Studies on the High-Pressure Phases of Polyethylene and Poly(tetrafluoroethylene) by Raman Spectroscopy

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ABSTRACT: Raman spectroscopic investigations of the high-pressure phase in polyethylene (PE) and each phase in poly(tetrafluoroethylene) (PTFE) under high pressure were performed using a hydrostatic high-pressure optical vessel. It was found that the molecular chain in the high-pressure phase of PE contains many *gauche* bonds similarly to the liquid phase, and it was confirmed that this phase is like a liquid crystal, which is consistent with the other results of X-ray, optical microscopic, and ultrasonic experiments. In the case of PTFE, the behavior of the two weak bands at 581 and 601 cm^{-1} , whose assignment has been the subject of discussion for some time in previous literatures, was investigated in detail throughout the whole range of PTFE phase diagram. It is suggested that the bands at 581 and 601 cm^{-1} should be attributed to 13_6 helical and transplanar conformations, respectively. Furthermore, the mechanism of untwisting in the PTFE molecular chain under high pressure is proposed.

KEY WORDS Polyethylene / Poly(tetrafluoroethylene) / High-Pressure Phase / Raman Spectroscopy / High-Pressure Optical Vessel / Liquid Crystal-Like Phase / Molecular Conformation /

The high-pressure phase of polyethylene (PE) which appears reversibly in melting and crystallization processes under high pressure above about 3000 kg cm^{-2} was discovered by Bassett and Turner,¹ and Yasuniwa and Takemura,² independently. The phase diagram in the melting process is shown in Figure 1.³ The structure of this phase was determined to be hexagonal (ordinary phase is orthorhombic) by Bassett and Piermarini.⁴ Further analyses of X-ray diffraction confirmed the existence of conformational disorder in this phase.^{3,5} On the other hand, the optical microscopic observation led to the concept that this phase has a liquid crystal-like structure.⁶ For ascertaining of these data, a direct measurement of chain conformation in this phase by Raman spectroscopy is the best method. This direct measurement is the first objective of this paper.

The high-pressure phase of poly(tetrafluoroethylene) (PTFE) was discovered by Bridgman⁷ and Weir,⁸ independently. The complete isobaric phase diagram was obtained by Hirakawa and

Figure 1. Schematic phase diagram of a folded-chain crystal of polyethylene.³ The region indicated by the shadow lines is the high-pressure phase (hexagonal). The region between the lower solid line and the dotted curve represents the coexistence region of the hexagonal and orthorhombic structures. The characteristics of the Raman skeletal-vibration bands are shown schematically in this figure.

Takemura as shown in Figure 2.⁹ The structure of the high-pressure phase (phase III) was proved by X-ray fiber pattern analysis to be an orthorhombic phase with a planar zigzag conformation.¹⁰ It was

Figure 2. Phase diagram of poly(tetrafluoroethylene).^{9,13} Molecular packings and chain conformations of phase II, IV, I, and III are the triclinic 13_6 helix, the hexagonal 15_7 helix, the hexagonal disordered 15_7 helix, and the orthorhombic planar zigzag, respectively. The hatched part represents the coexistence region of the orthorhombic and hexagonal crystals. The fiber pattern in the region I' in phase I shows the pattern of planar zigzag conformation. The characteristics of the Raman spectra for each phase are shown schematically in this figure.

also concluded from the physical properties in this phase that the rotational vibration of the chains in this phase is incoherent.^{11,12} Furthermore, the chain conformation of the region I' in phase I (hexagonal packing) was found to show a planar zigzag-like fiber pattern,¹³ which had been believed to be a disordered 15_7 helical structure. The order of I-I' transition is larger than two; therefore, this nature is interpreted as coming from emphasized molecular motion about the chain axis at this boundary, according to the results of NMR experiments.¹³ The X-ray diffraction pattern reflects a time-averaged molecular conformation in its long time scale, whereas the Raman spectrum reflects this in a short time scale. It is thus desirable and important to clarify the natures of phase III and the region I' in phase I by Raman spectroscopy. The clarification of these natures is the second objective of this paper.

EXPERIMENTAL

A high-pressure optical vessel with two sapphire (8 mm in diameter and 8 mm in length) windows, usable up to 300°C and 6000 kg cm^{-2} , was constructed as shown in Figure 3. The window aperture is 4 mm in diameter. The high-pressure cylinder (12 mm in diameter) and three plugs (two window plugs and one thermocouple plug which also serves as a sample holder) were made of heat treated DBC (Yasuki Steel) and maraging steels, respectively. To prevent leakage of pressure-transmitting fluid (silicone oil, Toshiba TSF 451 10 c.s.) at high temperatures, the sapphire windows were secured with an adhesive agent (Epicote 828, Mitsubishi Yuka Co.) on the optical flat surfaces of the plugs with 12° tapered aperture holes. Pure hydrostatic pressure was applied to a sample by the intensifier and high-pressure pipe system. The pressure was indicated digitally with an accuracy of $\pm 10\text{ kg cm}^{-2}$ by a homemade manganine-gauge-pressure meter. The focused incident beam ($4880\text{ \AA}$ or $5145\text{ \AA}$ radiation from an Ar ion laser, GLS 3200, NEC) passed through the lower window and encountered a specimen placed on the sample holder, and the 90° scattered light was collected

Figure 3. High-pressure optical vessel with sapphire windows.

through the side window. The scattered light was detected by a double monochromator (CT 25 ND, Nihon Bunko Co.) and a photon counting system (PC-543A, PL-545A, NF). The wavenumber of Raman peak was determined with an accuracy of $\pm 3 \text{ cm}^{-1}$.

Polyethylene samples used in this study were commercial "Hizex 2200" (Mitsui Co.) crystallized at atmospheric pressure. The sample sintered from powder "Polyflon F101" (Daikin Co.) was used as

a poly(tetrafluoroethylene) sample.

RESULTS AND DISCUSSION

Polyethylene (PE)

Figure 4 shows the Raman spectra of the orthorhombic phase (155°C), the lower-temperature region (233°C) in the coexistence region of the orthorhombic and hexagonal structures, the upper temperature region (238°C) in this region, the

Figure 4. Raman spectra of polyethylene at 5000 kg cm^{-2} for the orthorhombic phase (155°C), the lower-temperature region (233°C) in the coexistence region, the upper region (238°C) in this region, the hexagonal phase (240°C), the hexagonal phase (243°C) near the transition point from the hexagonal to the liquid phase, and the liquid phase (261°C). The symbol ▼ denotes the Raman lines of silicone oil.

Figure 5. Temperature shifts of the main Raman bands of polyethylene at 5000 kg cm^{-2} .

hexagonal phase (240°C), the hexagonal phase (243°C) near the transition point from the hexagonal to the liquid phase, and the liquid phase (261°C) at 5000 kg cm⁻², respectively. Temperature shifts of the main bands are shown in Figure 5. In the orthorhombic phase, there are no temperature shifts in the CH₂ stretching bands (2857 and 2889 cm⁻¹), but the other bands shift slightly to lower wavenumbers. The feature of the CH₂ bending bands is a well resolved triplet (1415, 1444, and 1464 cm⁻¹) at room temperature, but these lines grow into one broad peak with increasing temperature. The most important bands for understanding the chain conformational changes accompanied with the transition from the orthorhombic to the hexagonal phase are two skeletal vibration bands (1067 and 1135 cm⁻¹). At the orthorhombic to hexagonal transition point (233°C), obtained by the differential thermal analysis (DTA) endothermic peak (refer to Figure 1), these two bands begin to lose their intensities and take on a broad base curve. At the upper point (238°C) of the coexistence region, a new broad band appears at about 1085 cm⁻¹ at the center of the two weakened skeletal vibration bands. At the pure hexagonal phase (240°C), the 1135 cm⁻¹ band moves to a broad band located at 1000 cm⁻¹, and the 1067 cm⁻¹ band forms a large broad band located at 1085 cm⁻¹. The broadening of these bands is accelerated at temperatures above the melting point of the hexagonal phase (244°C) which is observed as DTA endothermic peak.

These facts can be explained by the use of a frequency dispersion map for a polyethylene chain. According to the theoretical calculation of these skeletal vibration modes (ν_4 branch) by Tasumi *et al.*,¹⁴ the wavenumber of this branch has a value of 1135 cm⁻¹ at $\delta=0$, decreases gradually with increasing δ to the minimum value of about 1000 cm⁻¹ at $\delta=4\pi/9$, increases gradually to the maximum value of about 1085 cm⁻¹ at $\delta=7\pi/9$, and tends to 1067 cm⁻¹ at $\delta=\pi$. For the planar zigzag-chain conformation, the Raman active frequencies in this branch are restricted to 1135 and 1067 cm⁻¹ which correspond to the values at $\delta=0$ and π , respectively. When the number of *gauche* bonds in the chain increases, the selection rule will be destroyed, and according to the zeroth approximation, the 1135 and 1067 cm⁻¹ bands will spread to the minimum (1000 cm⁻¹ at $\delta=4\pi/9$) and the

maximum (1085 cm⁻¹ at $\delta=7\pi/9$) frequencies of this branch, respectively.²⁶ These facts can be seen in Figure 4 as well as Figure 1 in which temperature dependence of these skeletal bands is schematically summarized in relation to the phase diagram. Thus, the molecular chain in the high-pressure phase must contain many *gauche* bonds similarly to the liquid phase. But, this phase has a hexagonal structure. This phase can thus be considered to be like a liquid crystal. This conclusion supports the results of X-ray measurements³ and the optical microscopic observation⁶ mentioned in the introduction of this paper. Further support for the liquid crystal-like nature of the hexagonal phase is given by the results of ultrasonic measurements¹⁵ that the shear modulus of high-pressure phase is the same as that of the liquid phase.

Why does a liquid crystal-like high-pressure phase exist above about 3000 kg cm⁻²? The answer to this question is very interesting, but also very difficult. However, a certain amount of pressure-induced cross-linking will play a role in determining the appearance of the hexagonal phase prior to melting under high pressure. That is, certain defects due to crossing of the molecular chains in the crystal will act as pressure induced cross-linking and prevent the melting of the orthorhombic phase.²⁷

Poly(tetrafluoroethylene) (PTFE)

The Raman spectra of phase II, III (high-pressure phase), and the region I' in phase I at 5500 kg cm⁻² are shown in Figure 6. There are no remarkable changes between these spectra, except the slight temperature shifts of each peak. Similar results were obtained at 4000, 3000, and 2000 kg cm⁻², and at atmospheric pressure. However, some characteristic changes can be observed for two weak peaks at 617 and 582 cm⁻¹. The details of the behaviour of these bands under 5500 and 3000 kg cm⁻², and under atmospheric pressure are shown in Figure 7. At 5500 kg cm⁻², the peak height of the 582 cm⁻¹ band (35°C), which seems to characterize the 13₆ helical conformation of phase II, decreases rapidly and disappears at the II-III transition temperature (71°C), while the 617 cm⁻¹ band (79°C), which seems to characterize the planar zigzag conformation of phase III, appears at this temperature and its intensity increases rapidly with increasing temperature. This peak maintains a constant intensity up to the region I' with a gradual wavenumber shift

Figure 6. Raman spectra of poly(tetrafluoroethylene) at 5500 kg cm^{-2} for phase II, III, and the region I' in phase I. The symbol ▼ denotes the Raman lines of silicone oil.

Figure 7. Raman spectra of poly(tetrafluoroethylene) at 5500 and 3000 kg cm^{-2} , and at atmospheric pressure in the $550\text{--}650 \text{ cm}^{-1}$ range.

to 608 cm^{-1} (142°C) at the III-I' transition region. At 3000 kg cm^{-2} , the peak height of the 581 cm^{-1} band (14.5°C), which seems to characterize phase II, decreases gradually from the II-I transition range (57°C) to the I-I' transition range (85°C), while the 606 cm^{-1} band (67.9°C), which seems to characterize the disordered 15_7 helical structure, appears at the II-I transition range and maintains a constant

intensity up to the region I' with a slight wavenumber shift to 603 cm^{-1} (123.3°C) at the I-I' transition range. At atmospheric pressure, the peak height of the 581 cm^{-1} band decreases very gradually over from the II-IV transition range to the I-I' transition range (120°C), while the 601 cm^{-1} band appears rapidly at the II-IV transition range and maintains a constant intensity up to the region I'. These characteristics are summarized schematically in Figure 2 with relation to the phase diagram.

The appearance of the 617 cm^{-1} band at the II-III transition point was reported as a characteristic of the planar zigzag phase by Wu *et al.*¹⁶ and Rabolt *et al.*¹⁷, based on their isothermal measurements at room temperature. Wu *et al.* interpreted this appearance as the wavenumber shift of the 582 cm^{-1} band due to the change in atomic contact induced by this first-order transition.

On the other hand, the appearance of the 601 cm^{-1} band at 20°C under atmospheric pressure is suggested as arising from a thermal defect, which is the reversal of the pitch of the helix, *i.e.*, the change from a left-handed to a right-handed helix, by DeSantis *et al.*,¹⁸ Brown,¹⁹ Koenig *et al.*,²⁰ Hannon *et al.*,²¹ and Zerbi *et al.*²²

Regarding the results concerning low-molecular fluorocarbons, Koenig and Boerio²³ reported that the 581 and 601 cm^{-1} bands should be attributed to the deformation of CH_2 groups adjoining transplanar and *gauche* backbone linkages, respectively. However, they finally reported that the 581 cm^{-1} band has to be assigned to a fundamental vibration of 13_6 helix, based on the fact that it splits at low temperatures.²⁴

Clark²⁵ reported a model based on this helix reversal point and interpreted the results of X-ray and NMR measurements. According to his model, these helix reversal points with transplanar conformation segregate into planes perpendicular to the chain axis forming the boundaries between the left- and right-handed crystal domains below the 20°C transition temperature, but above this temperature, such dislocation planes in the crystal gradually become more disordered as a result of the diffusion of the helix reversal points.

It is very disappointing that the vibrational assignment for PTFE chain is not complete. Particularly, the assignment of these two weak bands has been the subject of speculation and discussion for some time. In this paper, however, the

systematic investigation of the characteristic behaviour of these two bands over the whole range of the phase diagram is performed for the first time. As the character of these bands are shown schematically in Figure 2, our results must assign the 581 cm^{-1} band to a fundamental vibration of 13_6 helix as Koenig's final report must also do and the 617 cm^{-1} band to a fundamental vibration or overtone of transplanar chain since it appears at the planar zigzag orthorhombic phase (phase III). Furthermore, the $601\text{--}608\text{ cm}^{-1}$ bands in phase IV, I, and the region I' must be attributed to the thermal defect with transplanar conformation, since, at the II-IV and II-I transition temperatures, the abrupt growth of these bands is accompanied with an increase in rotational vibration along the chain axis, in phase I, the gradual decrease in the 581 cm^{-1} band intensity progresses with increasing temperature, and at the boundary of region I', the disappearance of this band can be observed along with a slight additional increase in rotational vibration along the chain axis.¹³

In view of our conclusions, Clark's model should be rewritten as follows: the helix reversal dislocation plane composed of C-C-C in the *trans* position below the 20°C transition grows and then unravels the chain from a 13_6 to a 15_7 helical symmetry at the 20°C transition. The helix reversal region (transplanar region) then grows and migrates along the chain axis at the 30°C transition, and spreads out over the chain at the boundary of the region I' in phase I. This feature can be understood by the following ordinary example. A vertically loosely stretched wet towel which is twisted into a right-handed helix in its upper part and into a left-handed helix in its lower part, is plane at the center, (this corresponds to the feature below the 20°C transition). When stretched (corresponding to an increase in the internal pressure due to emphasized thermal vibrational energy of the helical chain), the towel untwists and the plane portion spreads out over the towel (corresponding to the feature above the 20°C transition). Furthermore, the planar zigzag-like conformation obtained by X-ray measurements may be caused by a further untwisting of the helix in the region I'.

CONCLUSION

The molecular conformational changes of PE and

PTFE under high pressure and temperature are shown in this study, and the major conclusions may be summarized as follows.

PE

The molecular chain in the high-pressure phase (hexagonal phase) of PE contains many *gauche* bonds as is the case in the liquid phase. This phase can therefore be considered as being like a liquid crystal, and this is consistent with the other results of X-ray,³ optical microscopic,⁶ and ultrasonic¹⁵ experiments. A certain amount of pressure-induced cross-linking will play a roll in determining the appearance of this liquid crystal-like phase prior to melting under high pressure.

PTFE

The 581 cm^{-1} band in phase II and the 617 cm^{-1} band in phase III must be assigned to a fundamental vibration of 13_6 helix and to a fundamental vibration or overtone of the transplanar conformation, respectively. Furthermore, the $601\text{--}608\text{ cm}^{-1}$ bands in phase IV, I, and the region I' can be considered as arising from thermal defects of the helix reversal points with transplanar conformation. The helical chains in phase IV and I unravel gradually with increasing temperature because of the increased internal pressure due to the emphasized thermal vibrational energy of the chains, and at the same time, the helix reversal region (transplanar region) grows and spreads out over the chains.

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