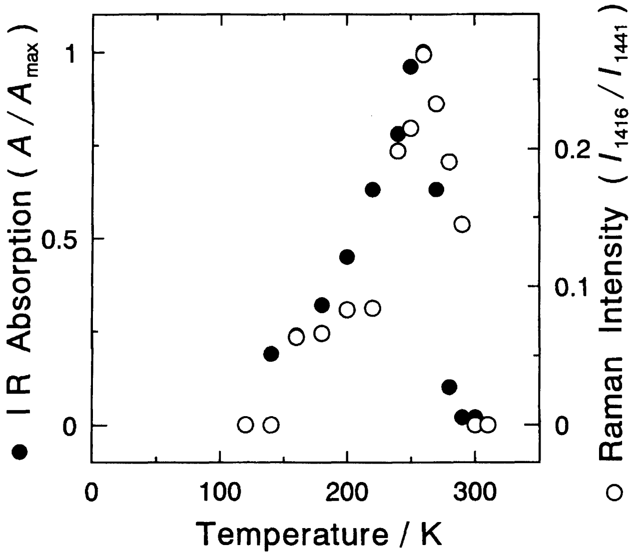

Fig. 7. Comparison of the intensity changes of 735 cm^{-1} infrared (Fig. 5) and 1416 cm^{-1} Raman (Fig. 6) bands which indicate the existence of the orthorhombic subcells. The infrared absorption (closed circles) is displayed by normalizing its maximum value. The intensity of the 1416 cm^{-1} Raman band (open circles) is displayed as the intensity relative to that of the 1441 cm^{-1} Raman band. A good correspondence between these two changes is seen for the temperature region in which the orthorhombic subcells existed.

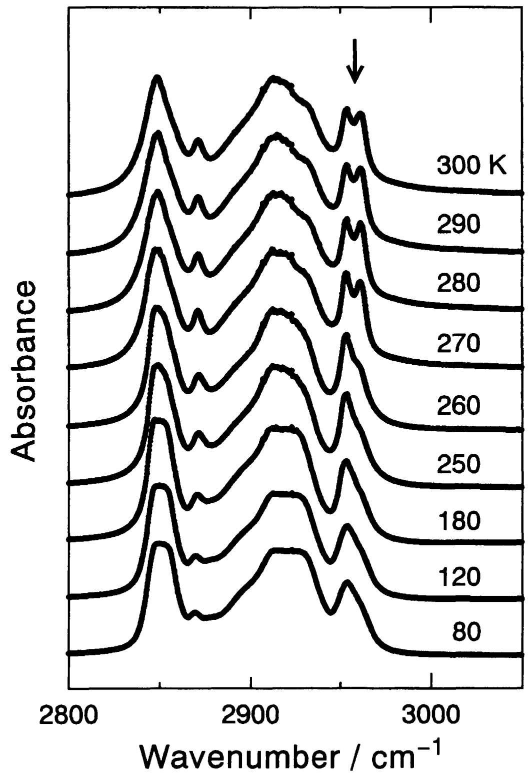

Fig. 8. Evolution of infrared spectra of the sample deposited at 80 K. The C–H stretching vibration region is displayed. The bands around 2960 cm^{-1} (indicated by an arrow) are attributed to the asymmetric stretching modes of the CH_3 group. The splitting becomes obvious above 270 K.

The conformation of the CH_3 groups, then, may still have some disorder. This is in harmony with the fact that the splitting of the CH_3 stretching band in the infrared spectra (Fig. 8) was incomplete below 260 K.

Taken together, these observations are consistent with the following microscopic picture. Around 270 K, translational displacements of molecules along the chain direction are considered to take place to make close contacts between the CH_3 groups along the chain direction. On this occasion, the molecules with the orthorhombic-type lateral contacts with adjacent molecules may undergo rotational reorientations around the chain axis simultaneously with the translational displacements (see Figs. 5 and 6). By these structural changes, the sample approaches to the structure of the stable triclinic crystal. Then, the asymmetric CH_3 stretching modes gives two clear infrared bands (Fig. 8), and the LAM frequency shifts to the value of the stable crystal (Fig. 4b). Around 300 K, the samples are considered to attain finally the structure almost the same as the stable crystal. In fact, the spectral feature observed at this stage were unchanged (except for the sharpening of the bands) when the samples were cooled again below 100 K.

(v) Summary of Annealing Process. The results of previous[3,4] and present studies have shown that the relaxation in amorphous normal hydrocarbons takes place in several distinguishable stages almost irrespective of the chain length. We illustrate schematically in Fig. 9 the main features of the relaxation in amorphous normal hydrocarbons.

In the initial state of the amorphous sample, we have disordered molecules with many *gauche* conformations (stage A). The conformational conversion from *gauche* to *trans* takes place in a wide temperature range centered around 100 K. Around 180 K, the molecules approach to the ordered *all-trans* conformation with a small number of the remaining *gauche* conformations (stage B).

In the range from 200 to 250 K, most of the molecules become *all-trans*, and the lateral alignment of the molecular chains is considered to attain some coherence much larger than the size of the molecule (stage C). However, the intermolecular packing at this stage is not of the stable crystal. The vertical lines in the picture of stage C are the guide to the eye to see the difference of the lateral arrangements. Note also that there remain large spaces between the head and tail of two molecules adjacent along the chain direction.

Finally, in a temperature range from 270 to 300 K, the adjustment of the mutual position of the *all-trans* molecules takes place, which includes presumably both the translational displacement in the chain direction and the rotational reorientation around the chain axis, and we have the sample with the structure of the stable

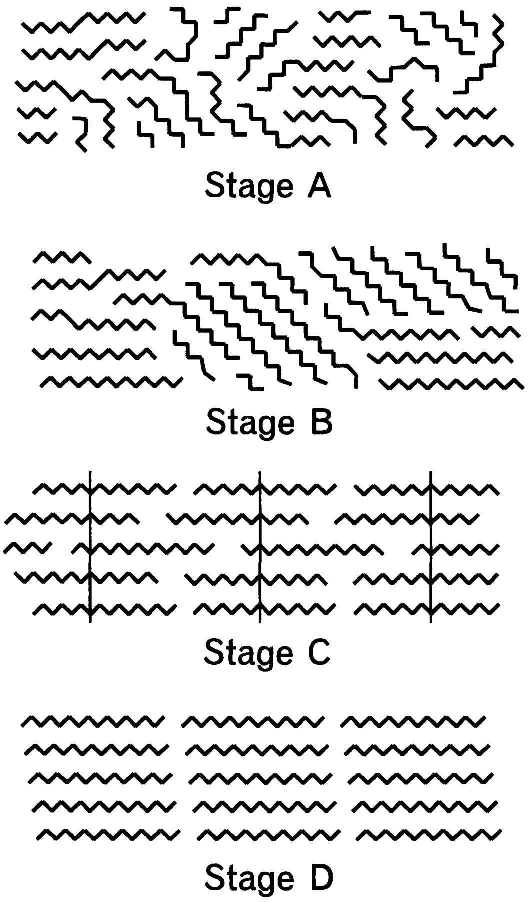

Fig. 9. Schematic illustration of the relaxation process of amorphous normal hydrocarbons. Stage A: the initial amorphous state as deposited on the cold substrate, many *gauche* conformations being incorporated. Stage B: the state around 180 K in which most of the *gauche* conformations have turned into *trans*, but a small number of the *gauches* still remain. Stage C: the state from 200 to 250 K where most of the molecules have become *all-trans*, but the intermolecular arrangement is still not of the structure of the stable crystal in both the longitudinal and lateral directions of the molecular chain. The vertical lines are the guide to the eye. Stage D: the final state of the relaxation in which the structure of the stable crystal is attained.

crystal (stage D). The temperature region in which the transition from stage C to stage D takes place is slightly dependent on the chain length of the molecule.[24)]

One should note that Fig. 9 is only for illustrating our image about the relaxation processes in amorphous hydrocarbons. As an effort to see structures of amorphous molecular systems, Eiermann et al.[25)] have measured electron diffraction of tetracene and pentacene films which were vacuum-deposited on a cold carbon film supported by a copper mesh. They confirmed the absence of the long-range order in their samples, and the structural coherence of a few lattice parameters seemed to remain. Their conclusion is essentially in harmony with our present image about the structure of amorphous molecular systems. We are now constructing an apparatus to study the structures of amorphous molecular systems by X-ray diffraction.

(vi) Some Comments and Conclusion. We have studied the relaxation processes in vacuum-deposited amorphous samples of three types of simple organic compounds; polyacenes, polyphenyls, and normal hydrocarbons.[7)] In comparison with the former two types of compounds, normal hydrocarbons are characterized by the high degree of internal freedom for deformation. Therefore, one would expect to distinguish many relaxation processes related to the internal freedom. However, since molecules such as C24 have a large number of CH_2 units in the chain, the feature of the relaxation of an unstable local conformation may not depend strongly on the position in the chain molecule. In addition, there may not be a strong preference for particular positions in the chain as the initiation point of the conformational transformation, although the atoms near the terminals of the molecule may naturally be more mobile compared with those in the midst. These may be the reasons that the conformational relaxation from *gauche* to *trans* takes place successively in a continuous temperature range around 100 K.

In the same context as described above, the structural transformation of conformationally-disordered normal hydrocarbon molecules may, in general, *not* occur in a single step. This contradicts the inference mentioned by Hagemann et al.[3)] The fact that the LAM-intensity increase (Fig. 4a) continues above 180 K where most of the *gauche* conformations disappeared (Fig. 3b) supports our view. In other words, some *gauche* conformations remain in the sample even in the annealing stage where the surroundings have become the structure almost the same as the crystal. To transfer such remaining *gauche* conformations into *trans*, it is necessary to raise the temperature above 200 K. Such a behavior of amorphous normal hydrocarbons is in contrast to the rather abrupt structural changes observed for the annealing processes in amorphous samples of naphthalene[26)] and biphenyl,[6)] and is understandable if one thinks of the long molecular shape and the large degree of intramolecular freedom for deformation of normal hydrocarbons.

Since the amorphous samples studied in the present work are not in thermodynamic equilibrium, the structure may change irreversibly and may be dependent on time. The former point has been confirmed as it has been described so far. However, in contradiction to the latter point, amorphous samples of normal hydrocarbons seem to keep their non-equilibrium structure for a fairly long time, at least for temperatures below 200 K. In addition, an almost instantaneous structural change takes place when the temperature is raised stepwise, at least on the time scale of the experiments described here. The same observations are reported by Hagemann et al.,[3] and also by us for amorphous terphenyl.[5] Such characteristic relaxation processes of some amorphous systems are considered to reflect the complex structure of their potential-energy surfaces.[25]

The electronic structure of amorphous C36 films and their annealing process have recently been studied by means of the photoemission spectroscopy.[27] The samples for the photoemission studies were prepared in a high vacuum of the base pressure of 5×10^{-10} Torr (1 Torr=133.322 Pa), and the film thickness was 6—7 nm. These conditions are considerably different from those of the vibrational studies.[3,4] In spite of such differences, a good correspondence has been found between the electronic and vibrational observations of the annealing process of amorphous C36. Thus, we consider that the vibrational observations described so far on the annealing process of amorphous C24 are not specific to the sample conditions we employed.

In conclusion, we have studied the relaxation process of amorphous C24 by infrared and Raman spectroscopies. Some microscopic features of the relaxation have been revealed, and the relaxation has been shown to proceed in several distinguishable stages. It has been demonstrated that these relaxation processes in amorphous normal hydrocarbons can be efficiently analyzed by applying both the infrared and Raman spectroscopies.

References

1) M. Tasumi and T. Shimanouchi, *J. Chem. Phys.*, **43**, 1245 (1965).

2) R. G. Snyder, *J. Chem. Phys.*, **47**, 1316 (1967).

3) H. Hagemann, H. L. Strauss, and R. G. Snyder, *Macromolecules*, **20**, 2810 (1987).

4) Y. Hibino, K. Ishii, and H. Nakayama, *Mol. Cryst. Liq. Cryst.*, **187**, 175 (1990).

5) H. Nakayama, M. Kawahara, K. Tanabe, and K. Ishii, *Mol. Cryst. Liq. Cryst.*, **218**, 183 (1992).

6) K. Ishii, H. Nakayama, K. Tanabe, and M. Kawahara, *Chem. Phys. Lett.*, **198**, 236 (1992).

7) K. Ishii, M. Kawahara, Y. Yagasaki, Y. Hibino, and H. Nakayama, *J. Phys. D*, **26**, B193 (1993).

8) H. Nakayama, M. Kawahara, and K. Ishii, *Chem. Phys.*, **178**, 371 (1993).

9) K. Ishii, H. Nakayama, Y. Yagasaki, K. Ando, and M. Kawahara, *Chem. Phys. Lett.*, **222**, 117 (1994).

10) A. R. Gerson, K. J. Roberts, and J. N. Sherwood, *Acta Crystallogr., Sect. B*, **B47**, 280 (1991).

11) A. E. Smith, *J. Chem. Phys.*, **21**, 2229 (1953).

12) N. M. M. Shearer and V. Vand, *Acta Crystallogr.*, **9**, 379 (1956).

13) P. W. Teare, *Acta Crystallogr.*, **12**, 294 (1959).

14) A. I. Kitaigorodsky, "Molecular Crystals and Molecules," Academic Press, New York (1973), Chap. I.

15) R. F. Schaufele and T. Shimanouchi, *J. Chem. Phys.*, **47**, 3605 (1967).

16) N. Jones, A. F. McKay, and R. G. Sinclair, *J. Am. Chem. Soc.*, **74**, 2575 (1952).

17) R. F. Holland and J. R. Nielsen, *J. Mol. Spectrosc.*, **8**, 383 (1962).

18) R. G. Snyder, *J. Mol. Spectrosc.*, **7**, 116 (1961).

19) R. G. Snyder, *J. Chem. Phys.*, **71**, 3229 (1979).

20) C. K. Wu and M. Nicol, *Chem. Phys. Lett.*, **24**, 395 (1974).

21) F. J. Boerio and J. L. Koenig, *J. Chem. Phys.*, **52**, 3425 (1970).

22) R. A. MacPhail, H. L. Strauss, R. G. Snyder, and C. A. Elliger, *J. Phys. Chem.*, **88**, 334 (1984).

23) S. L. Hsu and S. Krimm, *J. Appl. Phys.*, **48**, 4013 (1977).

24) M. Nukaga, H. Nakayama, and K. Ishii, to be publisehd.

25) R. Eiermann, G. M. Parkinson, H. Bässler, and J. M. Thomas, *J. Phys. Chem.*, **87**, 544 (1983).

26) K. Ishii, H. Nakayama, M. Kawahara, to be published.

27) K. Seki, N. Ueno, and H. Inokuchi, *Chem. Phys.*, **182**, 353 (1994).