

Elastic Moduli of Crystal Lattices of Polymers

Ichiro SAKURADA, Taisuke ITO and Katsuhiko NAKAMAE*

(Sakurada Laboratory)

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Lattice extension of crystalline regions of films or fibers of polyethylene, polyvinyl alcohol, isotactic polypropylene, isotactic polystyrene, polyoxymethylene, polyethylene terephthalate, polyvinylidene chloride, cellulose I, and polycaproatamide was measured by an X-ray diffractometer under a constant load, and the elastic moduli of these polymers were evaluated. Although the main purpose of the present work was the determination of the elastic modulus in the direction of the chain axis, some experiments were also carried out for the direction perpendicular to the chain axis.

The calculation of the elastic modulus was based on the assumption of a simple series model. This assumption seems to be valid at least for the evaluation of the modulus in the direction of the chain axis. Some discussions on the easiness of extension of molecular chains are also given.

INTRODUCTION

Knowledge of elastic moduli of crystalline regions in polymers seems to be interesting from two somewhat different points of view. The one is, of course, in connection with mechanical properties of polymers and the other is in connection with configuration of a polymer molecule in crystalline regions.

It was shown by Meyer and Lotmar¹⁾ in 1936 that the modulus of elasticity corresponding to the chain direction of cellulose may be calculated from the force constants of the chemical bonds of the chain derived from vibration frequencies of molecules. Mark²⁾ has carried out similar calculation for a straight chain hydrocarbon. More recently Lyons³⁾ and Treloar⁴⁾ have extended the treatment to the crystals of synthetic polymers such as polyethylene, nylon and polyethylene terephthalate.

Dulmage and Contois⁵⁾ have measured the extension of fiber identity period of eight condensation polymers with a Norelco Geiger Counter X-ray Diffractometer and calculated the elastic moduli of crystalline regions. When a polymer has fully extended chain configuration, the modulus is high; for example the elastic modulus of the crystalline regions of polyethylene terephthalate is 140×10^4 kg/cm². However, when the fiber identity period indicated contracted chain configuration the elastic modulus was found to be low and to lie between 3.7×10^4 and 6.8×10^4 kg/cm².

We have carried out experimental determination of elastic moduli of crystalline regions polyethylene⁶⁾, polyvinyl alcohol⁶⁾, isotactic polypropylene⁶⁾,

* 桜田 一郎, 伊藤 泰輔, 中前 勝彦

isotactic polystyrene, polyoxymethylene⁽⁶⁾, polyethylene terephthalate, polyvinylidene chloride⁽⁶⁾, cellulose I⁽⁶⁾, and polycaproatide. The lattice extension was measured by an X-ray diffractometer under a constant load, so that the relaxation did not occur during the measurements. Although the main purpose of the present work was the determination of the elastic modulus in the direction of the chain axis, some experiments were also carried out for the direction perpendicular to the chain axis.

The calculation of the elastic modulus is based on the assumption of the series model. In other words, it was assumed that the stress was homogeneous throughout the length and breadth of the specimen. As will be shown later, this assumption is valid at least for the evaluation of the modulus in the direction of the chain axis.

EXPERIMENTAL

1. X-Ray Determination of Lattice Extension

A Geiger counter X-ray diffractometer was constructed for the measurement of lattice extension under a constant load. Fig. 1 and 2 show the arrangement. The filament or film specimen was mounted horizontally in the stretching clamps which could be used as a specimen mount for the diffracto-

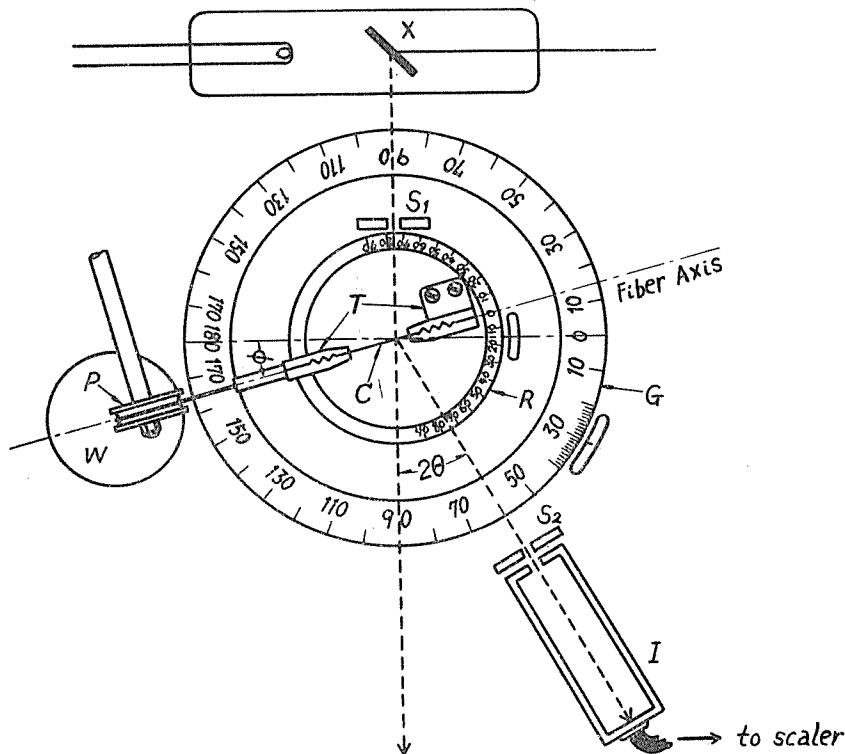


Fig. 1. X-ray diffractometer with stretching mechanism.

X: X-ray tube P: pulley I: G. M. counter W: weight S₁, S₂: slits
G: goniometer C: specimen R: rotary platform T: stretching clamps

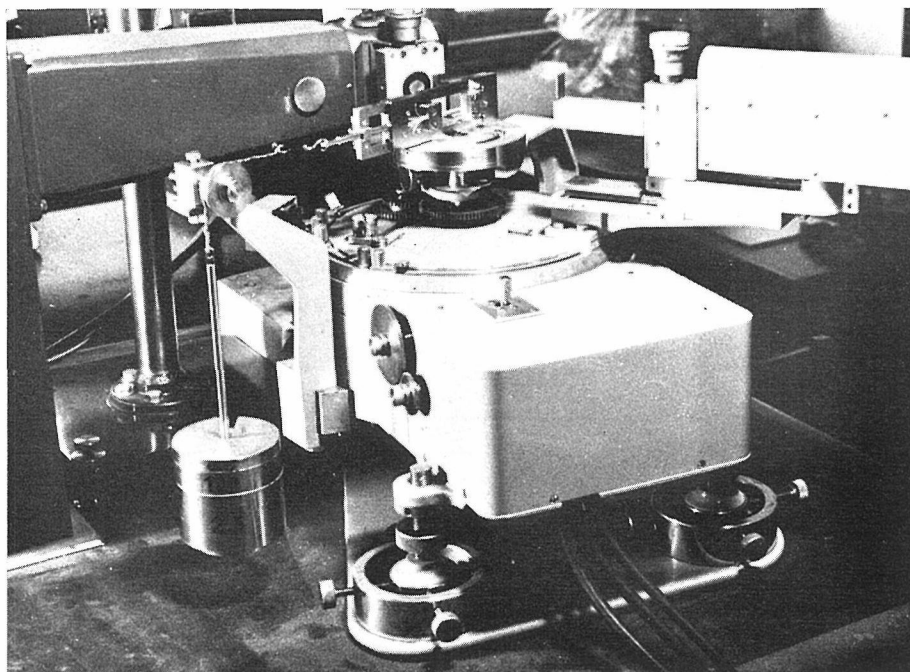


Fig. 2. X-ray diffractometer with stretching mechanism.

meter. Using a pulley, a constant weight was applied to the fiber bundle or film. The specimen length was ordinarily ca. 35 mm, and the specimen extension could be read to 0.03 mm. In the case of the measurement parallel to the fiber axis, the angle between X-ray beam and the fiber axis is 90° at the zero position of the mount. As a rule we inclined the fiber axis by an angle θ (Pragg angle) to obtain the most intense diffraction rays, when we were to measure the change of a diffraction angle of a meridional reflection. If the specimen did not exhibit an adequate meridional reflection, the fiber was so inclined that we could bring the four interference points on the meridian. Fractional change of fiber identity period, $\Delta I/I_0$, or of a net plane distance $\Delta d/d_0$, may be easily calculated from the displacement of the interference maximum.

$$\epsilon = \Delta I/I_0 = \Delta d/d_0$$

The experimental error of the measurements was $\pm 1'$. This corresponds to 0.00025 Å, when we are to measure an extension of a lattice distance of 1.25 Å; therefore we can measure the lattice extension ϵ up to 0.02%.

For the measurement of the lattice extension in the direction perpendicular to the fiber axis, film specimens were used exclusively. They were obtained by cutting from a larger drawn film as shown schematically in Fig. 3, and the displacement of the maximum of equatorial interferences was measured.

The stress σ may be obtained from the weight applied to the specimen and the calculated cross-sectional area. A correction was made for the latter, due to the elongation of the specimen. The elastic modulus E may

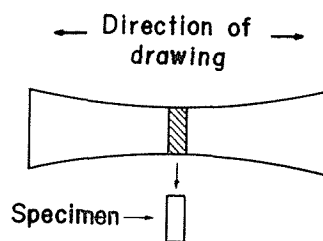


Fig. 3. Cutting a specimen from a drawn film.

be calculated by

$$\sigma = E\varepsilon.$$

2. An Example of the Measurement in the Direction of the Fiber Axis

Experiments with polyvinyl alcohol for the direction of the fiber axis should be mentioned as a first example of the measurement. The thickness of a fiber bundle used for the experiments was 2.72 mg/cm. Net plane employed for the measurement of lattice extension was (020)⁷⁾. At first a weight of 5 kg was applied, adding a dead weight (236 g) to 5 kg the load amounts

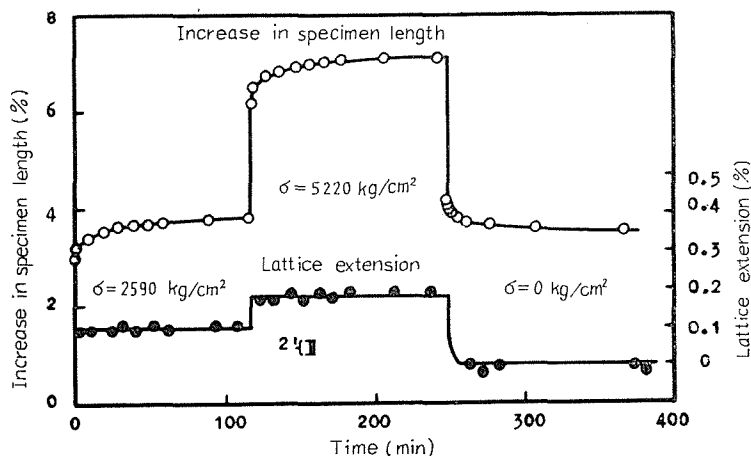


Fig. 4. Increase in specimen length and lattice extension of polyvinyl alcohol in the direction of the fiber axis.

Table 1. Stress-strain relationship for the polyvinyl alcohol lattice (parallel to the fiber axis).

σ kg/cm ²	ε %	σ kg/cm ²	ε %
1020	0.03	2590	0.10
1530	0.057	3060	0.125
2040	0.076	4080	0.15
2050	0.085	5140	0.19
2540	0.105	5220	0.18

to 2590 kg/cm². The weight was applied for 118 min. during which the specimen and lattice extension were measured. Time-extension curves are shown in Fig. 4 for the specimen and for the lattice. It may be seen from the figure that the lattice extension is reversible, whereas the specimen extension is not completely reversible. Similar experiments were carried out with varying thickness of the fiber bundle and the applied weight. The results are summarised in Table 1.

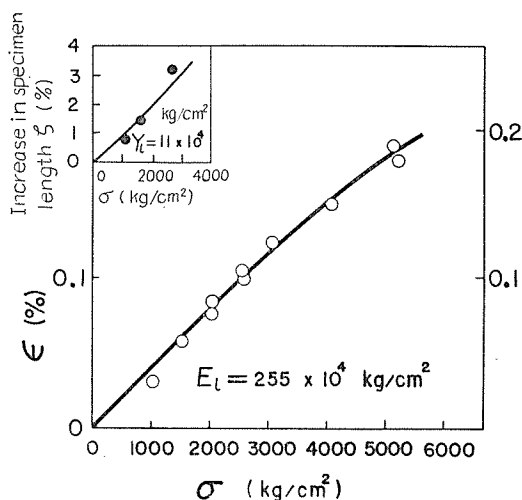


Fig. 5. Stress-strain curves for the lattice and the specimen of polyvinyl alcohol in the chain direction.

A stress-strain curve for the polyvinyl alcohol lattice is shown in Fig. 5; the elastic modulus E_l is found to be 255×10^4 kg/cm².

3. An Example of the Measurement Perpendicular to the Fiber Axis

As an example of the measurement of lattice extension perpendicular to the fiber axis, experiments with high density polyethylene film should be

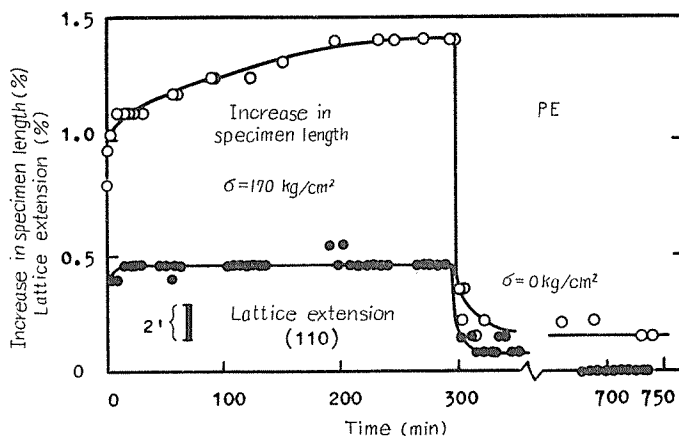


Fig. 6. Increase in specimen length and lattice extension of polyethylene in the perpendicular direction to the fiber axis.

mentioned. The form of the specimen has been already described in Fig. 3. Net planes (110), (CO00) and (020)⁸⁾ were employed for the measurement. Time-extension curves for the specimen and for the lattice, i.e. for the net plane distance (110), are shown in Fig. 6. In this case, the order of the magnitude of the specimen and lattice extension is similar. The recovery of the lattice extension is not instantaneous, although the percent extension becomes zero after a long time.

Stress-strain relationship for the net plane distance of (110) of polyethylene is given in Table 2.

Table 2. Stress-strain relationship for the net plane distance of (110) of polyethylene.

σ kg/cm ²	ϵ %	σ kg/cm ²	ϵ %
65	0.15	179	0.40
70	0.15	182	0.42
109	0.23	240	0.54
134	0.31	244	0.54
154	0.38	247	0.54
170	0.46	303	0.62

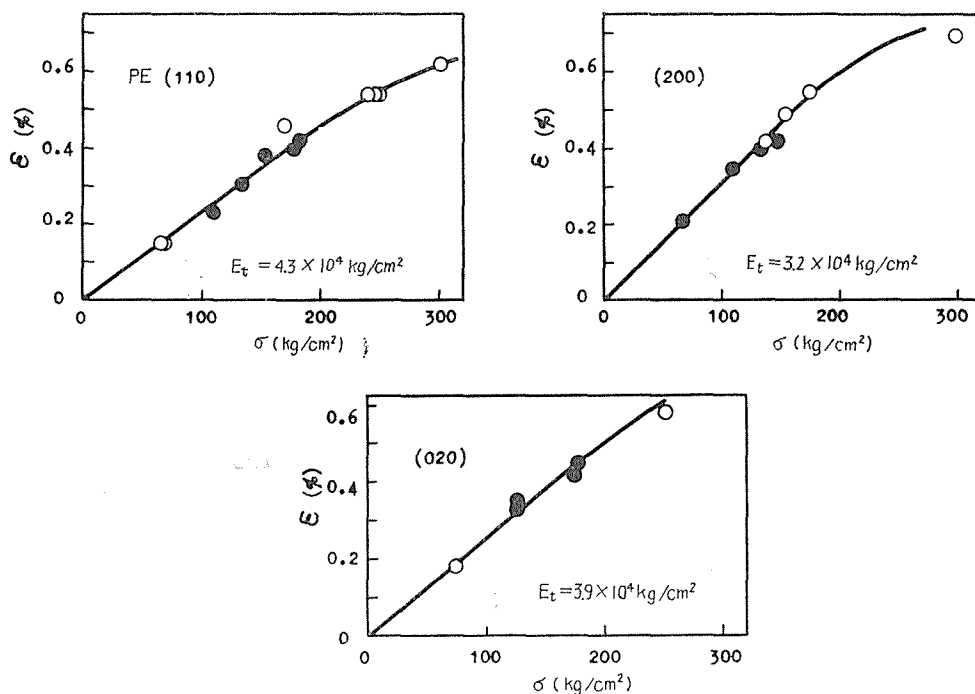


Fig. 7. Stress-strain curves for equatorial planes of polyethylene (20±1°C).

○...Plots for the specimen with no history of stress.

●...Plots for the specimen with history of stress (the lattice strain has been completely recovered before measurement.)

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Stress-strain curves for the net plane distances (110), (200) and (020) are shown in Fig. 7. The calculated values E_t of elastic modulus of the crystal-line lattice perpendicular to the fiber axis are summarised in Table 3, together with the specimen modulus Y_t , for the three different net plane distances. Although the difference of the three values lies in the range of the experimental error, it is possible or rather natural that different direction shows different modulus.

Table 3. Elastic modulus of polyethylene perpendicular to the fiber axis.

Net plane	Lattice modulus E_t kg/cm ²	Specimen modulus Y_t kg/cm ²
(110)	4.3×10^4	
(200)	3.2×10^4	2.0×10^4
(020)	3.9×10^4	

RESULTS

1. Measurements Parallel to the Fiber Axis

Polyethylene has fully extended planar zigzag chain structure like polyvinyl alcohol. Net plane (002) was employed for the measurement of the lattice extension parallel to the fiber axis, and a stress-strain curve is given in Fig. 8. The elastic modulus is found to be 240×10^4 kg/cm². Values for polyethylene and polyvinyl alcohol agree with one another within experimental error.

Both isotactic polypropylene⁹⁾ and polystyrene¹⁰⁾ molecules are known to have a helical structure, so that the extension of the lattice may chiefly

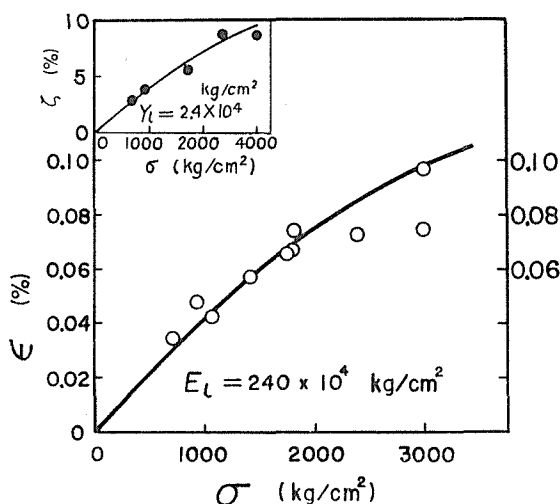


Fig. 8. Stress-strain curves for the lattice and the specimen of polyethylene in the chain direction.

depend on simultaneous rotations about the single bonds of the chain; whereas with a fully extended chain, the increase in the valence angles and or the valence distances is responsible for the lattice extension. For the measurement of the lattice extension the net planes (003) of polypropylene and (10 $\bar{2}$) of polystyrene were employed. Stress-strain curves for these two polymers are shown in Figs. 9 and 10, respectively; elastic moduli were found to be 42×10^4 (polypropylene) and 12×10^4 kg/cm² (polystyrene), values which are much lower than those of polyethylene and polyvinyl alcohol having an extended planar zigzag structure.

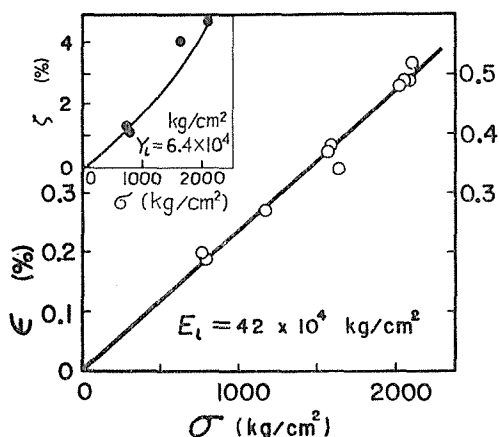


Fig. 9. Stress-strain curves for the lattice and the specimen of isotactic polypropylene in the chain direction.

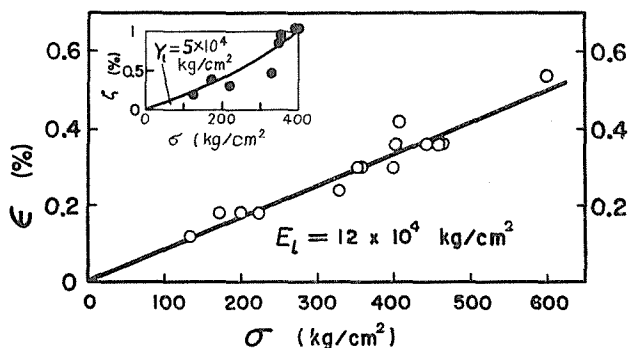


Fig. 10. Stress-strain curves for the lattice and the specimen of isotactic polystyrene in the chain direction.

Polyoxymethylene has also a helical structure¹¹⁾. The measurement of the lattice extension was carried out with (009). The stress-strain curve is shown in Fig. 11. It was possible with this polymer to raise the stress up to 6000 kg/cm² without breaking. It is interesting that the curve seems to be composed of two straight lines which cut each other at a stress of 2500 kg/cm². The mechanism of extension of lattice above and below the transition point may be different. The elastic modulus in a range of lower stress is 54

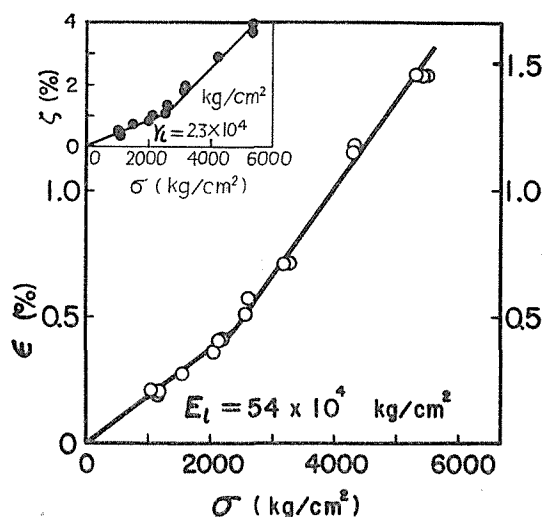


Fig. 11. Stress-strain curves for the lattice and the specimen of polyoxymethylene in the chain direction.

$\times 10^4 \text{ kg/cm}^2$, reasonable value when we assume for the polyoxymethylene molecule a helical structure, as for isotactic polypropylene.

Polyethylene terephthalate¹²⁾, polyvinylidene chloride¹³⁾ and cellulose¹⁴⁾ are the polymers which have nonplanar, not fully extended molecular structures. Measurements of the lattice extension were carried out with (105), (020) and (040) plane, respectively. Stress-strain curves are shown in Figs. 12~14. The obtained values of the elastic modulus were: 76×10^4 (polyethylene terephthalate), 41.5×10^4 (polyvinylidene chloride) and $137 \times 10^4 \text{ kg/cm}^2$ (cellulose I), respectively. The modulus of cellulose I is only half as large as that of polyethylene or polyvinyl alcohol, but attention must be paid to the fact that a cellulose molecule has a relatively large sectional area ($32.8 \text{ \AA}^2$ compared

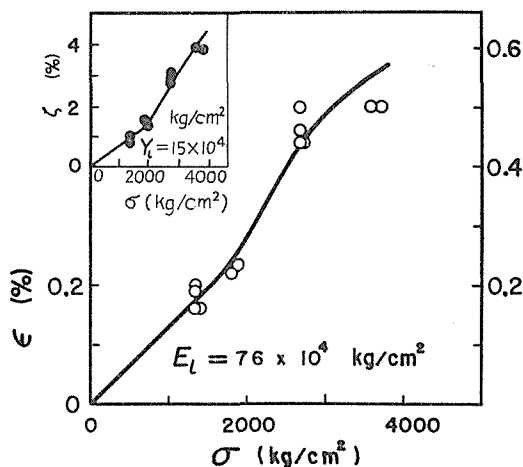


Fig. 12. Stress-strain curves for the lattice and the specimen of polyethylene terephthalate in the chain direction.

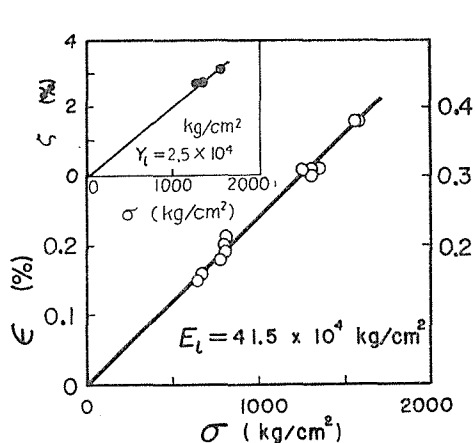


Fig. 13. Stress-strain curves for the lattice and the specimen of polyvinylidene chloride in the chain direction.

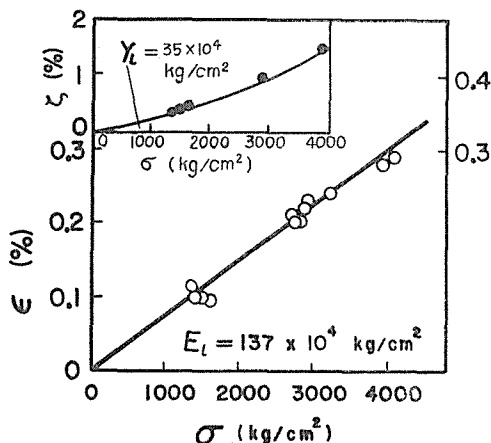


Fig. 14. Stress-strain curves for the lattice and the specimen of cellulose I in the chain direction.

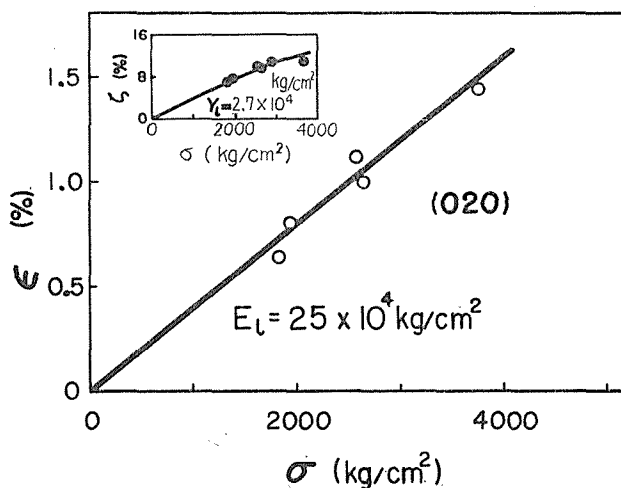


Fig. 15. Stress-strain curves for the lattice and the specimen of nylon 6 of α -form in the chain direction.

with that of 18.2 Å^2 for polyethylene).

Measurement of the stable form (α -form)¹⁶⁾ of polycapraamide (nylon 6) was somewhat difficult, because it had no adequate meridional, nor layer line reflections, but we succeeded to obtain a stress-strain curve for this polymer under employment of the (020) plane as shown in Fig. 15. The modulus was found to be 25×10^4 kg/cm², a value which was unexpectedly small, because the molecular configuration of the α -form of polycapraamide is believed to be nearly planar zigzag, so that a value larger by an order of magnitude than the observed one is expected as in the case of polyethylene and polyvinyl alcohol. The γ -form¹⁰⁾ of polycapraamide is the unstable form which may be obtained from the α -form, when we treat the latter with con-

centrated iodine solution to give a complex and afterward make this free from iodine by washing with sodium bisulfite solution. Fig. 16 shows X-ray fiber diagram of the γ -form. The diagram exhibits sharp meridional interferences on the 2nd, 4th and 6th layer line, so that the measurement of the lattice extension was very easy. Stress-strain curves are shown in Figs. 17~19. The average value of the modulus is $21 \times 10^4 \text{ kg/cm}^2$. Here it is not so surprising that the modulus is low, because the fiber identity period for the γ -form is 16.6Å instead of the calculated value of 17.3Å¹⁵⁾.

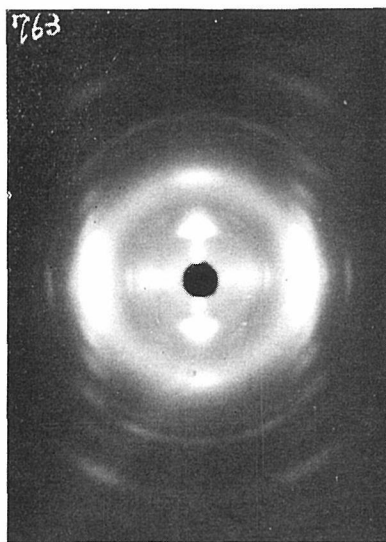


Fig. 16. X-ray fiber diagram of nylon 6 (γ -form).

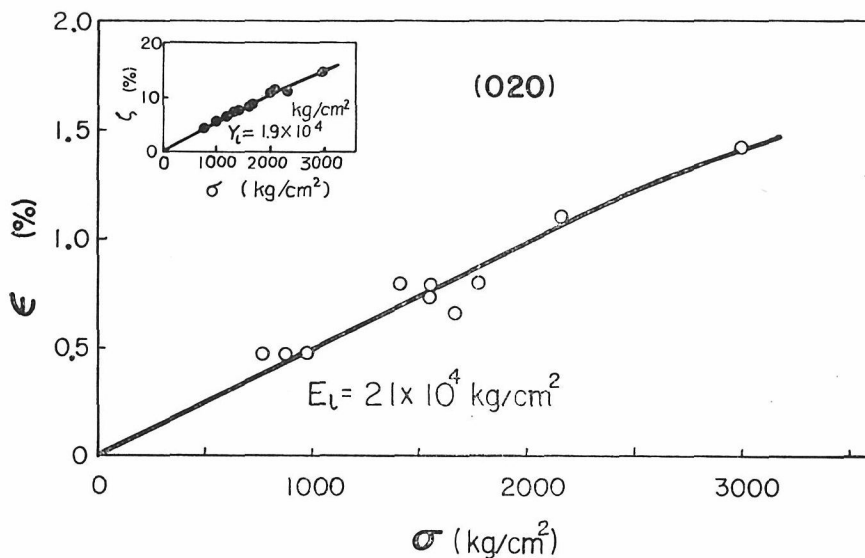


Fig. 17. Stress-strain curves for the lattice and the specimen of nylon 6 of γ -form in the chain direction.

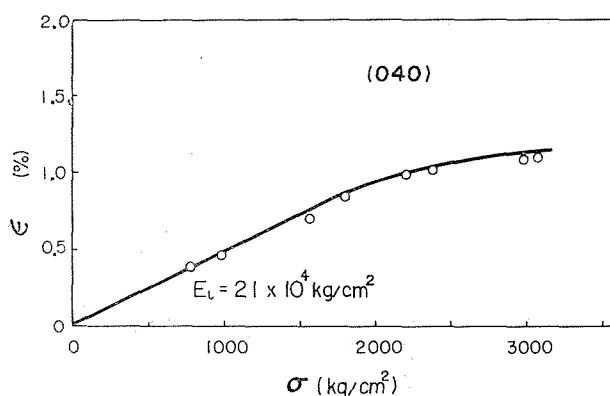


Fig. 18. Stress-strain curve for the lattice of nylon 6 of γ -form in the chain direction.

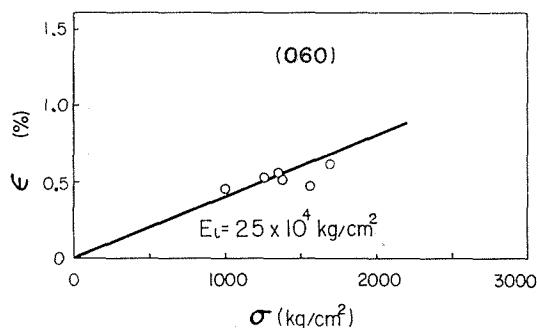


Fig. 19. Stress-strain curve for the lattice of nylon 6 of γ -form in the chain direction.

2. Measurement Perpendicular to the Fiber Axis

Measurements of the lattice extension perpendicular to the fiber axis were carried out for polyethylene, polyvinyl alcohol, polypropylene and polyoxymethylene. Except for polyvinyl alcohol where doubly oriented film, which

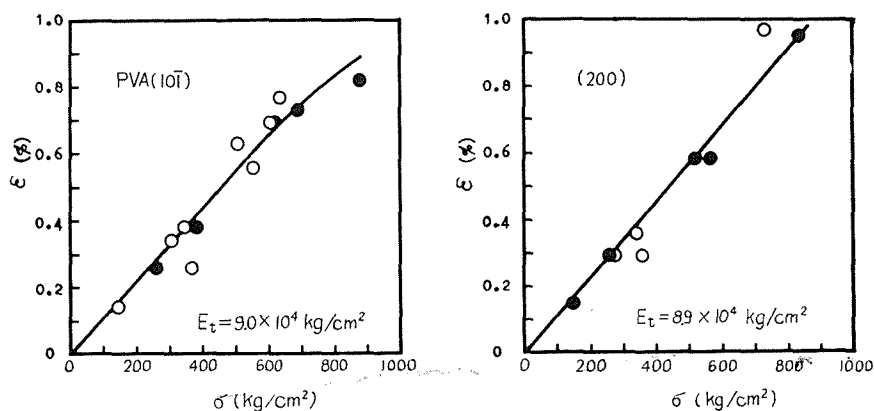


Fig. 20. Stress-strain curves for equatorial planes of polyvinyl alcohol ($25 \pm 1^\circ\text{C}$).

○...Plots for the specimen with no history of stress,

●...Plots for the specimen with history of stress (the lattice strain has been completely recovered before measurement).

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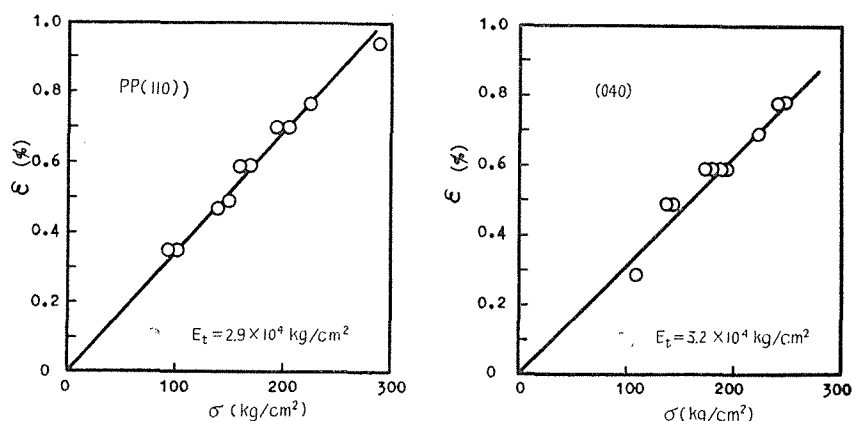


Fig. 21. Stress-strain curves for equatorial planes of isotactic polypropylene ($28 \pm 1^\circ\text{C}$).

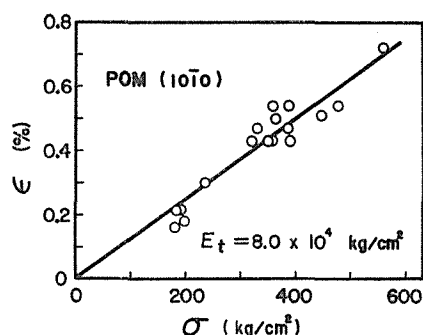


Fig. 22. Stress-strain curve for an equatorial plane of polyoxymethylene ($28 \pm 1^\circ\text{C}$).

Table 4. Elastic moduli of crystal lattices of various polymers perpendicular to the fiber axis.

Polymer	Net plane	Temp. $^\circ\text{C}$	Lattice modulus E_t kg/cm 2	Specimen modulus Y_t kg/cm 2	E_t/Y_t
Polyethylene	110	20	4.3×10^4	2.0×10^4	1.9
	200	20	3.2×10^4		
	020	20	3.9×10^4		
Polyvinyl alcohol	$10\bar{1}$	25	9.0×10^4	7.2×10^4	1.2
	200	25	8.9×10^4		
Polypropylene	110	28	2.9×10^4	2.3×10^4	1.3
	040	28	3.2×10^4		
Polyoxymethylene	$10\bar{1}0$	28	8.0×10^4	4.8×10^4	1.7

had been obtained by rolling a cast film, was used, ordinarily drawn film specimens with a simple fiber structure were employed for the measurements. Stress-strain curves are shown in Figs. 20~22; the results are summarised in Table 4.

It is noteworthy, that in all cases moduli perpendicular to the fiber axis (E_t) are much smaller than those parallel to the fiber axis (E_1). Specimen

modulus perpendicular to the fiber axis (Y_t) is of the same order of magnitude as E_t .

3. Measurements Parallel to the fiber axis with Various Specimens of the Same Polymer

For the purpose of testing the validity of an assumption of a simple series model for the calculation of the elastic modulus of crystalline lattice from the extension of a net plane distance, various specimens were prepared from the same polymer, stress-strain curves constructed and calculated values of modulus compared¹⁷⁾. For example, three specimens were employed for polyethylene. Specimen I is that which is already described and shown in Fig. 8. Its Y_1 is 2.4×10^4 kg/cm². Specimen II is a high tenacity polyethylene filament supplied from Prof. Ohya. Degree of orientation of this filament is very high and Y_1 is 15×10^4 kg/cm². Stress-strain relationships of these two specimens are shown in Fig. 23. All points lie on a curve. In spite of a large difference in Y_1 of the two specimens, there is no difference in E_1 .

Specimen III is the same drawn film that was employed for the measure-

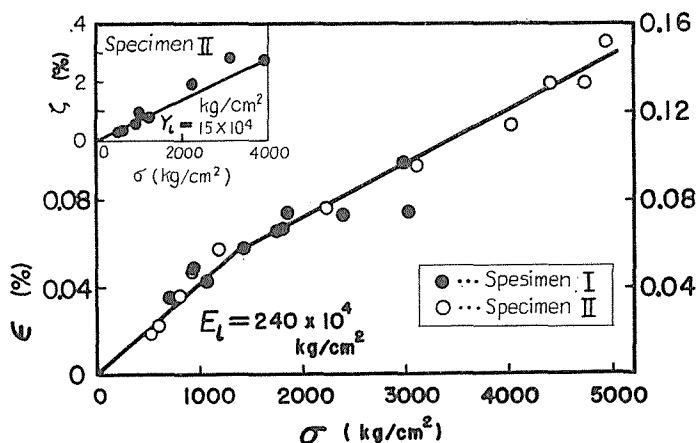


Fig. 23. Stress-strain relationships for the lattice of polyethylene for two different specimens in the chain direction.

Table 5. Elastic moduli of crystal lattice of various polymers parallel to the fiber axis.

Polymer	Nr. of specimen	Lattice modulus E_1 kg/cm ²	Specimen modulus Y_1 kg/cm ²	E_1/Y_1
Polyethylene	I	240×10^4	2.4×10^4	100
	II	240×10^4	15×10^4	16
	III	230×10^4	3.1×10^4	74
Polyvinyl alcohol	I	255×10^4	11×10^4	23
	II	250×10^4	12×10^4	21
Polypropylene	I	42×10^4	6.4×10^4	6.5
	II	48×10^4	7.0×10^4	6.9
Polyoxymethylene	I	54×10^4	23×10^4	2.4
	II	58×10^4	6.0×10^4	9.6

ment perpendicular to the fiber axis, and the E_1 of this specimen was found to be 230×10^4 kg/cm². The fact that various specimens with different micro-structure have the same E_1 value is a strong support for the validity of the above assumption.

Similar experiments were carried out for polyvinyl alcohol, polypropylene and polyoxymethylene. The results are summarised in Table 5. Specimen I is in all cases filaments E_1 value of which has been already reported in the foregoing paragraph and specimen II films which were employed for the measurement perpendicular to the fiber axis.

The agreement of E_1 values obtained for different specimens of the same polymer seems to be satisfactory.

DISCUSSION

Elastic moduli of crystal lattices parallel to the fiber axis, cross sectional area of a molecule, and the force required to stretch a molecule by 1% are summarised for various polymers in Table 6.

Table 6. Elastic moduli of crystal lattices parallel to the fiber axis, cross sectional area of a molecule and the force required to stretch a molecule by 1%.

Polymer	Lattice modulus E_1 kg/cm ²	Cross sectional area of a molecule, cm ²	Force required to stretch a molecule by 1%, dyne
Polyethylene	240×10^4	18.2×10^{-16}	4.28×10^{-5}
Polyvinyl alcohol	255×10^4	21.6×10^{-16}	5.40×10^{-5}
Polypropylene	42×10^4	34.4×10^{-16}	1.41×10^{-5}
Polystyrene	12×10^4	69.2×10^{-16}	0.81×10^{-5}
Polyoxymethylene	54×10^4	17.2×10^{-16}	0.91×10^{-5}
Polyethylene terephthalate	76×10^4	20.4×10^{-16}	1.52×10^{-5}
Polyvinylidene chloride	41.5×10^4	35.1×10^{-16}	1.43×10^{-5}
Cellulose I	137×10^4	32.8×10^{-16}	4.40×10^{-5}
Polycapraamide α	25×10^4	17.7×10^{-16}	0.43×10^{-5}
Polycapraamide γ	21×10^4	19.3×10^{-16}	0.40×10^{-5}

As already pointed out, such polymers with a planar zigzag configuration as polyethylene and polyvinyl alcohol have a very high elastic modulus, whereas elastic modulus of polymers with a helical configuration, for example that of isot. polypropylene, isot. polystyrene and polyoxymethylene is comparatively small; polyethylene terephthalate, polyvinylidene chloride and cellulose I have a nonplanar and not fully extended configuration and the modulus lie between the above two classes. These results are reasonable, but polycapraamide is an exception.

Polycapraamide molecule is believed to be nearly planar zigzag in the α -form of the crystal structure, therefore it is expected that its elastic modulus is nearly equal to that of polyethylene or polyvinyl alcohol, but the value experimentally found is much smaller than expected. Holmes, Bunn and Smith¹⁵⁾ have calculated the value of the fiber identity period of the α -form

of polycaproatamide to be 17.3 Å. According to our preliminary measurement it is 17.1 Å, Brill¹⁸⁾ gives experimentally 17.2 Å, Holmes, Bunn and Smith¹⁵⁾ 17.24 Å and Wallner¹⁹⁾ 17.08 Å. These results show that the fiber identity period of the α -form of polycaproatamide shortened by 0.4~1.7% in comparison to the calculated value. This shortening might be a reason for the low elastic modulus of polycaproatamide. Low elastic modulus of the crystal lattice of polycaproatamide seems to have some relation with low specimen modulus of nylon 6 fibers and filaments.

Comparison of the extensibility of various polymers by the elastic modulus of the crystal lattice is not convenient, because the cross sectional area is different from one polymer to another. So we have calculated the force which is required to stretch a molecule by 1%. There is nothing to alter the above conclusions, but the results are clearer.

In conclusion we wish to refer briefly to the results of the elastic modulus perpendicular to the fiber axis. In this case, there is yet some questions about the validity of a simple series model for the calculation, but it is true that the order of magnitude does not change when we apply other models for the evaluation. We think it is very important that the lattice modulus perpendicular to the fiber axis and the specimen modulus are of the same order of magnitude. It seems that the separation of a distance between two molecules play a significant role in a small and instanteneous deformation of polymer materials.

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