Poisson's ratio of the crystal lattice of poly(*p*-phenylene terephthalamide) by X-ray diffraction

Katsuhiko Nakamae*, Takashi Nishino and Xu Airu
Department of Industrial Chemistry, Faculty of Engineering, Kobe University, Rokkodai-cho, Nada, Kobe 657, Japan
(Received 24 December 1991; revised 16 March 1992; accepted 23 March 1992)

The longitudinal Poisson's ratios ν_{lt} of the crystal lattice of poly(*p*-phenylene terephthalamide), namely Kevlar 49 and Kevlar 29, were evaluated by X-ray diffraction. Linear contraction of the crystal lattice in the direction perpendicular to the chain axis was observed up to 800 MPa. The ν_{lt} values for the (1 0 0), (0 1 0) and (1 1 0) planes are obtained as follows:

(1 0 0) $\nu_{\mathrm{lt}} = 0.31$
(0 1 0) $\nu_{\mathrm{lt}} = 0.20$
(1 1 0) $\nu_{\mathrm{lt}} = 0.24$

The small ν_{lt} value for the (0 1 0) plane is considered to correspond to the hydrogen bonds that exist in the direction perpendicular to the plane. Information on the elastic anisotropy of the crystal lattice can be obtained through this measurement.

(Keywords: poly(*p*-phenylene terephthalamide); Poisson's ratio; X-ray diffraction; crystal modulus; mechanical properties)

INTRODUCTION

Aromatic polyamides have been developed as high-modulus, high-strength polymeric materials in the past two decades. Poly(*p*-phenylene terephthalamide) (PPTA) is the best-known example, and has been used in various environments not only because of its excellent physical properties but also because of its good chemical and thermal properties[1]. PPTA fibre is usually spun from the liquid-crystalline state. Hence it possesses an almost parallel chain orientation through molecular aggregation of rigid-rod chains, and the chain molecules are packed tightly in the crystalline region, being linked by strong intermolecular hydrogen bonds to each other. We have measured the elastic modulus E_{l} of the crystalline regions of various high polymers in the direction parallel to the chain axis by X-ray diffraction[2–7]. For PPTA, the E_{l} value was measured by using Kevlar, Kevlar 29, Kevlar 49, Kevlar 149 and Twaron HM, and 156 GPa was obtained at room temperature in every case[4,7]. Further, we investigated the temperature dependence of the E_{l} value of PPTA up to 350°C, and discussed the thermal mobility of chain molecules in the crystalline regions[8]. PPTA fibre shows highly anisotropic mechanical properties. The longitudinal Poisson's ratio ν_{lt} of the crystal lattice is defined as the ratio of the longitudinal crystal strain and the transverse-contraction crystal strain, when PPTA fibre is uniaxially stretched in its fibre direction. The value of ν_{lt} is one of the basic elastic constants of the crystal lattice and is important to understand the mechanical properties of the fibre.

In this paper, the longitudinal Poisson's ratio ν_{lt} of the crystal lattice of PPTA was measured by X-ray diffraction, and was discussed in terms of mechanical anisotropy of the crystalline regions.

EXPERIMENTAL

Kevlar 49 and Kevlar 29 (Du Pont) fibres were used as PPTA. The fibres were dried at 120°C for 4 h prior to measurements in order to remove adsorbed water, which may influence the results. In general, the fibres absorb *ca.* 5% water at 25°C under a relative humidity of 70%. A fibre bundle of PPTA was clamped in a stretching device and set on an X-ray diffractometer (Rigaku Denki, RAD-B system, operated at 40 kV, 20 mA) fitted with a load cell. In order to measure the longitudinal Poisson's ratio ν_{lt} of the crystal lattice, the lattice contraction by longitudinal stress was measured by using the equatorial reflections of PPTA. The crystal structure of PPTA is reported to be monoclinic with $a = 7.80$ Å, $b = 5.19$ Å, $c = 12.9$ Å and $\gamma = 90°$. In this study, equatorial reflections of the (2 0 0) and (1 1 0) planes of PPTA were employed for the measurements. A PPTA fibre was subjected to various tensile stresses in its chain direction and the diffraction profiles for these lattice planes were recorded.

Figure 1 shows the equatorial diffraction profile of PPTA (Kevlar 49) at room temperature. The observed profile can be separated into two peaks by the non-linear least-squares method assuming Cauchy shape, which is shown by the broken curves on the figure. The lower angle peak is the 1 1 0 reflection and the higher one is the

---

*To whom correspondence should be addressed

0032-3861/92/234898-03

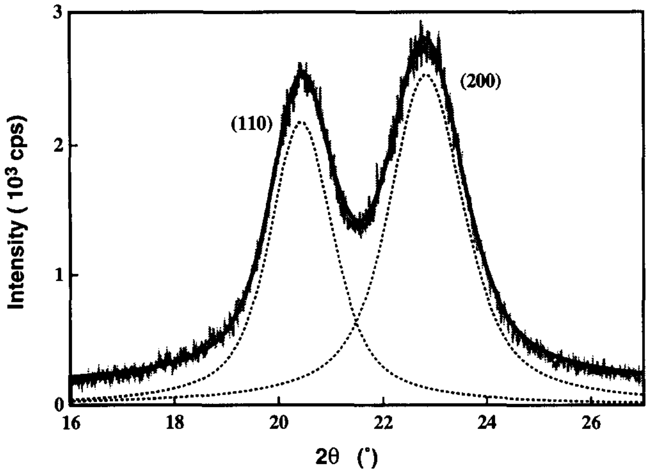

Figure 1 X-ray equatorial diffraction profile of PPTA (Kevlar 49 fibre) at room temperature. Broken curves indicate the results of curve fitting

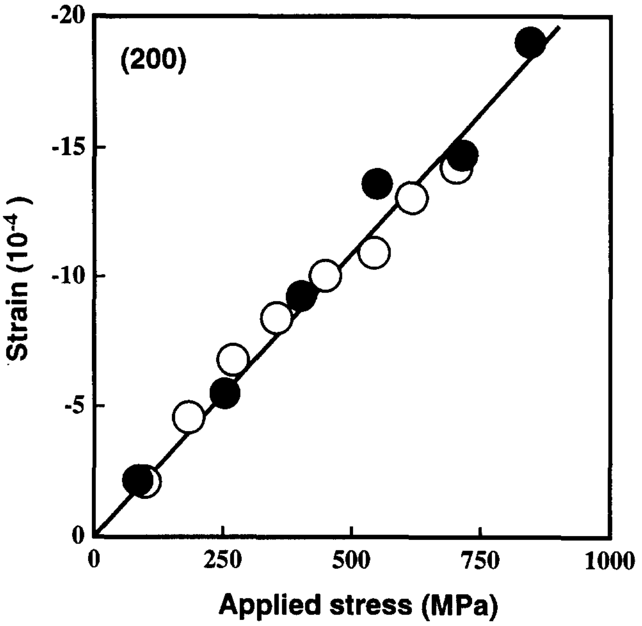

Figure 2 Relationship between strain of the (2 0 0) plane and the longitudinal applied stress for (○) Kevlar 49 and (●) Kevlar 29

2 0 0 reflection. The strain ε_{lt} of the crystal lattice was measured by the following equation:

$$\varepsilon_{lt} = \Delta d / d_0 \qquad (1)$$

where d_0 denotes the initial lattice spacing of the equatorial reflection and Δd is the change in lattice spacing induced by a constant stress applied along the chain axis. The experimental error in measuring the peak shift was evaluated ordinarily to be less than $\pm 0.001°$ in 2θ angle, which corresponds to 2% and 3% strains for the (1 1 0) and (2 0 0) planes, respectively, when the fibre was subjected to a stress of about 800 MPa. Chu *et al.*[9] performed a similar experiment on a single fibre of PPTA by using synchrotron radiation to detect the strain in the direction perpendicular to the applied stress. A high-power source enables a single fibre to be used for the measurement, by which means an inhomogeneous stress among the fibres can be avoided. This is a great advantage of using synchrotron radiation, but it should be mentioned that there are still inhomogeneities in the fibre structure as well as in the cross-sectional area along the fibre. As shown below, the ν_{lt} values estimated from Figure 4 in ref. 9 are about twice as large as those obtained in this study. The reason for the difference is not presently clear, but the experimental error in determining the peak position in this study is better than the angular resolution of 0.5 mrad by Chu *et al.*, since peak analysis software produced by Xu Airu was used in this study, with which multi-peak positions could be determined to high accuracy.

The stress induced in the crystalline regions is assumed to be equal to that applied to the bulk specimen. This assumption of homogeneous stress distribution has been proved experimentally for various polymers including PPTA[4,7], polyethylene[6], poly(vinyl alcohol)[2], cellulose[10], poly(ethylene terephthalate)[11] and so on.

As described previously[4,7], the elastic modulus E_l of the crystalline regions of PPTA in the direction parallel to the chain axis is 156 GPa for Kevlars and Twaron HM, though their specimen moduli change widely from 60 to 144 GPa. In these cases, the lattice extension was confirmed to be linear and reversible up to 800 MPa. Accordingly, the longitudinal Poisson's ratio ν_{lt} of the crystal lattice could be estimated by the following equation:

$$\nu_{lt} = -\varepsilon_{lt}/\varepsilon_{ll} = -(\varepsilon_{lt} \times E_l)/\sigma_l \qquad (2)$$

where ε_{ll} and σ_l are the lattice strain and stress along the chain direction. A more detailed description of the measurement method is given in earlier papers[2–8,10,11].

RESULTS AND DISCUSSION

Figure 2 shows the relationship between the lattice strain ε_{lt} for the (2 0 0) plane of Kevlar 49 (○), Kevlar 29 (●) and the applied stress σ_l at 20°C. When the stress is applied to its chain direction, ε_{lt} showed a negative value, i.e. the crystal lattice contracted in the direction perpendicular to the chain axis, and was always reversible. All the plots for the (2 0 0) plane could be expressed with a straight line through zero. From the slope of this line, the longitudinal Poisson's ratio ν_{lt} for the (2 0 0) planes can be obtained as 0.31.

Figure 3 shows the relationship between ε_{lt} for the (1 1 0) plane of Kevlar 49 (○), Kevlar 29 (●) and σ_l at 20°C. Again ε_{lt} was reversible and is linear with σ_l up to 800 MPa. The slope yields the ν_{lt} value for the (1 1 0) plane of 0.24.

Table 1 summarizes the measured values of ν_{lt} for the (2 0 0) and (1 1 0) planes and the estimated value of ν_{lt} for the (0 1 0) plane of PPTA at room temperature. The value of ν_{lt} for the (0 1 0) plane was calculated with the following equation:

$$(\nu_{lt,(110)})^2 = (\nu_{lt,(200)})^2 \cos^2 \psi + (\nu_{lt,(010)})^2 \sin^2 \psi \qquad (3)$$

where $\nu_{lt,(hkl)}$ is the ν_{lt} for the $(h\,k\,l)$ plane, ψ is the angle between the $(h\,k\,l)$ plane and the (1 0 0) plane, and $\psi = 33.64°$ for the (1 1 0) plane. The linear compressibility β of the crystal lattice of PPTA (Kevlar 49) by hydrostatic pressure[12], and the macroscopic ν_{lt} value, which was measured for Kevlar 29 by detecting the change in macroscopic fibre diameter[13], are also shown in *Table 1*.

The ν_{lt} values for the crystal lattice are smaller than

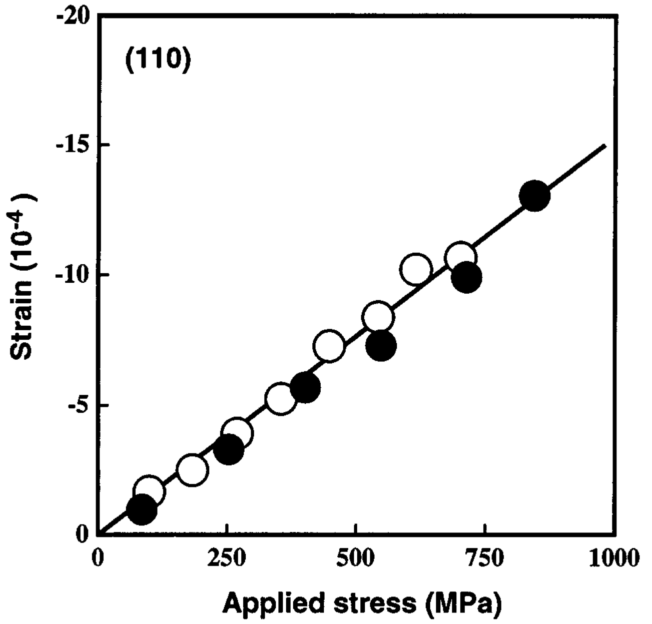

Figure 3 Relationship between strain of the (1 1 0) plane and the longitudinal applied stress for (○) Kevlar 49 and (●) Kevlar 29 at 20°C

Table 1 Microscopic and macroscopic longitudinal Poisson's ratio ν_{lt} and linear compressibility β of poly(*p*-phenylene terephthalamide)

	ν_{lt}		β
	Crystal lattice	Specimen	(GPa^{-1})
(2 0 0)	0.31		0.081^{c}
(1 1 0)	0.24	0.63^{b}	–
(0 1 0)	0.20^{a}		0.034^{c}

^{a}Calculated from ν_{lt} values for the (2 0 0) and (1 1 0) planes
^{b}Measured for Kevlar 29[13]
^{c}Linear compressibility of crystal lattice by hydrostatic pressure[3]

that of a macroscopic specimen. This indicates that the crystal lattice is harder to contract in the transverse direction than the bulk specimen. Kevlar fibre is known to have voids and/or defects along the chain direction, which can be revealed from the strong equatorial small-angle X-ray scattering[14]. This is considered to cause the larger ν_{lt} value for the macroscopic specimen. The value of ν_{lt} for the (0 1 0) plane is smaller than that for the (2 0 0) and (1 1 0) planes.

In order to investigate this point, the anisotropy of the ν_{lt} value in the *ab* plane of PPTA is superimposed on the crystal structure reported by Hasegawa *et al.*[15] in *Figure 4*. It is clear from the crystal structure that strong hydrogen bonds are expected to act along the *b* axis, but there exists only van der Waals forces along the *a* axis. This anisotropy is considered to affect that of ν_{lt} values directly, i.e. it can be predicted that it is harder to contract along the *b* axis, which corresponds to the low ν_{lt} value for the (0 1 0) plane. These tendencies are in accordance with the anisotropy of β values shown in *Table 1*.

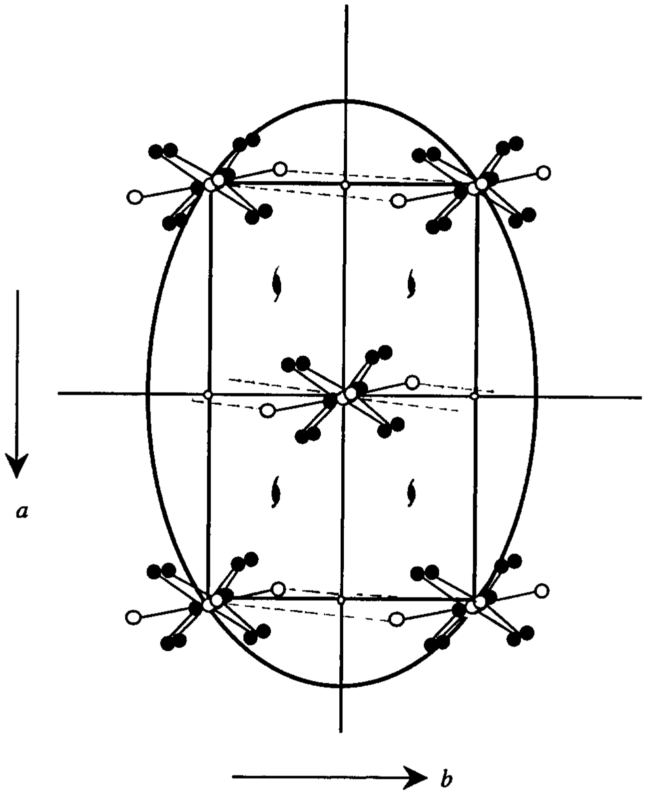

Figure 4 Schematic representation of anisotropy of ν_{lt} and crystal structure of poly (*p*-phenylene terephthalamide)

REFERENCES

1 Schaefgen, J. R., Bair, T. I., Ballou, J. W., Kwolek, S. L., Morgan, P. W., Panar, M. and Zimmerman, J. 'Ultra-High Modulus Polymers' (Eds. A. Ciferri and I. M. Ward), Applied Science, London, 1979, Ch. 6
2 Sakurada, I., Ito, T. and Nakamae, K. *J. Polym. Sci.* (*C*) 1966, **15**, 75
3 Sakurada, I. and Kaji, K. *J. Polym. Sci.* (*C*) 1970, **31**, 57
4 Nakamae, K., Nishino, T., Shimizu, Y. and Matsumoto, T. *Polym. J.* 1987, **19**, 451
5 Nakamae, K. and Nishino, T. Proc. 5th Rolduc Polym. Meeting, 1990, The Netherlands
6 Nakamae, K., Nishino, T. and Ohkubo, H. *J. Macromol. Sci.-Phys.* (*B*) 1991, **30**, 1
7 Nakamae, K., Nishino, T., Shimizu, Y. and Matsumoto, T. *Kobunshi Ronbunshu* 1988, **45**, 573
8 Nakamae, K., Nishino, T., Shimizu, Y., Hata, K. and Matsumoto, T. *Kobunshi Robunshu* 1986, **43**, 499
9 Chu, B., Wu, C., Li, Y., Harbison, G. S., Roche, E. J., Allen, S. R., McNulty, T. F. and Phillips, J. C. *J. Polym. Sci.* (*C*) *Polym. Lett.* 1990, **28**, 227
10 Nishino, T., Takano, K. and Nakamae, K. *Rep. Poval Committee* 1991, **98**
11 Nakamae, K., Nishino, T., Yokoyama, F. and Matsumoto, T. *J. Macromol. Sci.-Phys.* (*B*) 1988, **27**, 407
12 Maeda, Y. and Tanabe, Y. *Polym. Prepr. Jpn.* 1989, **38**, 964
13 Kawabata, S. 2nd Int. Conf. Adv. Mater. Tech,. Proc. Kobe, 1991, p. 51
14 Northolt, M. G. and van Artsen, J. J. *J. Polym. Sci., Polym. Symp.* 1977, **58**, 283
15 Hasegawa, R., Chatani, Y. and Tadokoro, H. Meeting Crystallographic Soc. Jpn., Osaka, 1973, p. 21