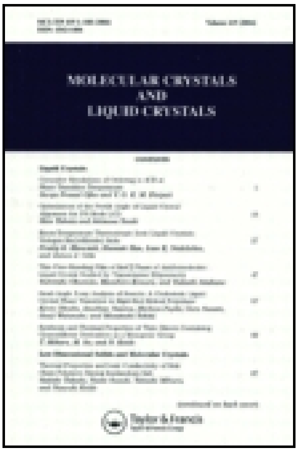

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Yukinobu Hibino [a], Kikujiro Ishii [a] & Hideyuki Nakayama [a]
[a] Faculty of Sience, Gakusuin University, Mejiro 1-5-1, Toshimaku, Tokyo, 171, JAPAN

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RAMAN SPECTRA AND ANNEALING PROCESSES IN GLASSY FILMS OF LONG-CHAIN ORGANIC COMPOUNDS

YUKINOBU HIBINO, KIKUJIRO ISHII,* and HIDEYUKI NAKAYAMA
Faculty of Sience, Gakusuin University, Mejiro 1-5-1,
Toshimaku, Tokyo 171 JAPAN

Abstract Glassy films of long-chain organic compounds were made by the evaporation onto cold metal surfaces. Raman spectra of these films are compared with those of crystal and liquid states. Annealing processes in these films were found to involve some molecular conformational changes which occur successively in several temperature regions. The results on hexatriacontane are shown as an example.

INTRODUCTION

It is very important to study the crystallization processes in polymer materials.[1] However, the studies carried out so far concerning these processes have mainly been focussed on the macroscopic properties of materials such as the density or the thermal properties. Very little has been known of the microscopic (molecular) processes of crystallization in polymer materials.

For studying the molecular processes, the samples are desired to be well characterized. Since most of the existing polymer materials cannot be regarded as homogeneous, they are not suitable for such basic researches. We have started, therefore, the studies of annealing processes of chemically-identified long-chain organic compounds in glassy states.

The vacuum evaporation method onto cold metal surfaces was employed to make the glassy states since it has been considered to be the best method to obtain glassy states of molecular materials.[2] Raman measurements were carried out on these evaporated films since vibrational spectroscopies give plentiful information on the molecular conformations of organic molecules. Thus, the evolution of Raman spectra was monitored during the annealing processes of the glassy films.

In this paper we describe, first the method of our study, and next report some results obtained for hexatriacontane, n-$C_{36}H_{74}$, one of the well studied long-chain organic compounds.[3] Similar studies on the annealing processes in some n-alkanes and low-molecular-weight polyethylene have recently been carried out by infrared spectroscopy[4] and ultraviolet photoelectron spectroscopy.[5]

EXPERIMENTAL

The vacuum evaporation of the sample onto the cold substrate and the in situ Raman measurements were carried out in our home-made cryostat. It consists of a liquid-nitrogen reservoir, a copper block equipped with a heater and a thermocouple, a furnace for the evaporation of the sample, a vacuum gauge, and a thickness monitor with a quartz oscillator. This cryostat was evacuated with an oil-diffusion pump during the experiment. The base pressure was 7×10^{-5} Pa.

The copper block is illustrated in Fig. 1. This block is attached to the bottom of the liquid-nitrogen reservoir by a stainless-steel cylinder to control the heat conduction. The tapered face of this block was polished and a several micrometer-thick copper layer was made on it by vacuum evaporation, in advance of the measurement. The lowest temperature reached with this was 105 K.

The 514.5 nm radiation from an Ar^+-ion laser was used as the excitation source in the Raman measurements, with s-polarization and a power of 30 mW. The apparatus for the Raman measurements were the same as reported previously.[6] The spectra were recorded with a resolution of 3.4 cm^{-1}.

Hexatriacontane (Tokyo Kasei Co.) was first recrystallized from benzene. This sample showed weak extra luminescence with 514.5 nm excitation, raising the base line of the Raman spectra very much. Then, the sample was purified further by the zone-refining. The luminescence of this sample was very weak and did not disturb the Raman measurement.

The samples with a thickness of about 800 nm were evaporated onto the copper substrate. The evaporation rate was kept very slow to avoid raising the local temperature at the sample surface.[5] Thus it took several hours to make the samples with the above thickness.

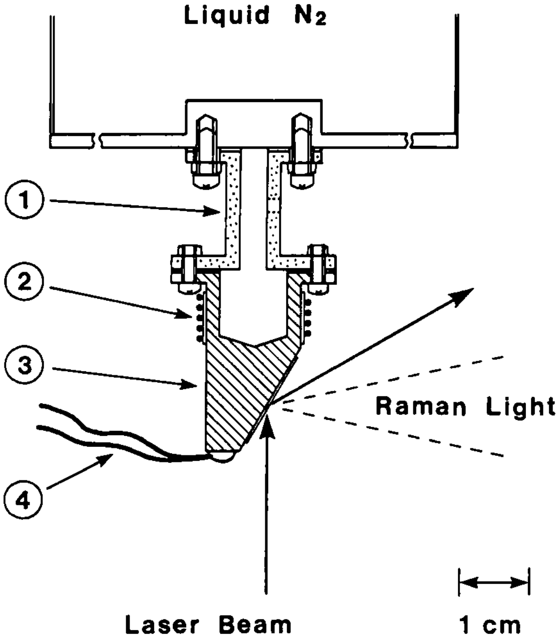

FIGURE 1. Illustration of the copper block onto which the sample is evaporated. ① Stainless steel cylinder, ② heater, ③ copper block, ④ thermocouple.

RESULTS AND DISCUSSION

Spectra of n-$C_{36}H_{74}$ Glassy Films

The n-$C_{36}H_{74}$ films evaporated onto the cold substrate were colorless and transparent. The Raman spectra of the films obtained at 150 K (sample C) and 108 K (sample D) are shown in Fig. 2 along with the spectra of the polycrystalline sample at 90 K (sample A) and liquid sample at 367 K (sample B). The main bands of sample A are numbered, and their assignments are described below.[7-11] We observed no indication of Raman bands of water, even two days after starting the measurement at low temperatures. The temperature difference between the liquid-nitrogen reservoir and the sample is believed to prevent the condensation of the residual gases on the sample.

Figure 2a displays the low-frequency region where A shows a strong band (band 1) arising from the longitudinal acoustic mode (LAM) which is characteristic of the extended all-trans structure of n-alkane molecules.[8] Sample C shows a weak band in this region, while D shows almost nothing. Therefore, it is inferred that C includes a small amount of all-trans molecules, while most of the molecules in D are disordered to some extent. The fact that the LAM frequency of C is smaller than that of A will be discussed elsewhere.[3]

Figure 2b displays the frequency region where the C-C stretching bands (bands 2 and 3) and the CH_2 rocking band (band 4) appear. It is noted that D does not show the rocking band, while C shows a small indication of this band. As for the C-C stretching bands, those seen in C and D are not blurred as those in B, but the band widths are rather broad compared with those in A.

Figure 2c displays the region of the CH_2 scissors bands. Bands 6 and 7 have been assigned to the scissors bands split by the Fermi resonance with the infrared-active CH_2-rocking mode.[9] Bands 5 and 6 are the pair which are split by the crystal field.[10] The fact that D does not show band 5 indicates that there is no correlation between vibrations in the neighboring molecules.

Figure 2d shows the region of the C-H stretching bands. Band 8 and the broad tail continuing to its high-frequency side are attributed to the CH_2 symmetrically stretching bands broadened by the Fermi resonance with the CH_2 scissors mode.[11] Band 9 is the CH_2 antisymmetrically stretching band. Comparison of the spectra of A and B indicates that the intensity of band 9 is sensitive to the structure of the molecule. Thus, one may use the apparent ratio of the peak-hights of bands 8 and 9 as a monitor of the degree of dis-

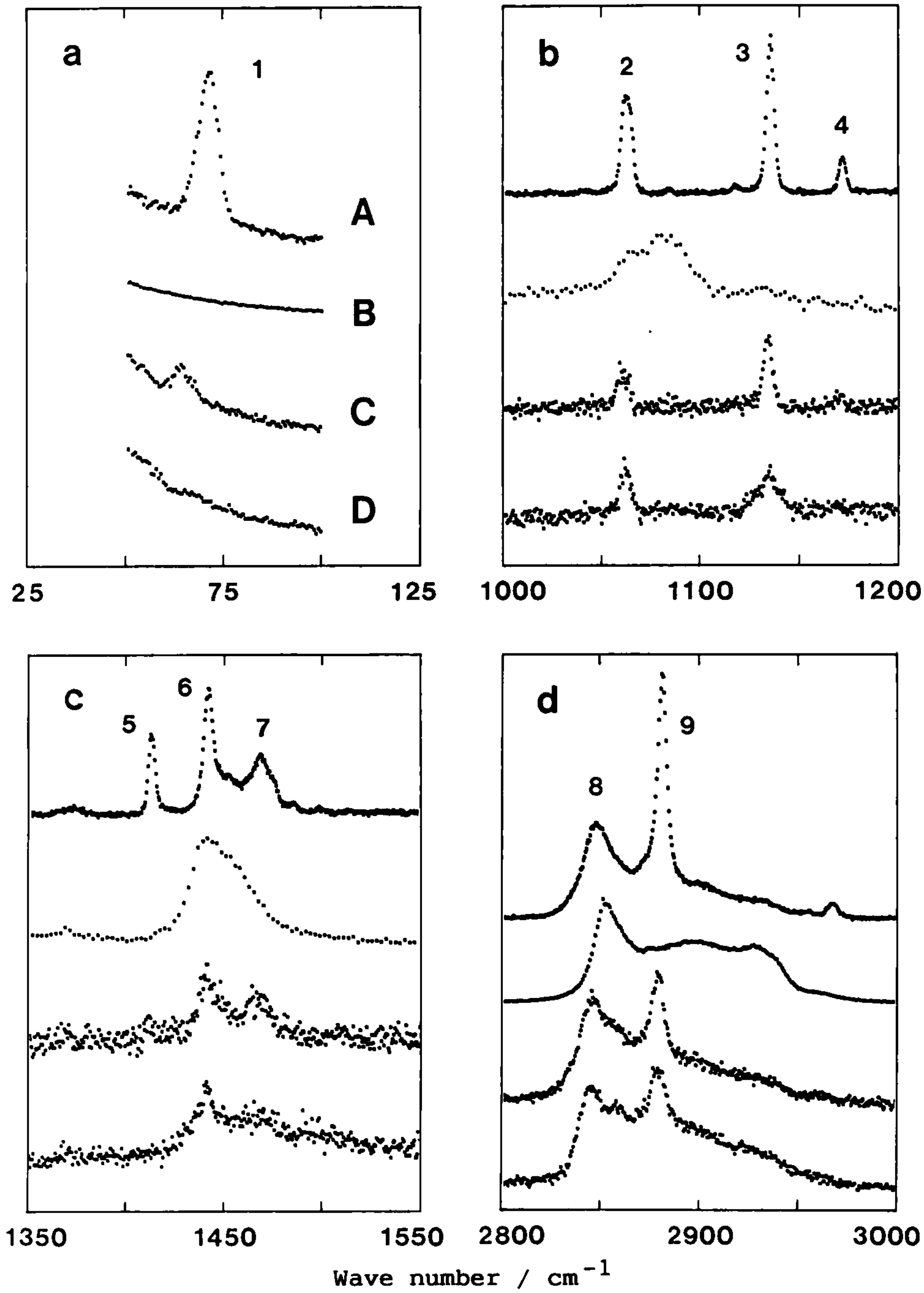

FIGURE 2. Raman spectra of n-$C_{36}H_{74}$ measured with (A) polycrystalline compacted sample at 90 K, (B) liquid sample at 367 K, (C) glassy film evaporated onto the block at 150 K, (D) glassy film evaporated on to the block at 108 K.

order in the molecule. Comparing these ratios of C and D, it is inferred that the degree of disorder in D is slightly larger than that in C.

All the above results indicate that the molecular structures in the films evaporated onto the cold substrates are disordered, although the degree of the disorder is not comparable to that of liquid as it is evident in Figs. 2b and 2d. The molecular structures of long-chain n-alkanes in the gaseous state are not known. However, it is inferred that the free molecules have tangled structures to minimize the electronic energy. In the evaporated films, these structures are considered to be frozen-in to some extent, including many gauche conformations in the molecular chains. The features of the Raman spectra of the evaporated films displayed above can, in fact, be interpreted with this model.

Annealing Process in n-$C_{36}H_{74}$ Film Evaporated at 108 K

The evolution of the Raman spectra were monitored during the annealing of this film. The sample temperature was raised stepwise. It took about 40 min to attain steady state at a new temperature, and it took about three hours to measure the set of the spectra at each temperature. At some temperatures, the measurements of some frequency regions were repeated within several hours. It was found that the molecules in the film attain the new conformations soon after the temperature is raised to the new point, and that the film structure does not change further substantially within several hours. Similar behavior has been observed by Hagemann et al.[4] for n-$C_{21}H_{44}$ by infrared measurement.

Figure 3a displays the evolution of the intensity ratio between bands 9 and 8 in Fig. 2d. Figure 3b displays the evolution of the LAM band intensity.

By comparing these and some other results, we devide the annealing process into three temperature regions as indicated at the top of Fig. 3. In region I, the gradual increase of band 9 is observed, indicating that the local conformational changes in the methylene chains occurs from gauche to trans. Most of these changes are completed below 190 K, but the remaining small number of these changes occur in the next temperature region from 190 K to 290 K. What happens in the second temperature region is inferred to be the final changes to the all-trans conformation. This is supported by the observation that the LAM band intensity

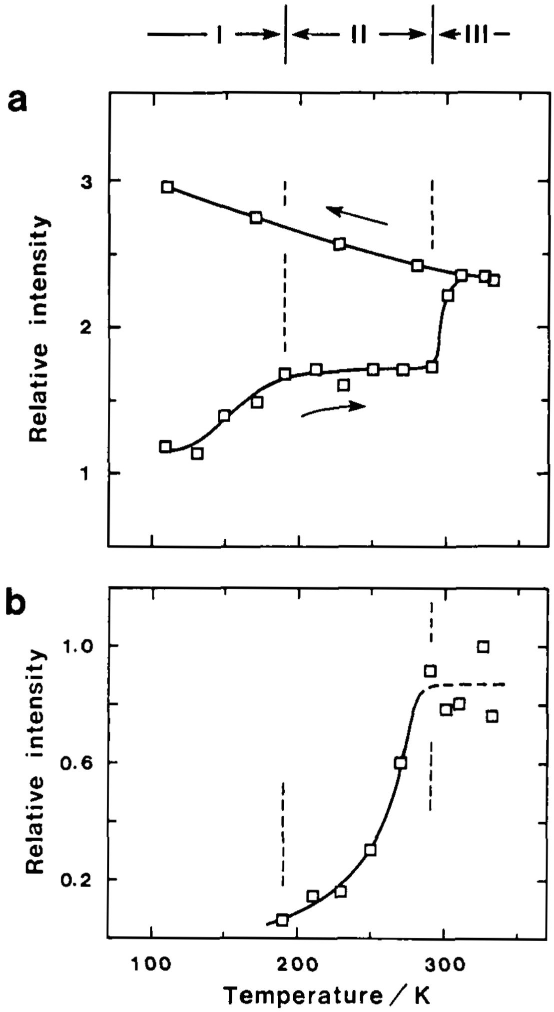

FIGURE 3. Evolution of Raman band intensities.
(a) Intensity of band 9 relative to that of band 8,
(b) intensity of band 1 normalized by the value at 326 K.

increses in region II as displayed in Fig. 3b.

Above 290 K, we observed a steep increase of the band 9 intensity (Fig. 3a). In the same narrow teperature region, we observed the shift of the LAM band frequency converging to that of the crystalline sample.[3] Therefore, we infer that the rearrangement of the all-trans molecules occurs in this temperature region along the molecular axes giving finally the polycrystalline film.

Once the polycrystalline film was obtained around room temperature, the features of the Raman spectra did not change when the sample cooled down again, except a small shift and sharpening of bands normally observed for the crystalline sample. Therefore, the evolution of the Raman spectra so far observed for the evaporated filmsof n-$C_{36}H_{74}$ is irreducible, and attributed to crystallization from the glassy state.

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