NOTE

Crystal Structure of Polynorbornene

INTRODUCTION

Polynorbornene (PN) is a special elastomer with the chemical structure shown in Figure 1 and has been noticed as one of shape-memorizable polymers. Recently, much attention has been paid to the ring-opening metathesis polymerization of norbornene,[1-5] which could control the stereo-regularity of the polymer. This is also interesting for a crystallographic study. On the other hand, it was found that drawing of PN gave rise to a strain-induced crystallization in our previous work.[6]

In this study, the unit cell parameters of crystals formed in an oriented sample were determined using the wide-angle X-ray technique (WAXD), taking the coexistance of stereo-isomers into account.

EXPERIMENTAL

Sample

PN was kindly supplied by Nippon Zeon Co. having a quoted average molecular weight of 3×10^6. A film was made by molding the fine powder sample at 150°C under a pressure of 90 kg/cm^2 for 15 min followed by quenching in ice water. An oriented sample was prepared by drawing the film 8 times in a boiling water bath and then quenching in ice water.

H-NMR Measurement

JEOL GX270 was employed to measure the H-NMR spectra of the PN solution using tetramethylsilane as a standard compound, after a 1.5 wt % solution of PN in carbon tetrachloride was diluted with deuterated chloroform.

X-ray Measurement

Wide-angle X-ray diffractograms were obtained with a Rigaku Denki model D-IA X-ray diffractometer equipped with a scintillation counter, utilizing nickel-filtered CuKα radiation. Wide-angle X-ray diffraction (WAXD) patterns were also recorded in a flat-plate camera.

Density Measurement

The density was measured by the flotation method using a mixture of carbon tetrachloride and n-heptane at 25°C.

RESULTS AND DISCUSSION

Configuration of Polynorbornene Molecule

PN may be expected to have both of the *trans-* and *cis-*configuration in the molecule, since it contains a double bond in the carbon skeleton of chemical structure. IR spectra of PN showed the absorption bands[7] of 965 and 738 cm^{-1}, attributed to the CH group on the *trans-* and *cis-*form of disubstituted ethylene, respectively. In order to obtain the exact content ratio of *trans-* and *cis-*form molecules, the H-NMR measurement was carried out. H-NMR spectra are shown in Figure 2, in which the absorptions corresponding to the two configurations are observed in the range of 5.1–5.3 ppm. From the integrated intensities, the content ratio was found to be 75 : 25 similar to that reported by Abboud et al.[7]

Determination of Unit Cell Parameters

WAXD photograph of the drawn film is shown in Figure 3(a) and is schematically illustrated in Figure 3(b). The highly oriented fiber pattern of crystals, with only several

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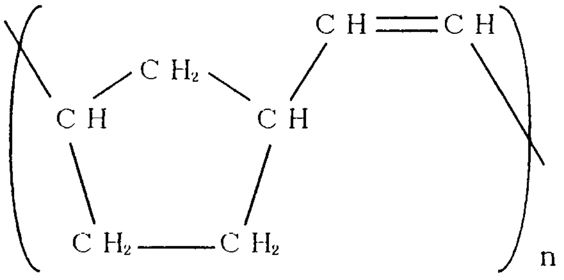

Figure 1 Chemical structure of polynorbornene.

reflections, can be seen. Here, we tried to determine the unit cell parameters of PN.

First, let us consider about two meridional reflections of H and I at spacings of 0.578 and 0.492 nm, respectively. They cannot give the relation between the orders of one crystal lattice. Accordingly, it leads us to conclude that two distinct crystal forms consisting of each molecule with the different configuration must appear.

Second, each reflection was classified into two groups corresponding to the *trans*- and *cis*-form crystal, denoted by the individual configurational molecules, assuming that the intensity of reflection spot simply depends on the content of each configurational molecule: the dense spots of A, B, D, H, and F are the reflections from the *trans*-form crystal, and the less intense ones of C, D, E, I, and G from *cis*-form. The spot D was assumed to be an overlap of the reflections from both crystals.

The crystal lattice was regarded as a monoclinic lattice. Three equatorial reflections were assumed to be (100), (010), and (110) in order of the spacing and the meridional one to be (002). The unit cell parameters of the *trans*- and *cis*-form crystals were calculated, given in Table I. The Miller indices and the calculated spacings for these two unit cells are listed in Tables II and III. The reflections F and G on the first layer line were indexed with the aid of a picture of the reciprocal lattice and WAXD photographs by trial and error, which are also shown in Tables II and III, respectively. A good agreement was obtained between the measured and calculated values.

On the other hand, the fiber repeat distances were calculated from the molecular model with the usual bond lengths and bond angles with the aid of the computer graphics,[8] assuming that the cyclopentane ring lies on a plane because we could not get the exact information about it. The values of 1.172 and 0.996 nm were obtained for the *trans*- and *cis*-form molecules, respectively. They agreed well with the results determined here from X-ray

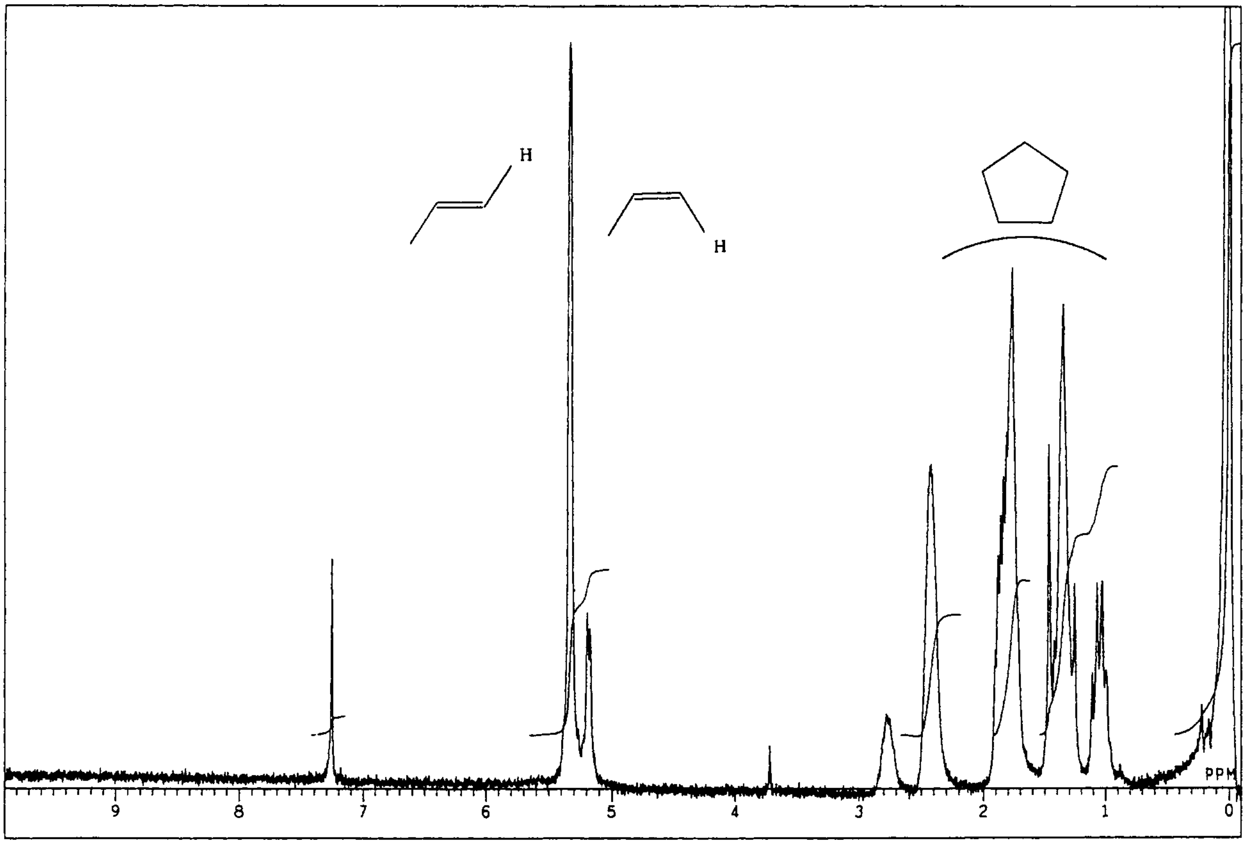

Figure 2 H-NMR spectra of polynorbornene.

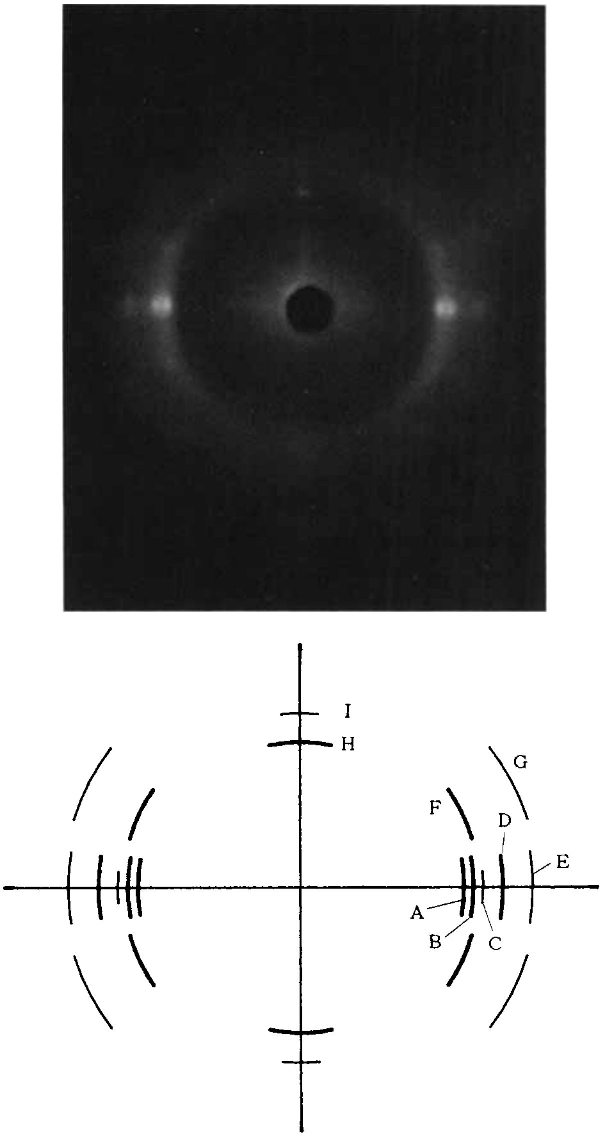

Figure 3 Wide-angle X-ray diffraction pattern of the drawn PN. (a) WAXD photograph, (b) schematic representation of (a).

analysis. Thus, the fiber distance contains two repeat units of the molecule, which implies that the 2_1-helix polymer chain lies along the c axis.

Table I Unit Cell Parameters of Crystals

Form	a (nm)	b (nm)	c[a] (nm)	γ (°)
trans	0.513	0.478	1.156	73.5
cis	0.464	0.422	0.984	68.1

[a] Fiber axis.

Table II Observed and Calculated X-ray Diffractions for *trans*-Form Crystal

		Observed		Calculated	
Spot[a]	Index	2θ (°)	d (nm)	2θ (°)	d (nm)
A	(100)	18.00	0.492	18.01	0.492
B	(010)	19.35	0.458	19.34	0.458
D	(110)	22.72	0.391	22.72	0.391
H	(002)	15.30	0.578	15.31	0.578
F	(101)	19.29	0.460	19.59	0.453

[a] The same sign as in Fig. 3(b).

Density

The density of the drawn sample, used for X-ray analysis, measured at 25°C was 1.22 g/cm^3. The density of crystal is theoretically calculated from the following equation:

$$\rho_{\text{calc}} = Z\frac{M}{V}\frac{1}{N_A} \tag{1}$$

where Z is the number of repeat units within the unit cell of crystal, M is the molecular weight of repeat units, V is the volume of the unit cell, and N_A is Avogadro's number. Before the calculation, a simple lattice was assumed, i.e., each unit cell contains only one polymer chain, leading to $Z = 2$. Now we can calculate the densities of each crystal using the lattice parameters determined here. Calculated values were 1.15 and 1.75 g/cm^3 for the *trans*- and *cis*-form crystals, respectively. If the content ratio of two-type crystals depends only on that of two distinct configurational molecules, the average density of crystals can be calculated by using their fractions of 0.75 and 0.25. The average density of crystals was obtained to be 1.30 g/cm^3. A good agreement was obtained between the observed and calculated densities, taking into account that the observed

Table III Observed and Calculated X-ray Diffractions for *cis*-Form Crystal

		Observed		Calculated	
Spot[a]	Index	2θ (°)	d (nm)	2θ (°)	d (nm)
C	(100)	20.65	0.430	20.63	0.430
D	(010)	22.72	0.391	22.72	0.391
E	(110)	24.33	0.365	24.34	0.365
I	(002)	18.00	0.492	18.00	0.492
G	(011)	24.49	0.363	24.47	0.363

[a] The same sign as in Fig. 3(b).

density is usually a little smaller than the calculated one because of the existence of the amorphous region. Accordingly, it is concluded that each unit cell of the *trans*- and *cis*-form crystals contains one polymer chain with 2_1-helix along the *c* axis and, at the same time, the unit cell parameters of two-type crystals determined here are to be reasonable.

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