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X-ray diffraction of polymer under load at cryogenic temperature

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An x-ray diffraction apparatus, consisting of a load cell, a stretching device, and a cryogenic cell, has been constructed to observe the mechanical deformation of the crystal lattice of polymers at cryogenic temperature. The polymer specimen could be cooled down to 18 K using this apparatus. The equatorial diffraction profiles of polymer specimens were observed under various temperatures and loads with 18 K minimum temperature. The equatorial lattice spacings of polyethylene (PE) decreased at 18 K compared with those at 300 K; however, they were elongated by a constant applied tensile stress. The elastic modulus E_t of the crystalline regions of PE in the direction perpendicular to the chain axis was evaluated. The E_t value for the (200) plane of PE increased to 11 GPa at 18 K from 3.2 GPa at 300 K. This is considered to be due to the increase of the van der Waals interactions between the chains in the crystal lattice at very low temperature, where the incoherent thermal vibrations of the atoms can be ignored. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1453501]

I. INTRODUCTION

X-ray diffraction is the most powerful method to investigate the crystal structures of materials. Many polymer crystal structures have been determined using x-ray diffraction,[1,2] and there are many reports on the relationship between the crystal structure and properties of polymers. We have been engaged particularly in measuring the elastic moduli (crystal moduli) of the crystalline regions of various polymers in the directions both parallel (E_l) and perpendicular (E_t) to the chain axis using x-ray diffraction.[3,5] The crystal moduli provide us with important information on the molecular conformation and the intermolecular forces in the crystal lattice. Furthermore, we have investigated the temperature dependencies of E_l and E_t for polymers both at high and low temperatures down to liquid nitrogen temperature and discussed these in terms of the thermal expansivity and stability of the crystalline regions for each polymer.[6–9] From the results of our past investigations, the E_l and E_t values are temperature dependent for some polymers. These indicate that crystal properties are influenced by thermal molecular motions in the crystalline regions. Therefore in order to obtain information on the crystal moduli purely based on the elasticity of polymer crystal (i.e., excluding the thermal effects), the moduli should be measured at very low temperatures. Similar measurements are also useful for direct comparison with the calculated values because most of the calculations of the crystal moduli neglect incoherent thermal effects.[10,11]

The liquid nitrogen temperature is well below the glass transition temperature of most polymers, however, it is still above the γ-relaxation temperature, where the molecular motions in the crystal lattice are reported to be significant.[12]

In this study we constructed the x-ray diffraction apparatus provided with a load cell, a stretching device, and a cryogenic cell, especially for measuring the crystal modulus of polymers at cryogenic temperature. Preliminary experiments on the lattice extension are also reported.

II. APPARATUS

In order to measure the crystal modulus of polymers, the lattice spacing under a constant stress should be measured by x-ray diffraction at cryogenic temperature. For this purpose, a stretching device and a load cell were combined with a cryostat cell (Ministat CRT-006-7000, Iwatani Industrial Gases Co.), and were mounted on an x-ray goniometer (RINT 2000, Rigaku).

Figure 1 shows a schematic setup of the apparatus. Helium gas was compressed and transported into the cold head attached to the top of the cryostat cell. Then helium was adiabatically expanded, so the cold head is cooled to cryogenic temperature. A polymer specimen was mounted to a stretching device, where the specimen was mechanically clamped. Full details were described in a previous paper.[5] The stretching device is connected with the cold head, and the sample is cooled by thermal conduction from the cold head via the stretching device. The stretching device is made of copper to ensure good thermal conduction. Gold was vapor deposited on the stretching device to avoid thermal radiation. In order to avoid thermal residual stress during cooling, the sample was allowed to shrink freely. The temperature of the sample was detected with a Au–chromel thermocouple attached to a reference specimen. The reference was the same kind of material as the measurement sample and was located just below the sample. The thermocouple was not attached to the sample directly because the thermocouple wire might interfere with the incident and the scattered x-ray beams depending on the diffraction angle.

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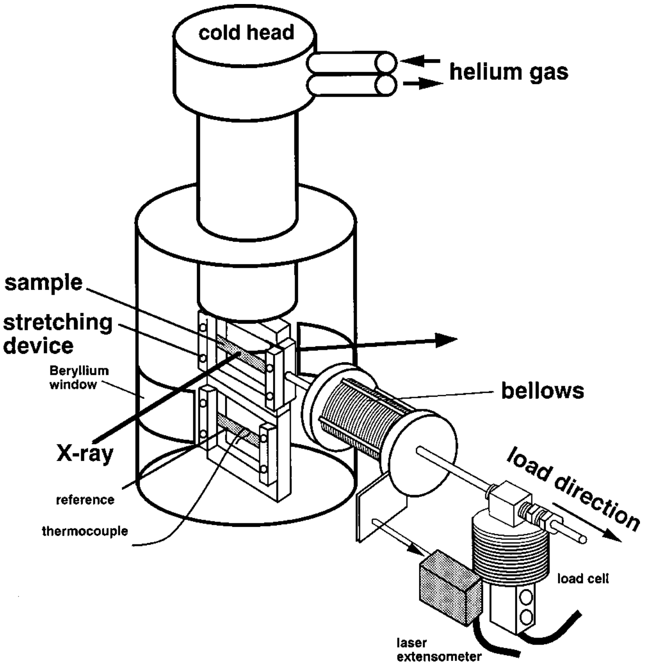

FIG. 1. Schematic setup of the cryogenic x-ray diffraction apparatus with a load cell and a stretching device.

The lowest temperature attained was 18±0.1 K during the measurements. The cooldown time from room temperature to 18 K was ~6 h and the actual measurements started at 4 h after reaching 18 K. The x-ray beam was irradiated on the specimen through a beryllium window, and the scattered beam was detected with a symmetric transmission geometry. Cu$K\alpha$ radiation (wavelength=1.5418 Å) was generated with the tube voltage of 40 kV and the tube current of 20 mA. The entire sample stage thermally contracts at cryogenic temperature, and this effect could disturb the precise setting of the sample for x-ray diffraction. However, the positional change of the specimen was found to be negligible. The photograph of the whole apparatus is shown in Fig. 2.

In order to apply stress to the specimen, the stretching device was connected to a load cell. This system is complicated since the inside of the cryostat with the stretching device was under vacuum. Therefore the load was applied to the sample from the outside of the cryostat through a bellows as schematically shown in Fig. 3. To determine the load (Fs) applied to the sample, an apparent load (F) was calibrated to the elasticity of the bellows (Fb) and the air pressure (Fa) against vacuum using

$$Fs=F-(Fa+Fb).$$

Figure 4 shows the relationship between the elongation of the bellows by the tensile load and the calibration force ($Fb+Fa$). The elongation of the bellows was measured with a laser extensometer (LC-2100, Keyence Co., Ltd.). The straight line through the origin can be the calibration curve to determine the Fs value.

III. SAMPLE

High density polyethylene (HDPE, Sholex 5551Z, from Showa Denko, Co., Ltd.) was melt pressed at 483 K then quenched into ice water. The rectangular film was uniaxially drawn six times at 368 K in water followed by annealing at 393 K for 1 h. The density of the specimen was 0.967 g/cm^3, measured by a flotation method at 300 K. This corresponds to a crystallinity of 87% assuming the crystal and amorphous densities are 1.0 (Ref. 13) and 0.855 g/cm^3,[14] respectively. The melting point of the specimen was 413 K, measured using a differential scanning calorimeter (Seiko Instruments, SSC-2200) at the heating rate of 10 K/min.

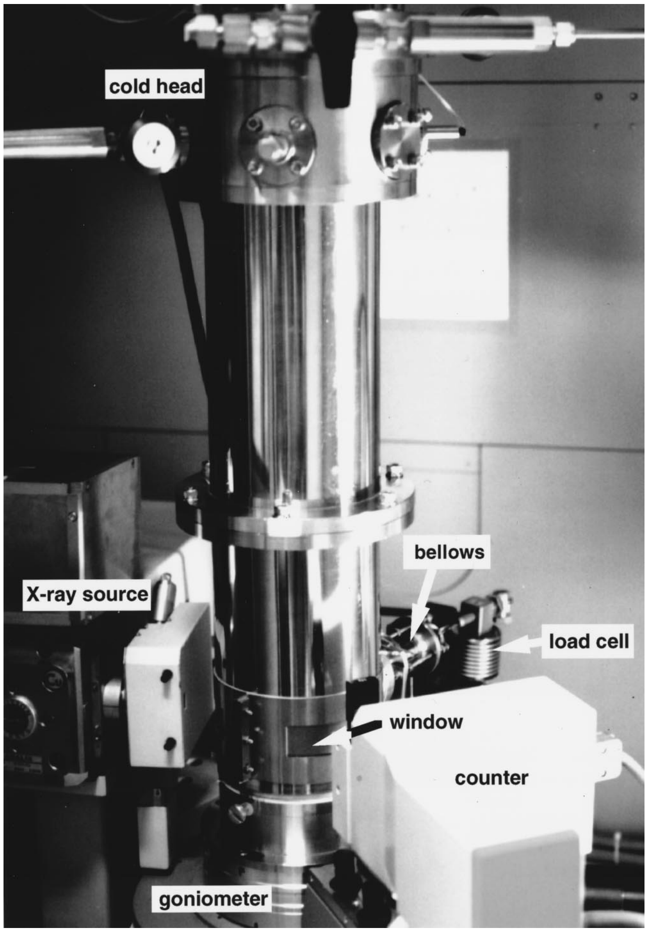

FIG. 2. Photograph of the whole apparatus on the x-ray goniometer.

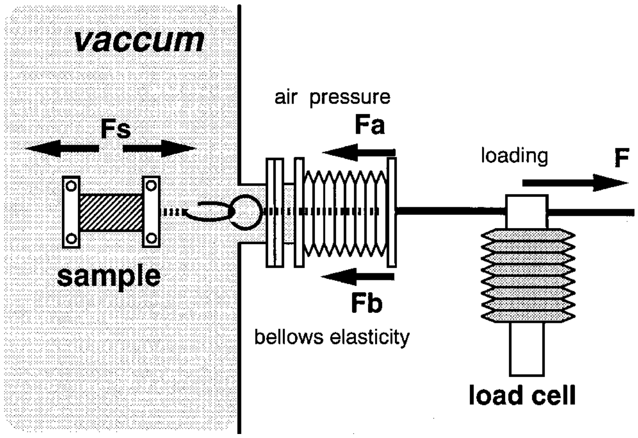

FIG. 3. Schematic representation of the system for applying stress on the sample through the stretching device and the bellows.

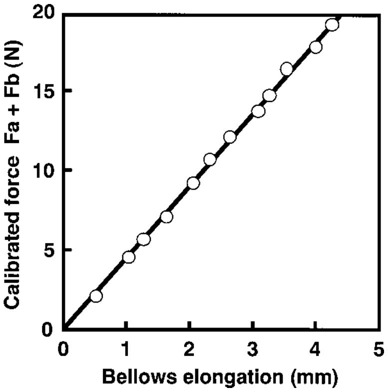

FIG. 4. Relationship between the bellows elongation by the tensile load and the calibrated force $(Fa+Fb)$.

IV. RESULTS AND DISCUSSION

Figure 5 shows the equatorial x-ray diffraction profiles of HDPE under (i) 0 MPa at 300 K, (ii) 0 MPa at 18 K, and (iii) 40 MPa at 18 K. The peak positions for the 110, 200, and 020 reflections at 300 K agreed with those measured by a second diffractometer and demonstrates that this cryosystem was suitably set on the goniometer. The peak positions shifted to higher angles at 18 K compared with those at 300 K. The 200 spacing changed from 3.70 Å at 300 K to 3.58 Å at 18 K. This showed the thermal shrinkage of the crystal lattice of PE. In addition, the peak intensities increased and the integral widths decreased at 18 K. These can be explained by the reduction of the temperature factor due to the frozen thermal vibrations of the atoms at 18 K.[15] On the other hand, the peak positions shifted to the lower angles under a constant tensile stress of 40 MPa at 18 K. This indicates that the crystal lattice was elongated by the stress. In this case, the interchain distance increased by the applied stress.

The strain ε in the crystalline regions was estimated by use of the relation

$$\varepsilon = \Delta d / d_0,$$

where d_0 denotes the initial lattice spacing, and Δd is the change in lattice spacing induced by a constant stress. The experimental error in measuring the peak shift was evaluated ordinarily to be less than ±0.01° in 2θ angle.

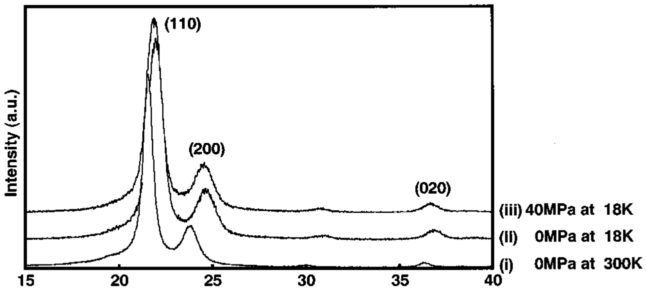

FIG. 5. X-ray diffraction profiles for the equatorial reflection of high density polyethylene: (i) 0 MPa at 300 K, (ii) 0 MPa at 18 K, and (iii) 40 MPa at 18 K.

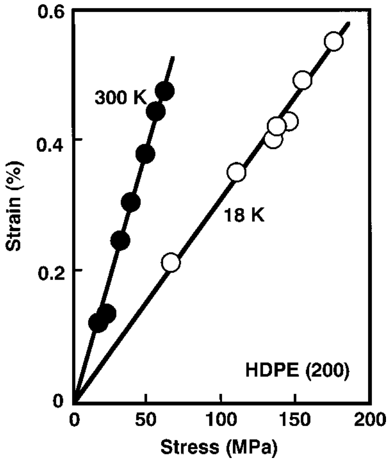

FIG. 6. Stress–strain curves for the (200) plane of high density polyethylene at ●: 300 K and ○: 18 K.

The stress σ in the crystalline regions was assumed to be equal to the stress applied to the sample. This assumption is valid since different PE specimens with different microstructures all have the same experimentally determined moduli.[5] The validity of this assumption of a homogeneous stress distribution has also been proven experimentally for polyvinyl alcohol,[16] cellulose,[8] poly(*p*-phenylene terephthalamide),[17] poly(ethylene terephthalate),[6] and so on. Furthermore, the amorphous regions would become more rigid at very low temperature, which becomes more appropriate for the effective measurements.

The elastic modulus E_t was calculated as

$$E_t = \sigma / \varepsilon.$$

By increasing the stress successively, the stress–strain curve of the crystal lattice could be drawn, from which the crystal modulus was obtained.

Detailed descriptions for the measurements of the crystal modulus were given in earlier papers.[4–6]

Figure 6 shows the stress σ–strain ε curve for the (200) plane of HDPE at (●) 300 K and (○) 18 K. The σ–ε curves could be expressed with a straight line through the origin, and the lattice extensions were always reversible. The slope gives the E_t value as 3.2 GPa at 300 K and 11 GPa at 18 K. The E_t value at 300 K coincides with that previously reported.[18] This confirms high accuracy of the measurements of the E_t value with this system. At 18 K, the E_t value increased more than three times compared with that at 300 K. This is considered to be due to the increase of the van der Waals interactions at very low temperature, where the incoherent thermal vibrations of the atoms can be ignored. The calculated E_t values for the (200) plane of polyethylene were 10.2 GPa (4 K),[19] 10.5 GPa (0 K),[20] and 10.9 GPa (0 K).[21] The calculated values agree with the experimentally determined moduli at 18 K within the experimental error.

This technique is being extended to the measurements of the crystal moduli in the directions both parallel and perpendicular to the chain axis for various polymers. The results are discussed purely based on the elasticity of polymer crystal without including the thermal vibrational effects, which will appear elsewhere.

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