

Experimental Determination of the Elastic Modulus of Crystalline Regions of Some Aromatic Polyamides, Aromatic Polyesters, and Aromatic Polyether Ketone

Dedicated to the Memory of the late Professor Ichiro Sakurada

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ABSTRACT: The elastic modulus E_t of the crystalline regions parallel to the chain axis was measured by X-ray diffraction for aromatic polyamides, *i.e.*, Kevlar 49, 29, HM-50, aromatic polyesters, *i.e.*, Ekonol, Vectran, and aromatic polyether ketone, *i.e.*, poly(ether ether ketone) (PEEK). The values of E_t for these polymers were obtained as follows; E_t (Kevlar 49, 29) = 156 GPa, E_t (Ekonol) = 130 GPa, E_t (Vectran) = 126 GPa, and E_t (PEEK) = 71 GPa. Except for PEEK, E_t of these polymer are very high and the ratio of the specimen modulus (Y_t) to E_t is close to unity. These E_t values were discussed from molecular structure and conformation in the crystalline regions. The molecular structure and conformation which are required for high modulus and high strength polymers were discussed from the value of E_t .

KEY WORDS Elastic Modulus / Crystalline Regions / Aromatic Polyamide / Aromatic Polyester / Aromatic Polyether Ketone / Crystal Modulus /

The elastic moduli of polymer crystals give us important information on the molecular conformation and intermolecular forces in the crystal lattice, and on the relation of these to mechanical properties of the polymers.¹⁻⁹ Sakurada and coworkers have been engaged in measuring the elastic moduli of various polymer crystals in the direction both parallel E_t and perpendicular E_n to the chain axis by X-ray diffraction since 1962.¹⁻⁶ Examinations of the data so far accumulated led us to success in relating the E_t value *viz.* the extensivity of a polymer molecule to the molecular conformation in the crystal lattice. The values of E_t for polymers with a fully extended planar zig-zag conformation, *i.e.*, polyethylene (PE) and polyvinyl alcohol (PVA) are found to be 235 and 250 GPa respectively, while those for polymers with contracted conformation in the

crystal lattice are smaller, *i.e.*, 35 and 2.59 GPa for isotactic polypropylene and poly(trimethylene terephthalate), respectively.

Knowledge of the elastic modulus E_t of crystalline regions of polymers is of interest from another point of view. That is in connection with mechanical properties of polymer, because it gives us the maximum value for the specimen modulus of a polymer.

Recently, studies to obtain ultra high modulus and high strength polymers, and high heat resistant polymers with rigid chain molecules have been done actively, being stimulated by the development of Kevlar.¹⁰ As mentioned above, E_t value is a monitor of practical achievement in process aimed at obtaining high modulus oriented polymers.

In this paper, we report the determination of E_t for aromatic polyamides, aromatic polyes-

ters, aromatic polyether ketone, namely Kevlar 49, HM-50, Ekonol, Vectran, and PEEK. These polymers have been investigated for the purpose to obtain ultra-high modulus and high strength, and heat-resistant engineering polymers.

EXPERIMENTAL

Specimen

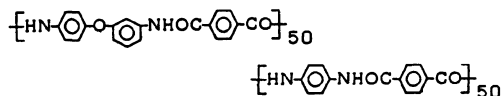
Chemical structure of polymers investigated in this study are as follows:

Aromatic polyamides

a) Poly(*p*-phenylene terephthalamide) (PPTA); Kevlar 49, Kevlar 29, Du Pont, diameter of a fiber $d = ca. 13 \mu\text{m}$.

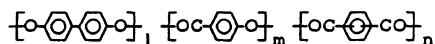


b) HM-50, Teijin Co., Ltd., $d = ca. 12.7 \mu\text{m}$.

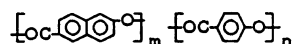


Aromatic polyesters

c) Ekonol, Sumitomo Chemical Co., Ltd., $d = ca. 17.4 \mu\text{m}$.

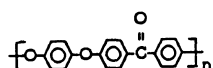


d) Vectran, Kuraray Co., Ltd., $d = ca. 23.6 \mu\text{m}$.



Aromatic polyether ketone

e) Poly(ether ether ketone) (PEEK), Sumitomo Chemical Co., Ltd.



All these samples are used as supplied except for PEEK. PEEK film ($150 \mu\text{m}$) is drawn 4 times its original length at 170°C and annealed at 300°C for 1 h at constant length.

The degree of crystal orientation π is defined

by equation,

$$\pi = (180 - H^0)/180$$

where, H^0 is the half-width of the intensity distribution curve along the Debye-Scherrer ring of each meridional reflection.

Measurement of the Elastic Modulus E_l of Crystalline Regions

The elastic modulus E_l was measured by means of an X-ray diffractometer (Rigaku Denki Co., Ltd.) equipped with stretching device.

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 the constant stress.

The stress σ in the crystalline regions was assumed to be equal to the stress applied to the sample. This assumption of the homogeneous stress distribution have been proved experimentally.^{3,5,9}

The elastic modulus E_l was calculated as

$$E_l = \sigma/\varepsilon$$

More detailed description of the measurement was given in earlier papers.¹⁻⁹

Stress-strain curves for the specimen were measured by a tensile tester (Shimadzu Autograph IS-100). The initial length of the specimen was 150 mm and the extension rate was 5 mm min^{-1} .

All the measurements were performed at 25°C .

RESULTS AND DISCUSSION

Figure 1 shows the X-ray fiber photographs of various polymers studied. From these fiber patterns, chain molecules are not well oriented in the crystalline regions and reflections are not so sharp except for Kevlar 49 and PEEK. Particularly on the equator, only a few reflections can be observed. This means that the lateral molecular packing is poor because of

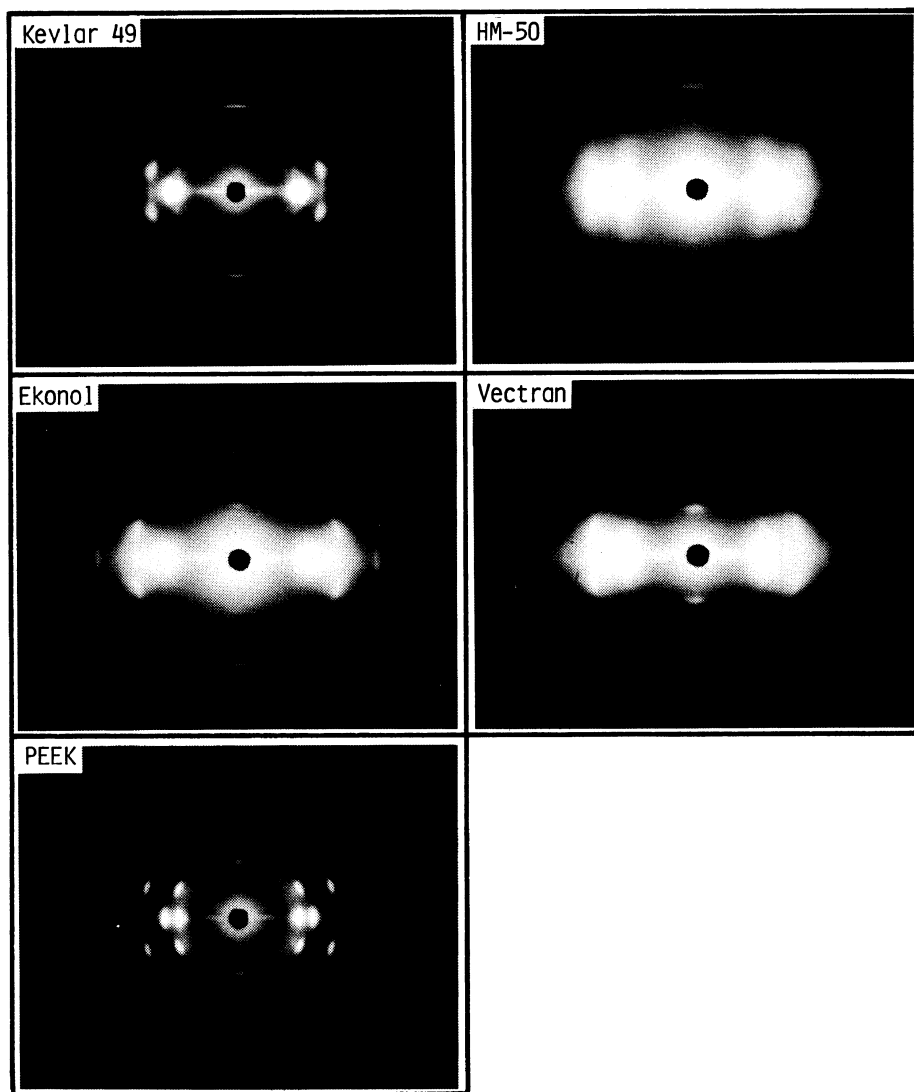


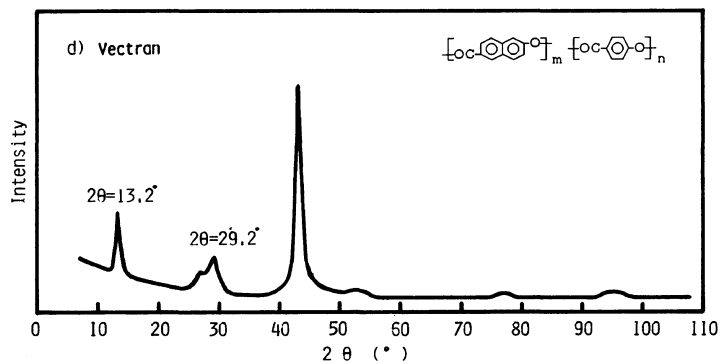
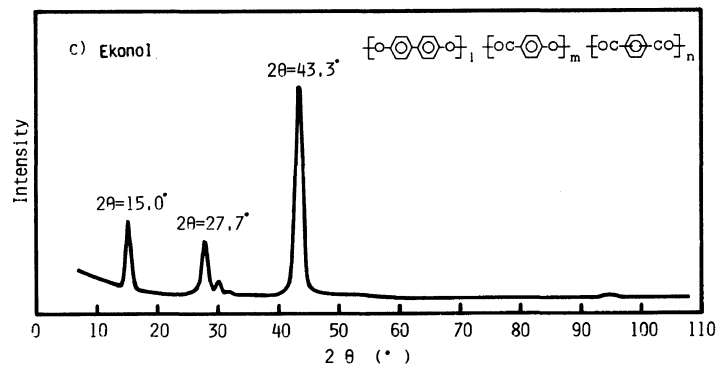
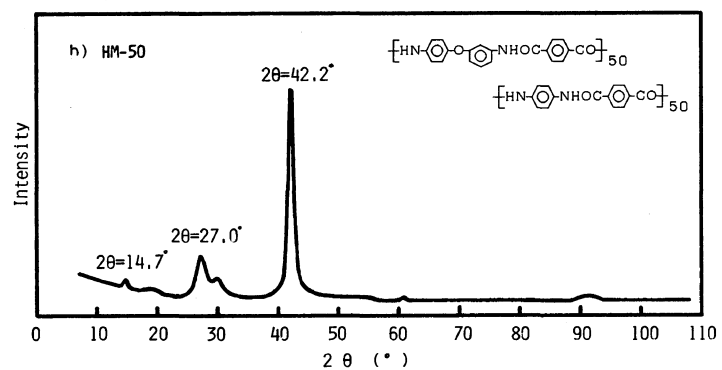
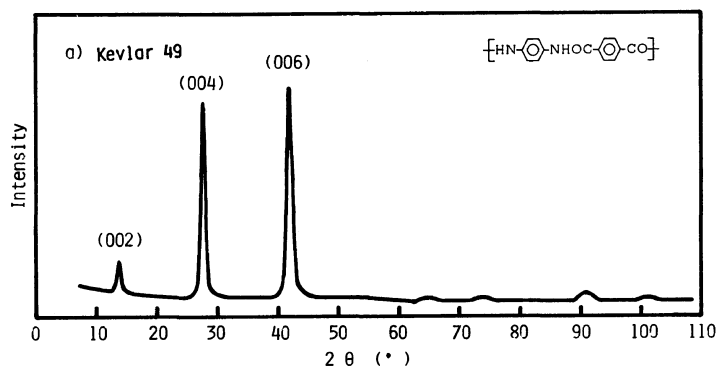
Figure 1. X-Ray fiber photographs of various polymers.

the stiffness of molecule. However, they have some sharp meridional reflections corresponding to the periodicity parallel to the chain axis.

Figure 2 shows the meridional diffraction patterns obtained by diffractometer.

For Kevlar 49, *i.e.*, poly(*p*-phenylene terephthalamide) (PPTA), some crystallographic studies have been reported.^{11,12} According to Hasegawa *et al.*,¹² PPTA has a monoclinic structure, $a=7.80 \text{ \AA}$, $b=5.19 \text{ \AA}$, c (fiber

identity period) (FIP)= 12.9 \AA , and $\gamma=90^\circ$, cross-section area of one molecule S is 20.2 \AA^2 . In Figure 2(a), it could be observed the reflections indexed as (002), (004), (006). However, in the meridional reflections observed in Figure 2(b), (c), and (d) for HM-50, Ekono1, and Vectran, respectively, the ratio of d -spacing of each reflections is not an integer, and there are shoulder peaks near $2\theta=27^\circ$.^{13,14} Further, the unit cell parameter



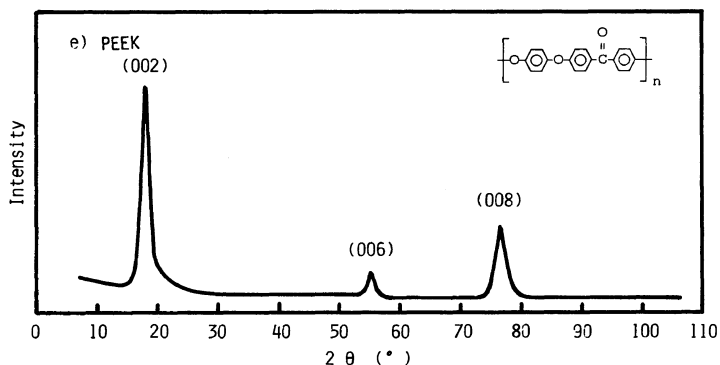


Figure 2. Meridional diffraction patterns of a) Kevlar 49, b) HM-50, c) Ekonol, d) Vectran, and e) PEEK.

of PEEK was reported as $a=7.80 \text{ \AA}$, $b=5.92 \text{ \AA}$, $c \text{ (FIP)}=10.0 \text{ \AA}$, $S=23.1 \text{ \AA}^2$, and the meridional reflections in Figure 2(e) can be indexed as (002), (006), and (008),¹⁵ but precisely the fiber identity periods calculated from various meridional reflections did not agree each other (FIP=9.85, 9.97, and 10.0 \AA calculated from (002), (006), and (008) reflections, respectively).

Figure 3 shows the stress σ -strain ϵ curves for the meridional reflections of Kevlar 49. For comparison, the stress-strain curve of the specimen (broken line) and that for the (006) plane of Kevlar 29 are also superposed on the Figure. The lattice extension is linear up to 560 MPa and the slope gives the E_l of 156 GPa. This E_l value coincides with the observed and calculated values previously reported.¹⁶ Particularly the observed E_l value (153 GPa) reported by Kaji and Sakurada¹⁷ is equal to this. They used "Kevlar" fiber for the measurement of E_l , and its specimen modulus Y_l was 62 GPa. The specimen modulus Y_l of Kevlar 49 used in this study is 131 GPa. The values of E_l of Kevlar, Kevlar 29 and Kevlar 49 agree within experimental error with each other, although values of Y_l differ widely. This may be regarded to be a strong support for the assumption of a homogeneous stress distribution. The f -value, the force required to stretch a molecule by 1%, calculated from

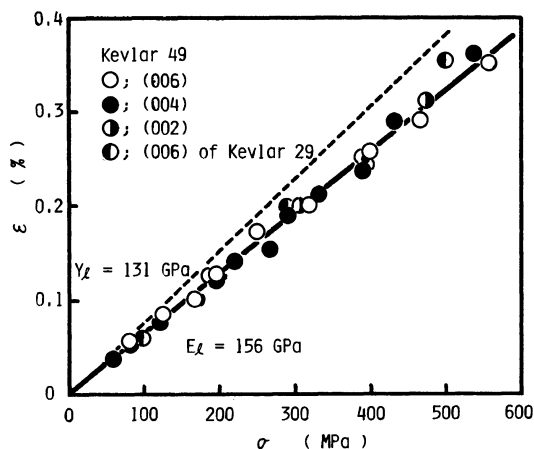


Figure 3. Stress σ -strain ϵ curve for the meridional reflections of Kevlar 49 and Kevlar 29, Broken line indicates the stress-strain curve of the specimen.

both E_l and the cross-sectional area of one molecule in a crystal lattice is 3.16×10^{-5} dyn for Kevlar 49. The E_l and f -value for PE, fully extended planar zig-zag conformation, are 235 GPa and 4.28×10^{-5} dyn. These value for PPTA, even though the Y_l/E_l is close to the unity, are smaller than those for PE.

Figure 4 shows the stress σ -strain ϵ curves for the meridional reflections of the crystal lattice of various polymers. Broken lines indicate the stress-strain curves of the specimens. The stress-strain curves for different meridional

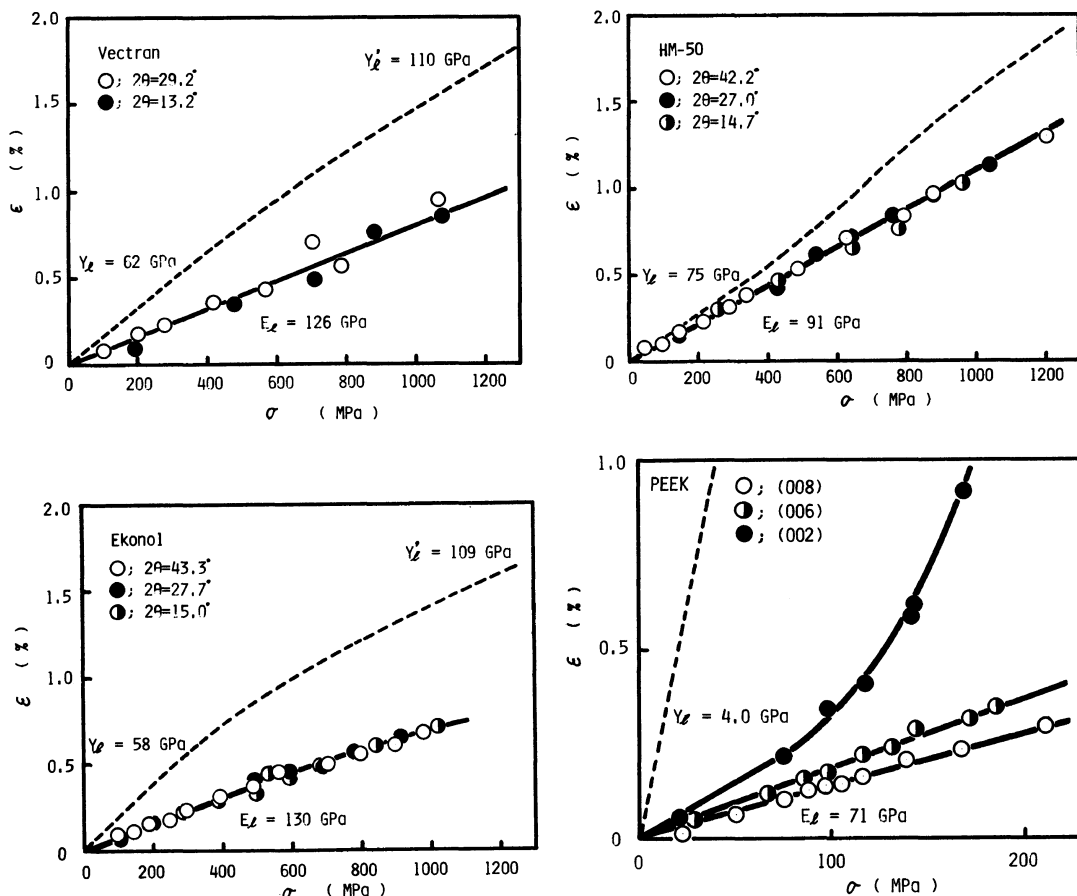


Figure 4. Stress σ -strains ϵ curves for the meridional reflections of various polymers. Broken lines indicates the stress-strain curves of the specimens.

reflections coincide each other except those for PEEK. Reflections ($2\theta = 13.2^\circ$, 29.2°) were used for the measurement of E_L of Vectran. The most intense reflection of Vectran ($2\theta = ca. 43.4^\circ$) is not used because it is not a meridional reflection but inclines about 4° from its fiber axis. It is clear from Figure 4, aromatic polyamide and polyesters can be stressed over 1 GPa stably and lattice extension is always reversible. All the stress-strain curves of the crystal lattice give straight lines through zero point and we got the E_L value from the slope of each line.

Table I shows the summary of E_L and Y_L , Y_L' , Y_L/E_L and some other properties of various

polymers. Where, Y_L , Y_L' mean the initial specimen modulus and the specimen modulus at large strain, respectively.

From this table, the E_L values of these high modulus fibers and some of super engineering plastics are not so high compared with those of PE and PVA, even though their specimen modulus are relatively high.

HM-50 is known as a high strength and tough polymer.¹⁸ One of its reason is that an ether linkage and asymmetric phenyl group are introduced to decrease molecular linearity and then the rigidity of its molecule. From these reasons, the E_L value of HM-50 decreases to 91 GPa compared with that of Kevlar 49. The E_L

Table I. Properties of various polymers

	d_4^{30} g/cm ³	π	E_l GPa	Y_l GPa	Y_l' GPa	Y_l/E_l
Kevlar 49	1.450	—	(002) 156 (004) (006)	131	145	0.84
HM-50	1.407	0.926	(2 θ = 14.7°) 91 (2 θ = 27.0°) (2 θ = 42.2°)	75	75	0.82
Ekonol	1.395	0.912	(2 θ = 15.0°) 130 (2 θ = 27.7°) (2 θ = 43.3°)	58	109	0.45
Vectran	1.436	0.961	(2 θ = 13.2°) 126 (2 θ = 29.2°)	62	110	0.49
PEEK	1.303	0.950	31 (002) 55 (006) 71 (008)	4.0	—	0.06

values of HM-50 determined from three meridional reflections coincide with each other as mentioned above, but the shoulder peak near $2\theta = 29.7^\circ$ seems to show a larger shift to lower angle under stress. This may be due to the soft copolymer component which mainly contributes to this shoulder peak. Further investigation is continued now.

Aromatic polyesters, Ekonol and Vectran, are thermotropic liquid-crystalline polymers. The development of random copolymer of rigid units enabled the decrement of melting point with the stabilization of liquid-crystalline phase where spinning and processing is performed, utilizing their ability to orient in the melt.¹⁹ However, the randomness of the different rigid units along the chain axis causes the complicated meridional reflections as shown in Figure 2 and this is considered to be the origin of the fact that the E_l value of these polymers are not so high. On the other hand, the specimen moduli Y_l of aromatic polyamides and aromatic polyesters are very high compared with conventional polymers despite the degree of orientation is not so high. The Y_l/E_l values are also high. Further, the Y_l'

values are close to the E_l values. These mean that the properties of crystalline regions control strongly the mechanical properties of the specimens. Particularly in the region of large strain, E_l , mainly determined the specimen modulus.

The stress σ -strain ϵ curve of PEEK depends on the lattice plane employed for the measurement of E_l . For the polymer an inherent E_l value should be obtained independent of the order of reflections. However, higher-ordered reflections give higher E_l values, and the highest E_l value is obtained as 71 GPa for PEEK. Same phenomenon was observed for Nylon 6.²⁰ In the case of Nylon 6, the disagreement was found to be due to the increase of crystallite size by the stress. By correcting for this effect, the values of E_l measured for another reflections agreed well with each other.²⁰ It may reasonable to conclude that the E_l value (71 GPa) for the (008) plane is valid judging from the similarity with the calculated E_l value (69 GPa)²¹ using Treloar's method. PEEK has a large arm zigzag conformation bended at the ether and ketone linkages in the crystal lattice.¹⁵ The

deformation is concentrated to the bendings of these linkages and the length of the arm (5.8 Å) is much longer than that of PE (0.9 Å). Because of above two factors, the value of E_l of PEEK is smaller than the others. The value of Y_l is also small because the rigidity of PEEK prevents the chain molecules from aligning to the draw direction with conventional drawing process.

Figure 5 shows the relationship between the E_l values and the maximum specimen modulus already reported for various polymers. Y_l of Kevlar 49 and HM-50 are very close to the E_l . Kevlar, HM-50, Vectran and Ekonol are the group of the largest specimen modulus, except the specially oriented ultra high molecular weight polyethylene.²² From Figure 5, it is reasonable to conclude that the purpose of synthesis for getting high modulus and high strength polymers from aromatic polyamide and aromatic polyester is achieved even E_l values for these polymers are smaller than those of PE, PVA. PE and PVA have the highest E_l values because these polymer crystals are composed with a fully extended planar C-C zig-zag conformation with the smallest cross-section area of a chain molecule.

These E_l values give us important information about molecular structure and conformation which high modulus and high strength polymers should have.

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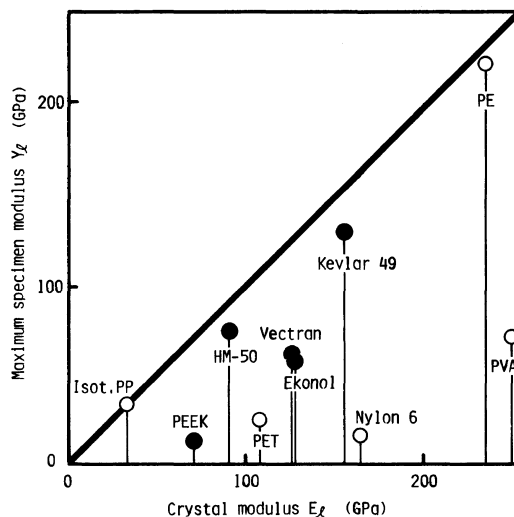


Figure 5. Relationship between the crystal modulus E_l and the maximum specimen modulus Y_l already reported for various polymers. Abbreviations indicate as follows: PET, poly(ethylene terephthalate); Isot. PP, isotactic polypropylene.

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