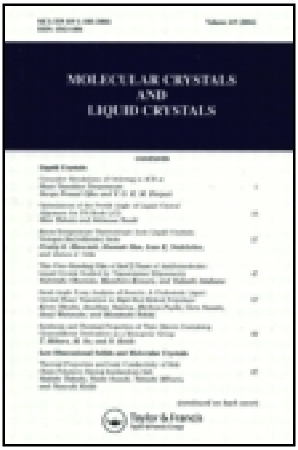

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Raman Studies of Annealing Processes in Glassy Films Of P-Terphenyl

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RAMAN STUDIES OF ANNEALING PROCESSES IN GLASSY FILMS OF P-TERPHENYL

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Abstract Glassy films of p-terphenyl were prepared by evaporation onto cold metal substrates. Raman spectra in the lattice and intramolecular vibrational regions were measured to observe the annealing processes of the glassy films for temperatures ranging from 99K to 270K, and compared with those of liquid and polycrystalline samples. It was found that the intramolecular conformational change of the molecule takes place before the long-range ordering in the intermolecular packing.

INTRODUCTION

The study of the crystallization process in glassy molecular systems is important to know the dynamical properties both of the disordered and crystalline systems. Vibrational spectroscopies are powerful for this purpose, because informations of the molecular level are obtained by them. We have previously studied the annealing processes in glassy films of long-chain hydrocarbons, and long-chain alcohols by Raman and infrared spectroscopies.[1] It was found that the long-chain compounds crystallize through several steps which involve intramolecular conformational changes in the methylene chains and the rearrangement of the molecular packing to attain the long-range ordering. The existence of the OH group in the molecule of long-chain alcohols was found to raise the temperature where the latter process starts to take place.

p-Terphenyl (PT) has intramolecular freedoms of twisting beetween the phenyl rings. It has been known that the balance between the intramolecular energy of twisting and intermolecular energy of packing give rise to the interesting phase-transition phenomena of this compound.[2] Thus, we studied the annealing process in glassy films of PT. The results of Raman measurements are briefly reported in this parper.

EXPERIMENTAL

Glassy films were prepared by evaporation onto cold metal substrates. Raman measurements were carried out in a liquid-nitrogen cryostat which has been reported previously.[1]

The sample with a thickness of 3μm was evaporated onto the substrate at an evaporation rate of about 10Å/sec in a vacuum of $< 10^{-6}$ Torr. The substrate was a thin film of copper or gold evaporated onto the polished surface of a copper block. There was no significant dependence on the substrate metals.

The 514.5nm radiation from an Ar^+-ion laser was used as the excitation source with a power of 40mW. The laser beam were focused by a cylindrical lens to reduce the heating effect. The sample temperature was raised stepwise and kept constant during the measurement.

Commercial PT (Tokyo Kasei Co.) was first refluxed with benzene and maleic anhydride. The sample was purified further by the recrystallization and the zone-refining.

RESULTS AND DISCUSSION

The PT films evaporated onto the cold substrate (99K) were colorless and almost transparent. Fig. 1 shows the evolution of the Raman spectra in the lattice vibrational region during the heating process. Spectrum E was measured after the annealing for about 10 hours at 270K. The fact that no Raman band was seen in spectrum A indicates that the long-range order did not exist in the initial film at 99K. As the temperature was raised, Raman bands appeared and increased their intensity gradually. However, we do not consider that these increases in the intensity reflect the degree of crystallization directly, because the similar increases were observed for the intramolecular vibrational bands. Some macroscopic structural changes (e.g., the change of the size of the crystalline particles) might change the effective path length of the laser beam in the film

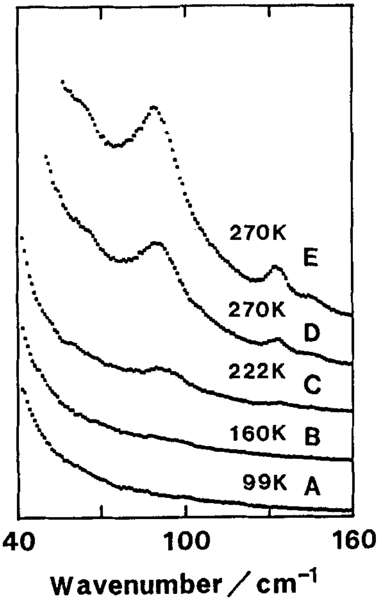


FIGURE 1 Evolution of the Raman spectra of evaporated film of p-terphenyl. E was measured after the annealing for sustained about 10 hours at 270K.

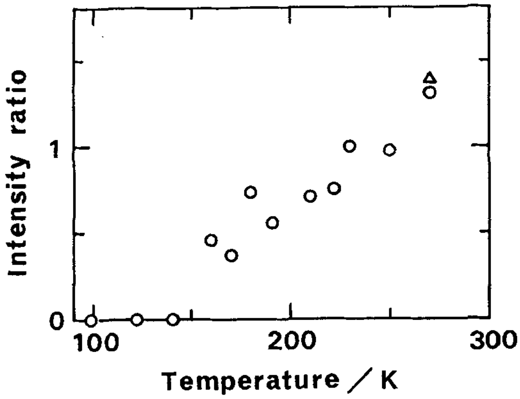


FIGURE 2 Evolution of the intensity ratio between the band around 90cm^{-1} and the band around 1595cm^{-1}. The point Δ was measured after the annealing for about 10 hours at 270K.

and cause the increase in the spectral intensity.

To see the evolution of the intrinsic intensity of the lattice-vibrational band, the intensity ratio between the band around 90cm^{-1} and an intramolecular vibrational band around 1595cm^{-1} is plotted in Fig. 2. The evolution of this ratio indicates that the crystallization begins around 120K and progresses gradually with the increase in the temperature. On the other hand, no prominent change in the ratio was observed after keeping sample for about 10 hours at 270K. Therefore, it is inferred that the microscopic crystallization did not progress further substantially after the temperature was raised to 270K. However, by comparing the spectra D and E in Fig. 1, it is seen that the apparent intensity increased after the temperature was raised to 270K. This fact suggests that the macroscopic change continued even after the microscopic process allowed at that temperature was completed.

Fig. 3 shows the spectra of intramolecular vibrational region of the evaporated film at 99K along with the spectra of the liquid sample at 508K and the polycrystalline sample at 88K. The band at 330cm^{-1}of the spectrum C in Fig. 3a is assinged to the symmetric stretching vibration between the phenyl groups. This band is very week in the spectrum of the evaporated film, which is similar to the spectrum of the liquid. Two strong bands shown in the spectra in Fig. 3b are those arising from the modes equivalent to the degenerate stretching vibration of benzene. The bands in spectrum A are broad and the intensity of the higher-frequency band is stronger than that of another one. Furthermore, the peak positions of the bands of the evaporated film are close to those of the liquid sample rather than the polycrystalline sample. These results indicate that local structure of the evaprated film at 99K, particularly the intramolecular conformation concerning the twisting freedom between the phenyl rings, is similar to that in the liquid state.

Fig. 4 shows the evolution of the width of the band at 1595cm^{-1} (99K) of the evaporated film along with corresponding data of the polycrystalline sample. The band width of the evaporated film

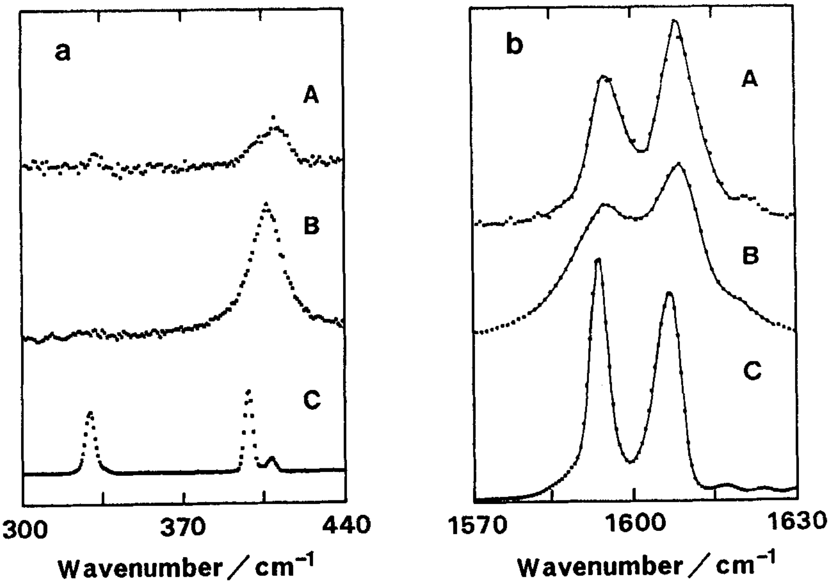
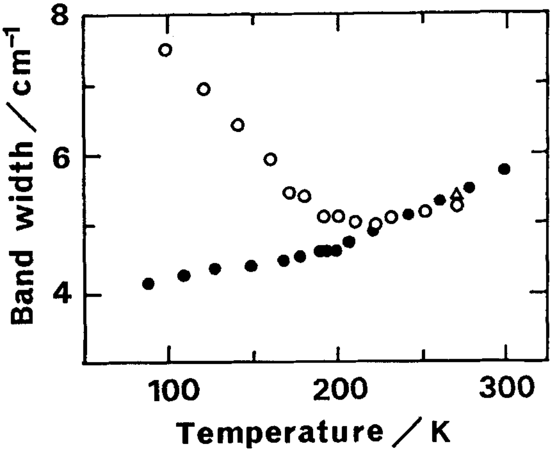


FIGURE 3 Raman spectra of p-terphenyl.

(A) Evaporated film at 99K. (B) Liquid sample at 508K.

(C) Polycrystalline sample at 88K.



FIGUER 4 Evolution of the width of the Raman band around 1595cm^{-1}.

(○) Evaporated film.

(△) Evaporated film annealed about 10hours at 270K.

(●) Polycrystalline sample.

decreased first as the temperature was raised, and above 220K, it was almost the same as the width of the polycrystalline sample. The initial decrease of the width of the evaporated film with an increase in the temperature is considered to show that the number of molecules with similar molecular conformation is increasing. By comparing the Figs. 2 and 4, it is seen that the temperature region where the width of 1595cm^{-1}(99K) band decreases is different from the region where the increase in the lattice-band intensity was observed. Thus the long-range ordering in the molecular packing is attained in the temperature region higher than that where the intramolecular conformational change of the individual molecule takes place.

Similar behaviors have been observed for the long-chain hydrocarbons in the annealing processes of their glassy films.[1] It should be noted that both PT and the long-chain hydrocarbons have the intramolecular freedom of deformation with small energies. In the glassy films of these compounds, it is considered that the change in the intramolecular conformation takes place first at low temperatures to rearrange the contact with the nearest neighbors. Then, the long-range ordering in the intermolecular packing starts to take place to give the final crystalline state. It is interesting that the phase-transition temperature 193K of the PT crystal[2] falls in the region where the two temperature regions, in which the above two annealing processes take place respectively, overlap each other.

REFERENCES

1. The results are partially reported in : Y. Hibino and H. Nakayama, and K. Ishii, Mol. Cryst. Liq. Cryst., 187, 175 (1990).
2. A. Girard, Y. Delugeard, and H. Cailleau, J. Physique, 48, 1751 (1987).