

Elastic Moduli of Isotactic Poly(4-methyl-1-pentene) Crystals

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Elastic moduli of the crystalline regions for isotactic poly(4-methyl-1-pentene) (PMP) were determined by an X-ray diffraction method. The observed modulus $E_{1,obs}$ for the chain-axial direction is 2.9 GN/m² at room temperature; the force required to stretch a polymer chain by 1% or f value is 0.026 nN. The modulus for the chain-axial direction was also calculated by Shimanouchi's method according to the 7/2 helix model of this polymer. The result is $E_{1,calc}=2.62$ GN/m², which agrees well with the observed one. Further the observed value $E_{t,obs}$ for the direction perpendicular to the chain axis is 2.9 GN/m² at room temperature, which is equal to $E_{1,obs}$. Thus, PMP may be isotropic concerning the initial moduli of elasticity in the crystalline regions.

From the results for the measurement of E_1 the ratio of the lateral contraction to the axial strain or the Poisson's ratio for the PMP crystals was obtained as 0.33.

INTRODUCTION

The purpose of this paper is to determine the elastic moduli of the crystalline regions for isotactic poly(4-methyl-1-pentene) (PMP). The moduli have been determined for two different directions; one is for the chain-axial direction and the other is for the direction perpendicular to the chain axis.

In the previous paper¹⁾ we reported only a numerical value of the modulus E_1 along the chain axis without details: $E_{1,obs}=6.6$ GN/m². This value is, however, reliable only in the order of magnitude since the intensity of the meridional reflection of (002) used in the measurement is weak and the reflection angle is very small, *i.e.*, the accuracy was not good. To avoid the above difficulties a strong reflection near the meridian of (113) was employed in the present work. In this case the normal of the lattice plane inclines at an angle of about 19° to the chain axis. A correction for the inclination of the plane is, therefore, necessary to estimate the E_1 -value from the (113) reflection. Thus the contraction of the lateral lattice spacings must be taken into account when the tensile stress is applied to the fibers. From the extensibilities and the lateral contractions we can also estimate the Poisson's ratio of PMP crystals. As E_1 is closely connected with the conformation of a crystalline molecular chain, it is interesting to compare the observed E_1 -value with the value calculated for the conformation of the main chain. The calculation was carried out by Shimanouchi's method.²⁾

The modulus E_t for the direction perpendicular to the chain axis depends on the intermolecular chain forces. In polyolefins it was shown that E_t decreases with increasing

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length of the side chain: 4 GN/m² for polyethylene,³⁾ 3 GN/m² for isotactic polypropylene,⁴⁾ and 2 GN/m² for isotactic poly (1-butene).⁵⁾ This is due to the enlargement of the inter-chain distances by the side chains, which results in the decreased interchain forces. On the other hand if the side chains have branches, E_t will be expected to increase since the number of effective attraction centers per unit area increases with the degree of branching. For this purpose PMP is suitable because it is a polyolefin and has a branched side chain of $-\text{CH}_2\text{CH}(\text{CH}_3)_2$. In this study, therefore, the E_t -value for PMP was also determined.

EXPERIMENTAL

Material

PMP was supplied in the form of film by the kindness of Professor Dr. Waichiro Tsuji. The polymer is a fractionated residue of Sample G in the study of "Dynamical Mechanical Properties of Poly(4-methyl-1-pentene) Fractions" by Sakaguchi, Tsuji, and Kitamaru.⁶⁾ The polymer films were drawn at 150~170°C; the draw-ratios of the specimens for the measurements of E_1 and E_t were about 6 and 3, respectively. The densities of these specimens obtained by a floatation method were 0.830 and 0.834 Mg/m³, respectively. Figure 1 is the X-ray fiber pattern of the specimen for E_1 ; it shows that the specimen is highly oriented. The degrees of orientation were determined from the azimuthal scans of a reflection. If the orientation is expressed by the practical standard of orientation, *i.e.*, $H = (180^\circ - H^\circ)/180^\circ$ where H° is the width in degrees of the azimuthal peak at half-maximum intensity, the degrees of orientation for the above two specimens are 0.96 and 0.73, respectively.

Measurements

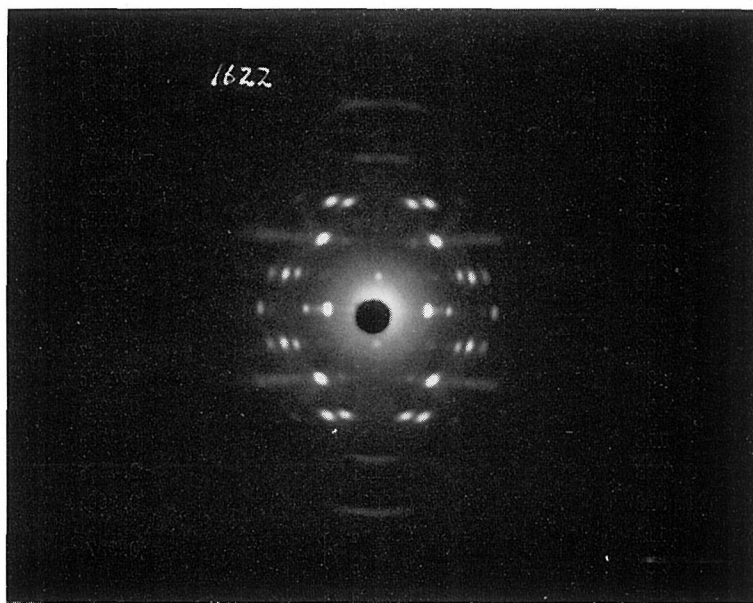


Fig. 1. X-ray fiber photograph of the highly oriented film of poly(4-methyl-1-pentene). Ni-filtered CuK α radiation.

Crystallographic data for PMP have been reported by several authors.⁷⁻⁹⁾ In order to examine these data we re-determined the lattice parameters using the highly oriented specimen. X-ray photographs were taken with a flat-plate camera where the quartz powder was used as a standard. Ni-filtered $\text{CuK}\alpha$ radiation was used throughout the present work. The lattice spacings observed are listed in Tables I and II; the equatorial

Table I. Comparison of the Calculated and Observed Lattice Spacings, d_c and d_o , of the Equatorial Planes for Poly(4-methyl-1-pentene).

Author	Present work		Litt ⁹⁾		Frank <i>et al.</i> ⁷⁾
hkl	d_c/nm	d_o/nm	d_c/nm	d_o/nm	d_o/nm
200	0.926 ₅	0.926 ₆	0.925	0.925	0.93
210	0.828 ₇	(0.79)	—	—	0.835
220	0.655 ₁	0.654 ₄	0.654	0.650	0.66
320	0.513 ₉	(0.521 ₀)	—	—	—
400	0.463 ₃	(0.452 ₉)	0.463	0.460	0.465
410	0.449 ₄		—	—	0.45
420	0.414 ₃	0.415 ₁	0.414	0.415	0.415
430	0.370 ₃	0.370 ₆	0.370	0.371 ₀	0.312 ?
440	0.327 ₆	0.331 ₇	0.327 ₀	0.328 ₇	0.33
600	0.308 ₉	0.309 ₇	0.308 ₃	0.308 ₄	0.31

Table II. Comparison of the Calculated and Observed Lattice Spacings, d_c and d_o , for the Reflections on the Layer Lines of Isotactic Poly(4-methyl-1-pentene). Present Data.

hkl	d_c/nm	d_o/nm
001	1.376	1.37
211	0.709 ₉	0.711 ₂
221	0.602 ₁	0.593 ₉
311	0.539 ₁	0.536 ₁
321	0.481 ₅	0.480 ₉
411	0.427 ₂	0.428 ₅
112	0.609 ₁	0.609 ₂
212	0.529 ₃	0.525 ₅
222	0.474 ₄	0.476 ₁
312	0.446 ₁	0.446 ₉
322	0.411 ₇	0.411 ₆
402	0.384 ₃	0.384 ₇
422	0.354 ₉	0.357 ₆
432	0.326 ₃	0.325 ₃
113	0.432 ₉	0.433 ₃
203	0.411 ₁	0.409 ₈
313	0.361 ₂	0.360 ₄
114	0.332 ₇	0.327
204	0.322 ₅	
115	0.269 ₃	0.266
205	0.263 ₈	

lattice spacings agree well with those by Litt⁹⁾ and Frank, Keller, O'Connor.⁷⁾ The observed lattice spacings give the reciprocal lattice rotation diagram as shown in Fig. 2. The unit cell is tetragonal with lattice constants $a=1.853\pm0.003$ nm and $c=1.376\pm0.003$ nm; the calculated density of the crystalline regions is 0.828 Mg/m^3 . These parameters agree well with those by Litt: $a=1.850$ nm and $c=1.376$ nm; 0.831 Mg/m^3 . In this study the lattice constants determined by us were employed; the crystal density calculated from these lattice constants agrees completely with the value estimated by Griffith and Rånby:¹⁰⁾ $0.828\pm0.002\text{ Mg/m}^3$ at 20°C .

For the measurement of E_1 the (113) plane was used; the normal of the lattice plane makes an angle of $19^\circ22'$ with the chain axis. The Bragg angle of the (113) plane for CuK α radiation is $10^\circ16'$; the X-ray beam was, therefore, incident on the specimen in the direction of about 81° to the fiber axis. Figure 3 shows an X-ray fiber pattern of PMP when the specimen was inclined at about 80° to the incident X-ray beam. The (113) reflection is seen on the meridian. The lattice extension under each constant stress was

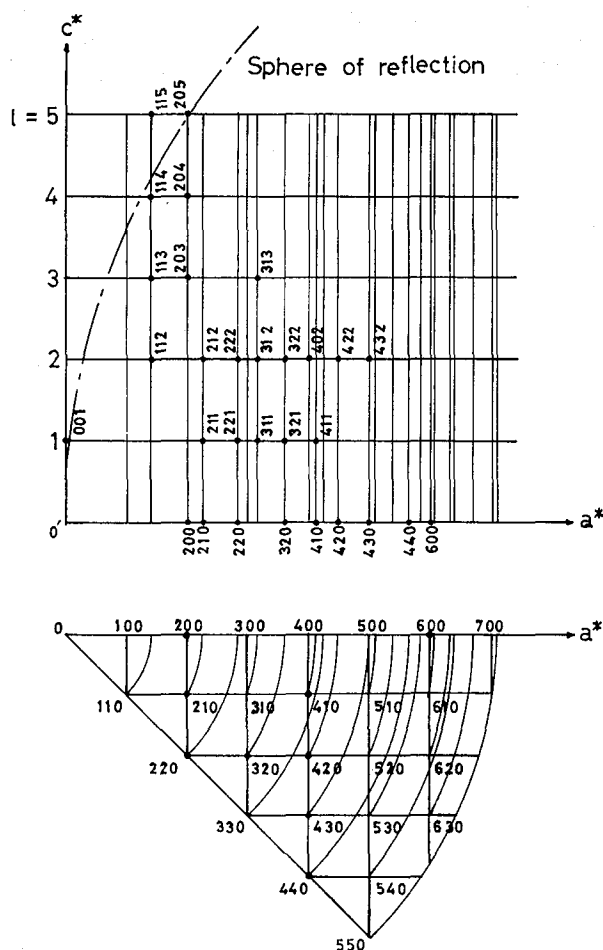


Fig. 2. Reciprocal lattice rotation diagram of poly(4-methyl-1-pentene). Tetragonal system with parameters $a=b=1.853\pm0.003$ nm and $c=1.376\pm0.003$ nm (chain axis).

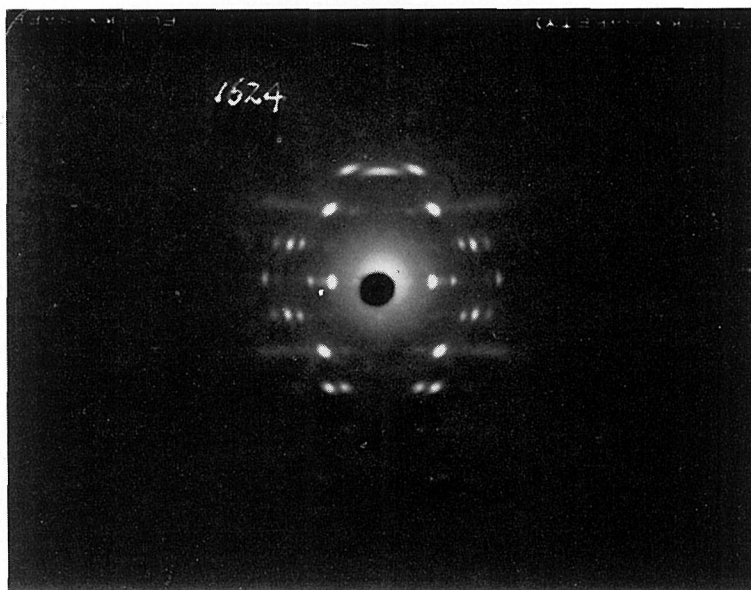


Fig. 3. The (113) reflection of poly(4-methyl-1-pentene), which appeared on the meridian. The fiber axis was inclined about 9° to the incident X-ray beam. Ni-filtered $\text{CuK}\alpha$ radiation.

measured with a Geiger-Müller counter X-ray diffractometer and a horizontal stretching device as reported in early papers.^{11,12} The specimen film was mounted on the device so that its fiber axis would be parallel to the stretching direction. For the measurements of the lateral contraction by the tensile stress applied in the chain-axial direction three equatorial strong reflections of (200), (220), and (420) were used. These measurements were carried out by use of a vertical stretching device;¹³ the stretching or fiber-axial direction is parallel to the goniometer axis. In this case X-ray beam was incident perpendicularly on the film surface of the specimen since the specimen is uniaxially oriented.

E_t was determined from the strongest reflection of (200) in the same manner³) as in the case of E_1 .

The data for all of the lattice planes used are listed in Table III. The experimental error in reading off the peak shift of the reflection by the stress was less than $\pm 1'$ in a reflection angle.

Table III. Lattice Planes Used for the Measurement of the Elastic Moduli of Poly(4-methyl-1-pentene) Crystals and Their Data.

Lattice plane (<i>hkl</i>)*	Lattice spacing, <i>d</i> /nm	Reflection angle for $\text{CuK}\alpha$, 2θ	Lattice extension or contraction corresponding to 2θ of $-1'$ or $+1'$, respectively, %
(113)	0.433	$20^\circ 31'$	0.0803
(200)	0.927	$9^\circ 33'$	0.174
(220)	0.655	$13^\circ 32'$	0.123
(420)	0.414	$21^\circ 27'$	0.0768

* The chain axis is c .

RESULTS

The stress-strain curve for the (113) plane of PMP is shown in Fig. 4. The observed points are shown only below a stress of about 50 MN/m² although the strength of the specimen is more than 90 MN/m², because the intensity of the (113) reflection begins to decrease abruptly from a stress of about 30 MN/m² and above 50 MN/m² its decrease is too great to read off the peak position exactly. As seen from the stress-strain curve for the macroscopic specimen in the corner of Fig. 4, the decrease of the intensity is partly due to the large elongation of the specimen. Figure 5 shows the stress-strain relationship for the equatorial lattice spacings of (200), (220), and (420); the observed points for these three lattice planes are on the same curve within experimental errors. This result shows that the crystal system does not change by the tensile stress along the chain axis. It is also seen in Fig. 5 that the curve has an inflection point at a stress of about 60 MN/m²; the reason for this phenomenon was not investigated in the present study. Therefore, the discussions will hereinafter be made below this stress.

From Figs. 4 and 5 we can calculate the elastic modulus of the crystalline regions along the chain axis. In the tetragonal system such as PMP the relation between the interplanar spacings d_{hkl} of (hkl) planes and the lattice constants is given as follows:

$$1/d_{hkl}^2 = (h^2 + k^2)/a^2 + l^2/c^2 \quad (1)$$

For the (113) plane Eq. (1) becomes

$$1/d_{113}^2 = 2/a^2 + 9/c^2 \quad (2)$$

When the crystal system does not change by stresses, the small change of d -spacing is given by

$$\Delta d = (\partial d / \partial a) \Delta a + (\partial d / \partial c) \Delta c \quad (3)$$

From Eqs. (2) and (3) the rate of lattice strain along the chain axis, *i.e.*, $\Delta c/c$ can be derived

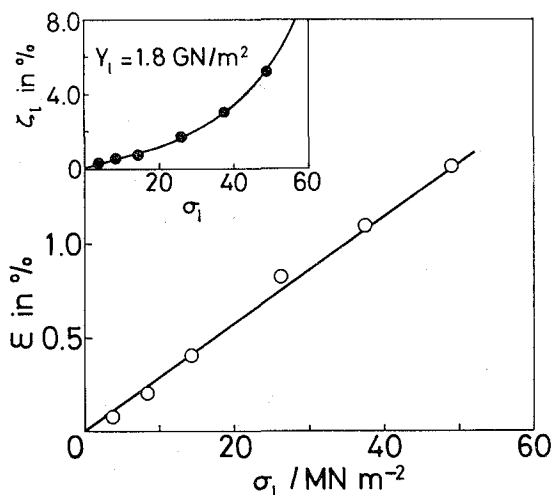


Fig. 4. Stress-strain (σ_1 - ϵ) curve for the (113) plane of poly(4-methyl-1-pentene) at $20 \pm 1^\circ\text{C}$. The stress-elongation (σ_1 - ζ_1) curve for the macroscopic specimen is shown at the corner of the figure.

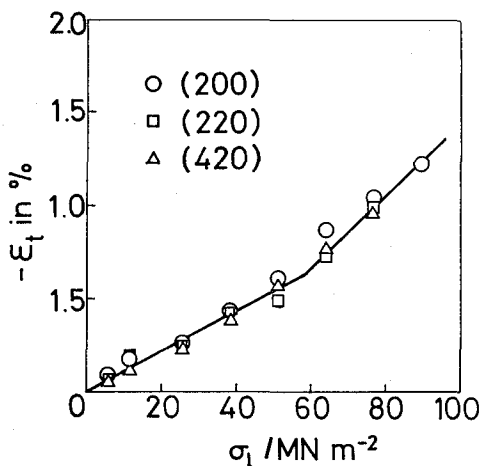


Fig. 5. Stress-strain (σ_1 - ϵ_t) relationship for the equatorial lattice spacings of (200), (220), and (420) of poly(4-methyl-1-pentene) at $20 \pm 1^\circ\text{C}$ when the stresses were applied along the chain axis.

immediately:

$$\frac{9}{c^2} \left(\frac{\Delta c}{c} \right) = \frac{1}{d_{113}^2} \left(\frac{\Delta d}{d_{113}} \right) - \frac{2}{a^2} \left(\frac{\Delta a}{a} \right) \quad (4)$$

Substituting the numerical values of the lattice parameters in the Eq. (4) we obtain

$$\Delta c/c = 1.1225(\Delta d/d_{113}) - 0.1221(\Delta a/a) \quad (5)$$

Thus the $\Delta c/c$ can be calculated from the observed values of $\Delta d/d$ for the (113) plane and $\Delta a/a$. Figure 6 shows the stress-strain curve for the chain-axial direction, which was obtained through Eq. (5) from Figs. 4 and 5. The initial slope of this curve gives rise to the modulus along the chain axis: $E_{l, \text{obs}} = 2.9 \text{ GN/m}^2$ at $20 \pm 1^\circ\text{C}$, from which the force required to stretch a polymer chain by 1% or f value is calculated as 0.026 nN by use of

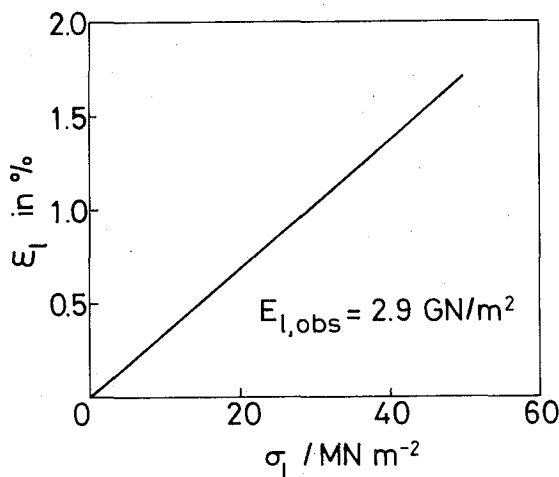


Fig. 6. Corrected stress-strain (σ_1 - ϵ_t) curve for the chain-axial direction of poly(4-methyl-1-pentene).

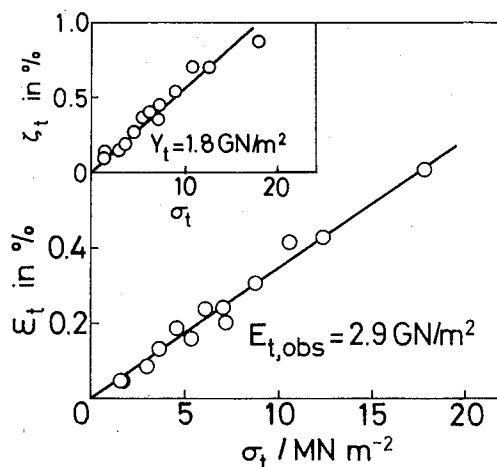


Fig. 7. Stress-strain curve (σ_t - ϵ_t) for the (200) plane of poly(4-methyl-1-pentene) at $25 \pm 1^\circ\text{C}$ when the stresses were applied in the direction normal to this lattice plane. The stress-elongation (σ_t - ζ_t) curve for the macroscopic specimen is shown at the corner of the figure.

the effective cross-sectional area of a single chain of 0.858 nm^2 .

The ratio of the lateral contraction to the chain-axial strain or the Poisson's ratio ν for the PMP crystals can also be estimated from Figs. 5 and 6: $\nu = 0.33$. It is noteworthy that this value for crystals is comparable to the values for the macroscopic specimens of usual synthetic polymers.

For the determination of E_t the equatorial plane of (200) was used; in this case the stress was applied in the direction perpendicular to the lattice plane. The stress-strain curve for the (200) plane of PMP is shown in Fig. 7. The observed values are on a straight line within experimental error. The slope of this curve gives rise to the modulus in the direction perpendicular to the chain axis: $E_t = 2.9 \text{ GN/m}^2$ at $25 \pm 1^\circ\text{C}$. This value is equal to the value of E_1 ; PMP is isotropic concerning the initial moduli of elasticity in the crystalline regions. This is valid for the macroscopic moduli Y of the specimen; $Y_1 = Y_t = 1.8 \text{ GN/m}^2$.

DISCUSSION

As was previously reported,¹⁾ E_1 depends mainly on the conformation of a main chain of the linear polymer and is independent of its side groups. It will, therefore, be expected that the observed E_1 -value agrees with the value calculated for the conformation of the main chain. The molecular conformation of PMP used for the calculation of E_1 has the following parameters:¹⁴⁾ normal bond length $r_{\text{C-C}} = 0.154 \text{ nm}$; tetragonal bond angles $\phi_1 = \phi_2 = 109^\circ 28'$; internal rotation angles $\tau_{12} = 172^\circ$, $\tau_{21} = -75^\circ$; and FIP of 1.380 nm .* The calculation was carried out by Shimanouchi's method.²⁾

E_1 is calculated from the equation

$$E_1 = (F_1/A) / (\Delta l/l) = (l/A) / (\Delta l/F_1) \quad (6)$$

* More recently the model was modified as follows: $\phi_1 = 110^\circ$, $\phi_2 = 113^\circ$; $\tau_{12} = 72^\circ 30'$, $\tau_{21} = 193^\circ$.¹⁵⁾

where A is the effective cross-sectional area of a molecular chain, and Δl is the change of the structural unit length l caused by the force F_1 applied on the chain along the chain axis. Thus,

$$\Delta l/F_1 = \Sigma T^r(\Delta r/F_1) + \Sigma T^\phi(\Delta \phi/F_1) + \Sigma T^\tau(\Delta \tau/F_1) \quad (7)$$

where

$$\begin{aligned} T^r &= \partial l / \partial r \\ T^\phi &= \partial l / \partial \phi \\ T^\tau &= \partial l / \partial \tau \end{aligned} \quad (8)$$

Here T^r , T^ϕ , and T^τ can be calculated from the chain conformation by the use of Miyazawa's relationships.¹⁶⁾ If we adopt the Urey-Bradley type of force field, the potential energy per structural unit of the chain is

$$V = \frac{1}{2} \Sigma K(\Delta r)^2 + \frac{1}{2} \Sigma H(R\Delta \phi)^2 + \frac{1}{2} \Sigma K^\tau(R'\Delta \tau)^2 + \frac{1}{2} \Sigma F(\Delta q)^2 \quad (9)$$

where K , H , K^τ , and F are the stretching, bending, torsion, and repulsion force constants; r , ϕ , and τ are bond length, bond angle, and internal rotation angle, respectively. Further

$$\begin{aligned} R &= (rr')^{\frac{1}{2}} \\ R' &= (r_{-1}r_{+1})^{\frac{1}{2}} \\ q &= r^2 + r'^2 - 2rr' \cos \phi \end{aligned} \quad (10)$$

where r and r' are bond lengths making an angle of ϕ : r_{-1} and r_{+1} are the two bond lengths neighboring the bond about which the internal rotation angle is τ . From Eq. (9) we can obtain

$$\begin{aligned} \partial V / \partial r &= T^r F_1 \\ \partial V / \partial \phi &= T^\phi F_1 \\ \partial V / \partial \tau &= T^\tau F_1 \end{aligned} \quad (11)$$

By solving the simultaneous equations of Eq. (11) we obtain $\Delta r/F_1$, $\Delta \phi/F_1$, and $\Delta \tau/F_1$.

In the case of PMP we used the following set of the force constants:

$$\begin{aligned} K_{CC} &= 247 \text{ N/m} \\ H_{CCC} &= 35 \text{ N/m} \\ F_{CC} &= 40 \text{ N/m} \\ K^\tau &= 5 \text{ N/m} \end{aligned}$$

which were chosen from the values for isotactic polypropylene¹⁷⁾ and poly(ethylene oxide).¹⁸⁾ Then the following results are obtained:

$$\begin{aligned} \Delta r_{12}/F_1 &= -1.23 \text{ mm/N} \\ \Delta r_{21}/F_1 &= 2.43 \text{ mm/N} \\ \Delta \phi_1/F_1 &= \Delta \phi_2/F_1 = 7.22 \text{ rad/N} \\ \Delta \tau_{12}/F_1 &= 77.1 \text{ rad/N} \\ \Delta \tau_{21}/F_1 &= 1.86 \text{ rad/N} \end{aligned}$$

and

$$\Delta l/F_1 = 38.07 \text{ mm/N}$$

The effective cross-sectional area of a PMP chain is $A = 0.858 \text{ nm}^2$ and the structural unit length is $l = 0.197 \text{ nm}$. From Eq. (6) we obtain

$$E_{1,\text{calc}} = 2.62 \text{ GN/m}^2$$

This calculated value agrees well with the observed one of 2.9 GN/m^2 . The slight difference between them is not due to the observed value but to the calculated one; in the calculation the contribution of the side chains is neglected.

As described in the introduction the E_t for polyolefins decreases with the length of the side chain. Thus E_t decreased from 4 GN/m^2 for polyethylene with no side chains to 2 GN/m^2 for isotactic poly(1-butene) (PB) with the ethyl side chains. PMP has the isobutyl side chains of $-\text{CH}_2\text{CH}(\text{CH}_3)_2$ which is longer than ethyl group and has a methyl branch at the end. The effect of branching on the intermolecular forces or E_t is large since PMP is a vinyl polymer and the density of side chains is considerably high. It may, therefore, be expected that the branching effect cancels or exceeds the effect of the side-chain length, *i.e.*, the E_t for PMP is equal to or larger than that for PB. The observed E_t for PMP is 2.9 GN/m^2 , which is larger than that for PB. This shows that the effect of branching is considerably large.

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