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General Analysis of the Measurement of the Crystal Lattice Modulus of Semicrystalline Polymers by X-ray Diffraction

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ABSTRACT: A mathematic representation based on a linear elastic theory is proposed by which one may investigate the dependences on molecular orientation and crystallinity of the crystal lattice modulus and linear thermal expansion coefficient in the chain direction as commonly measured by X-ray diffraction. The proposed model includes polymeric systems with a low degree of molecular orientation and low crystallinity, in which the oriented crystalline layers are surrounded by an anisotropic amorphous phase. It is assumed that the strains of the two phases at the boundary are identical. The mathematical analysis indicates that the crystal lattice modulus and linear thermal coefficient as measured by X-ray diffraction may be different from the intrinsic crystal lattice modulus and linear thermal expansion coefficient, depending on the structure of the polymer solid.

I. Introduction

The ultimate value of the Young's modulus of polymer materials generally is taken to be equivalent to the crystal lattice modulus in the direction of the polymer chain axis. Frequently, the crystal lattice moduli that have been reported were measured by X-ray diffraction. Sakurada et al. in particular have investigated a number of oriented crystalline polymers.[1-3] An essential question in the determination of crystal lattice moduli by X-ray measurements is whether or not the critical assumption in this method is valid, that the specimen is under homogeneous stress. In order to verify the validity of this assumption, we previously conducted a study in which ultradrawn polyethylene and polypropylene films with different draw ratios were used as specimens.[4,5] It was established that the crystal lattice modulus indeed is independent of the degree of orientation of the *c* axes, crystallinity, and crystal size if draw ratios were greater than 50 for polyethylene and 30 for polypropylene, respectively. In addition, a mathematical representation based on a linear elastic theory was proposed, by which one may investigate the dependence of the derived crystal lattice modulus on molecular orientation and crystallinity using a composite model of crystalline and amorphous phases.[6] In this model system, it is assumed that anisotropic noncrystalline layers lie adjacent to oriented crystalline layers with the interface perpendicular to the stretching direction, so that the strains of the two phases at the boundary are identical. The mathematical description indicates that, even within the homogeneous stress hypothesis, the crystal lattice modulus and the linear thermal coefficient as measured by X-ray diffraction are different from the intrinsic crystal lattice modulus and the intrinsic linear thermal expansion coefficient. Numerical calculations indicated, however, that at high degrees of molecular orientation and crystallinity the calculated values were independent of the parameters of these materials. Thus, we concluded that X-ray diffraction is an excellent technique for measuring the crystal lattice modulus of polyethylene and polypropylene, provided that samples of high draw ratios are used.

Generally, crystal lattice moduli have been measured for crystalline polymers whose degree of the chain orientation is not high, such as poly(ethylene terephthalate), nylon 6, and cellulose. In such cases, there is no indication whether or not crystal lattice moduli reported are in agreement with the intrinsic lattice modulus.

The present paper further investigates possible discrepancies between the crystal lattice modulus measured by X-ray diffraction and the intrinsic crystal lattice modulus. A composite unit is proposed to describe the polymer specimen, in which anisotropic amorphous layers lie adjacent to oriented composite layers with the interface perpendicular to the three principal directions. This means that the oriented crystallites are surrounded by an anisotropic amorphous phase where amorphous chain segments are oriented predominantly in the stretching direction. This model system satisfies the morphological characteristic of a specimen with a low degree of molecular orientation and low crystallinity. The mathematical description presented can also be applied to systems where there exists no detectable crystal plane whose reciprocal lattice vector is parallel to the molecular chain axis, such as polypropylene and poly(ethylene terephthalate). Using the apparent crystal lattice modulus of the plane whose reciprocal lattice vector, among all the crystal planes, is most closely parallel to the crystal chain axis, one can estimate the real value of the crystal lattice modulus. The crystal lattice modulus is formulated as a function of crystallinity and molecular orientation. The numerical calculation shall be carried out elsewhere[7,8] using the experimental results of several crystalline polymers.

II. Theory

A mathematical representation is proposed to estimate the crystal lattice modulus and the Young's modulus, as well as the thermal expansion coefficients of crystal lattice and bulk specimen, as a function of crystallinity and molecular orientation. The description is presented for a system with a triclinic unit cell, as a general case. The procedure for calculating the mechanical anisotropy of a single-phase system from the orientation of the structural units is discussed in relation to mutual conversion of the orientation distribution function of the structural unit with respect to Cartesian coordinates fixed within the bulk specimen.

1. Structural Unit. Figure 1a shows Cartesian coordinates $0{-}U_1U_2U_3$ fixed within a structural unit, with respect to Cartesian coordinates $0{-}X_1X_2X_3$, fixed in the bulk specimen. The U_3 axis may be taken along the reference axis but has random orientation around the X_3

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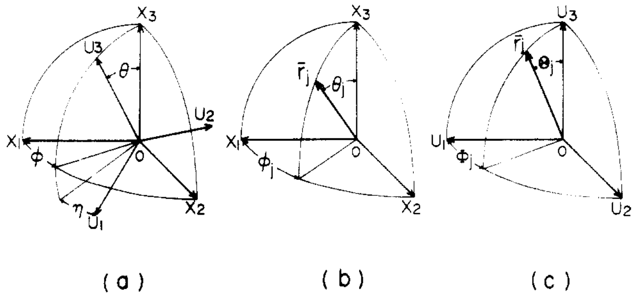

Figure 1. Cartesian coordinates illustrating geometrical relations. (a) Eulerian angles θ, ϕ, and η, which specify the orientation of coordinate $0\text{-}U_1U_2U_3$ of the structural unit with respect to coordinate $0\text{-}X_1X_2X_3$ of the specimen. (b) Angles θ_j and ϕ_j, which specify the orientation of the jth axis of the structural unit with respect to the coordinate $0\text{-}X_1X_2X_3$. (c) Angles Θ_j and Φ_j, which specify the orientation of the jth axis of the structural unit with respect to the coordinate $0\text{-}U_1U_2U_3$.

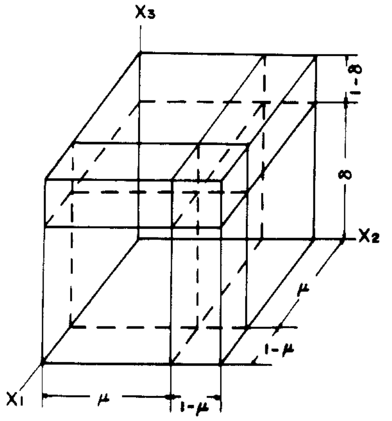

Figure 2. Composite structural unit of a semicrystalline polymer whose crystallites are surrounded by amorphous phase.

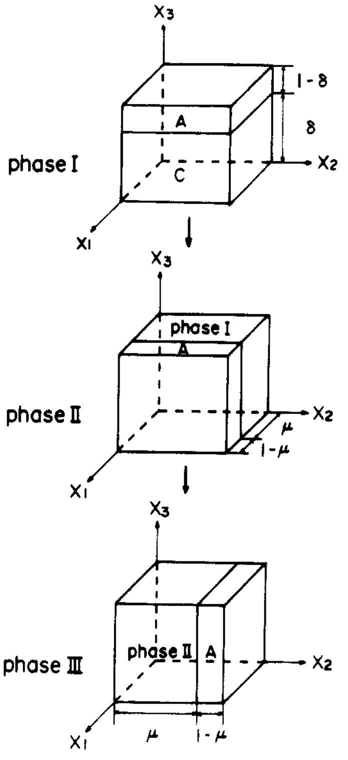

Figure 3. A procedure to construct a model in Figure 2: (a) amorphous phase attached to the X_3 face of the crystallite to construct phase I; (b) amorphous phase attached to the X_1 face of phase I to construct phase II; (c) amorphous phase attached to the X_2 face of phase II to construct phase III.

axis in the present case. Parts b and c of Figure 1 show a given jth axis $\mathbf{r}_j$ within the unit, specified by the polar angle θ_j and the azimuthal angle ϕ_j with respect to the Cartesian coordinates $0\text{-}X_1X_2X_3$ and specified by polar angle Θ_j and the azimuthal angle Φ_j with respect to the Cartesian coordinates $0\text{-}U_1U_2U_3$ of the unit.

Let the composite structural unit be as shown in Figure 2, in which oriented crystallites are surrounded by amorphous phases. This model is thought to be a realistic representation of the morphology of crystalline polymers with a low degree of molecular orientation and low crystallinity, as pointed out by Hibi et al.[9] The volume fraction X_c is represented by $\delta\mu^2$ by use of the fraction lengths δ and μ in the directions of U_3 and U_2 (and U_1) axes.

2. Stress/Strain Behavior. This paper is focused on the crystal lattice modulus and the thermal expansion coefficients of the jth crystal plane, detectable by X-ray diffraction when the external stress in the X_3 direction is applied to the crystalline phase in this model system. In this model system, amorphous layers are adjacent to oriented crystalline layers with the interfaces perpendicular to the X_1, X_2, and X_3 axes. The strains of the two phases at the boundary are assumed to be identical. This model is constructed by three components shown in Figure 3. In model a, an anisotropic amorphous layer lies adjacent to the crystallite with the interface perpendicular to the X_3 axis, and in model b an anisotropic amorphous layer with fraction length $1 - \mu$ is attached to the structure of phase I in a plane normal to the X_1 direction. The final phase III can be constructed by adding an anisotropic amorphous layer with fraction length $1 - \mu$ to phase II. This method was proposed by Maeda et al.[10] for representation of an undeformed semicrystalline polymer system. This procedure is convenient for analysis of the stress–strain relationships in each phase, and the mechanical constants of two phases can be written by using the average mechanical constants of their phases. It is well-known, of course, that at $\mu = 1$, this model corresponds to a series model, while at $\delta = 1$, it corresponds to a parallel model.[11]

When the uniaxial external tensile stress σ_{33} is applied along the X_3 axis in model a in Figure 3, the inner stresses of the crystalline and amorphous phases, $(\sigma_{11}^{c}, \sigma_{22}^{c}, \sigma_{33}^{c}, 0, 0, 0)$ and $(\sigma_{11}^{a}, \sigma_{22}^{a}, \sigma_{33}^{a}, 0, 0, 0)$, are applied to the two phases, respectively, inducing the following strains in the respective phases:

$$\begin{aligned}
\epsilon_{11}^{c} &= S_{11}^{cv}\sigma_{11}^{c} + S_{12}^{cv}\sigma_{22}^{c} + S_{13}^{cv}\sigma_{33}^{c} + \alpha_{11}^{cv}\Delta T \\
\epsilon_{22}^{c} &= S_{12}^{cv}\sigma_{11}^{c} + S_{11}^{cv}\sigma_{22}^{c} + S_{13}^{cv}\sigma_{33}^{c} + \alpha_{22}^{cv}\Delta T \\
\epsilon_{33}^{c} &= S_{13}^{cv}\sigma_{11}^{c} + S_{13}^{cv}\sigma_{22}^{c} + S_{33}^{cv}\sigma_{33}^{c} + \alpha_{33}^{cv}\Delta T \\
\epsilon_{12}^{c} &= \epsilon_{23}^{c} = \epsilon_{31}^{c} = 0
\end{aligned} \qquad (1)$$

and

$$\begin{aligned}
\epsilon_{11}^{a} &= S_{11}^{av}\sigma_{11}^{a} + S_{12}^{av}\sigma_{22}^{a} + S_{13}^{av}\sigma_{33}^{a} + \sigma_{11}^{av}\Delta T \\
\epsilon_{22}^{a} &= S_{12}^{av}\sigma_{11}^{a} + S_{11}^{av}\sigma_{22}^{a} + S_{13}^{av}\sigma_{33}^{a} + \alpha_{22}^{av}\Delta T \\
\epsilon_{33}^{a} &= S_{13}^{av}\sigma_{11}^{a} + S_{13}^{av}\sigma_{22}^{a} + S_{33}^{av}\sigma_{33}^{a} + \alpha_{33}^{av}\Delta T \\
\epsilon_{12}^{a} &= \epsilon_{23}^{a} = \epsilon_{31}^{a} = 0
\end{aligned} \qquad (2)$$

where S_{uv}^{cv} and S_{uv}^{av} represent the average elastic compliances of the crystalline and amorphous phases, respectively. Parameters α_{uv}^{cv} and α_{uv}^{av} represent the average thermal expansion coefficients of the crystalline and amorphous phases, respectively. ΔT is given by $T - T_0$, where T_0 is the reference temperature. The uniaxial stress condition with respect to the X_3 axis leads to the relations

$$\sigma_{11} = \delta\sigma_{11}^{c} + (1-\delta)\sigma_{11}^{a} = 0$$
$$\sigma_{22} = \delta\sigma_{22}^{c} + (1-\delta)\sigma_{22}^{a} = 0$$
$$\sigma_{33} = \sigma_{33}^{c} = \sigma_{33}^{a} \tag{3}$$

where σ_{uv} corresponds to the stress of the bulk specimen. Because of the above restriction upon the strains, it follows

$$\epsilon_{11} = \epsilon_{11}^{c} = \epsilon_{11}^{a}$$
$$\epsilon_{22} = \epsilon_{22}^{c} = \epsilon_{22}^{a}$$
$$\epsilon_{33} = \delta\epsilon_{33}^{c} + (1-\delta)\epsilon_{33}^{a}$$
$$\epsilon_{12} = \epsilon_{23} = \epsilon_{31} = 0 \tag{4}$$

Equation 1 (and eq 2) has been used as a generalized Hooke's law expanded to thermal elasticity. Here it should be noted that the thermal expansion coefficient is related to higher order elastic theory associated with unharmonic problems and is described in relation to the difference between adiabatic and isothermal compliances. Accordingly, eq 1 cannot be formulated strictly; for convenience, it has been used widely in terms of infinitesimal elastic theory.

Assuming the homogeneous stress hypothesis for a polycrystalline material, the relation between the intrinsic compliance of a structural unit and the bulk compliance is given by

$$S_{ijkl}^{cv} = \sum_{o=1}^{3}\sum_{p=1}^{3}\sum_{q=1}^{3}\sum_{r=1}^{3}\langle a_{io}a_{jp}a_{kq}a_{lr}\rangle S_{opqr}^{co} \tag{5}$$

$$S_{ijkl}^{av} = \sum_{o=1}^{3}\sum_{p=1}^{3}\sum_{q=1}^{3}\sum_{r=1}^{3}\langle a_{io}a_{jp}a_{kq}a_{lr}\rangle S_{opqr}^{ao} \tag{6}$$

Here S_{ijkl}^{cv} and S_{ijkl}^{av} are averaged compliances of the crystal and amorphous phases, respectively, and S_{opqr}^{co} and S_{opqr}^{ao} are their intrinsic compliances. a_{io} is, for example, the direction cosine of the U_0 axis with respect to the X_i axis, which is given for the geometrical arrangements in Figure 1a as follows:

$$[a] = \begin{bmatrix} \cos\phi\cos\theta\cos\eta - \sin\phi\sin\eta & -\cos\phi\cos\theta\sin\eta - \sin\phi\cos\eta & \cos\phi\sin\theta \\ \sin\phi\cos\theta\cos\eta + \cos\phi\sin\eta & -\sin\phi\cos\theta\sin\eta + \cos\phi\cos\eta & \sin\phi\sin\theta \\ -\sin\theta\sin\eta & \sin\theta\sin\eta & \cos\theta \end{bmatrix} \tag{7}$$

Average values in eq 5 and 6, $\langle a_{io}a_{jp}a_{kq}a_{lr}\rangle$, can be given by

$$\langle a_{io}a_{jp}a_{kq}a_{lr}\rangle = \int_0^{2\pi}\int_0^{2\pi}\int_0^{\pi}\omega(\cos\theta,\phi,\eta) \times a_{io}a_{jp}a_{kq}a_{lr}\sin\theta\,\mathrm{d}\theta\,\mathrm{d}\phi\,\mathrm{d}\eta \tag{8}$$

where $\omega(\cos\theta,\phi,\eta)$ is a normalized orientation distribution function of the structural unit $0\text{–}U_1U_2U_3$ with respect to the coordinate $0\text{–}X_1X_2X_3$ in Figure 1a.

In accordance with the analysis of Krigbaum and Roe,[12,13] we can write the orientation functions F_{l0n} and G_{l0n} with some changes of the notation using $\omega(\cos\theta,\eta)$ in the case when the structural unit of a triclinic system has a uniaxial orientation distribution around the X_3 axis:

$$F_{l0n} = \int_0^{2\pi}\int_0^{\pi}\omega(\cos\theta,\eta)P_l^n(\cos\theta)\cos(n\eta)\sin\theta\,\mathrm{d}\theta\,\mathrm{d}\eta \tag{9}$$

$$G_{l0n} = \int_0^{2\pi}\int_0^{\pi}\omega(\cos\theta,\eta)P_l^n(\cos\theta)\sin(n\eta)\sin\theta\,\mathrm{d}\theta\,\mathrm{d}\eta \tag{10}$$

$P_l^n(\cos\theta)$ are the associated Legendre polynominals. By use of eqs 7–10, S_{ij}^{cv} in eq 5 can be formulated as a function of F_{l0n}, G_{l0n}, and S_{ij}^{co}.

The amorphous chain segments have uniaxial symmetry around the U_3 axis, and therefore S_{ij}^{av} in eq 6 may be written as a function of F_{l00}^{am} and S_{ij}^{ao} in simple form.

The average linear thermal expansion coefficients α_{uv}^{cv} and α_{uv}^{av} in crystalline and amorphous phases, respectively, in eqs 1 and 2 are given by

$$\alpha_{11}^{cv}\ (=\alpha_{22}^{cv}) = \frac{1}{12}(-F_{202} + 2F_{200} + 4)(\alpha_{11}^{co} + \alpha_{22}^{co}) + \frac{1}{6}(-2F_{200} + F_{202} + 2) \tag{11}$$

$$\alpha_{33}^{cv} = \frac{1}{3}(1 - F_{200})(\alpha_{11}^{co} + \alpha_{22}^{co}) + \frac{1}{3}(2F_{200} + 1)\alpha_{33}^{co} \tag{12}$$

$$\alpha_{11}^{av}\ (=\alpha_{22}^{av}) = \frac{1}{6}(F_{200}^{am} + 2)(\alpha_{11}^{ao} + \alpha_{22}^{ao}) + \frac{1}{3}(1 - F_{200}^{am}) \tag{13}$$

$$\alpha_{33}^{av} = \frac{1}{3}(1 - F_{200}^{am})(\alpha_{11}^{ao} + \alpha_{22}^{ao}) + \frac{1}{3}(2F_{200}^{am} + 1)\alpha_{33}^{ao} \tag{14}$$

where α_{uv}^{co} and α_{uv}^{ao} are the intrinsic linear thermal expansion coefficients of the crystal and amorphous phases, respectively.

When stresses $(0, \sigma_{22}^{I}, \sigma_{33}^{I}, 0, 0, 0)$ and $(0, \sigma_{22}^{a}, \sigma_{33}^{a}, 0, 0, 0)$ are applied to each layer in model II, the following strains are induced in the respective phases:

$$\epsilon_{11}^{I} = S_{12}^{I}\sigma_{22}^{I} + S_{13}^{I}\sigma_{33}^{I} + \alpha_{11}^{I}\Delta T$$
$$\epsilon_{22}^{I} = S_{11}^{I}\sigma_{22}^{I} + S_{13}^{I}\sigma_{33}^{I} + \alpha_{22}^{I}\Delta T$$
$$\epsilon_{33}^{I} = S_{13}^{I}\sigma_{22}^{I} + S_{33}^{I}\sigma_{33}^{I} + \alpha_{33}^{I}\Delta T \tag{15}$$

and

$$\epsilon_{11}^{a} = S_{12}^{av}\sigma_{22}^{a} + S_{13}^{av}\sigma_{33}^{a} + \alpha_{11}^{av}\Delta T$$
$$\epsilon_{22}^{a} = S_{11}^{av}\sigma_{22}^{a} + S_{13}^{av}\sigma_{33}^{a} + \alpha_{22}^{av}\Delta T$$
$$\epsilon_{33}^{a} = S_{13}^{av}\sigma_{22}^{a} + S_{33}^{av}\sigma_{33}^{a} + \alpha_{33}^{av}\Delta T \tag{16}$$

Here, one considers a case where the composite unit is subjected to a tensile stress in the direction of the X_3 axis as shown in Figure 3b, leaving the other directions free from external force. Under this condition, one obtains

$$\sigma_{11}^{II} = 0$$
$$\sigma_{22}^{II} = \mu\sigma_{22}^{I} + (1-\mu)\sigma_{22}^{a} = 0$$
$$\sigma_{33}^{II} = \mu\epsilon_{33}^{I} + (1-\mu)\sigma_{33}^{a} \tag{17}$$

For the above restriction upon the stress, one derives

$$\epsilon_{11}^{II} = \mu\epsilon_{11}^{I} + (1-\mu)\epsilon_{11}^{a}$$
$$\epsilon_{22}^{II} = \epsilon_{22}^{I} = \epsilon_{22}^{a}$$
$$\epsilon_{33}^{II} = \epsilon_{33}^{I} = \epsilon_{33}^{a}$$
$$\epsilon_{12}^{II} = \epsilon_{13}^{I} = 0 \tag{18}$$

The elastic compliances S_{ij}^{I} of the phase I in eq 15 can be formulated as a function of S_{ij}^{cv}, S_{ij}^{av}, and δ according to the method of Hibi et al.,[9,10] and the thermal expansion coefficients α_{ii}^{I} are written in the Appendix.

When stresses $(\sigma_{11}^{II}, 0, \sigma_{33}^{II}, 0, 0, 0)$ and $(\sigma_{11}^{a}, 0, \sigma_{33}^{a}, 0, 0, 0)$ are applied to each layer in model III, the following relationships are obtained:

$$\begin{aligned}\epsilon_{11}^{\mathrm{II}} &= S_{11}^{\mathrm{II}}\sigma_{11}^{\mathrm{II}} + S_{13}^{\mathrm{II}}\sigma_{33}^{\mathrm{II}} + \alpha_{11}^{\mathrm{II}}\Delta T\\ \epsilon_{22}^{\mathrm{II}} &= S_{12}^{\mathrm{II}}\sigma_{11}^{\mathrm{II}} + S_{23}^{\mathrm{II}}\sigma_{33}^{\mathrm{II}} + \alpha_{22}^{\mathrm{II}}\Delta T\\ \epsilon_{33}^{\mathrm{II}} &= S_{13}^{\mathrm{II}}\sigma_{11}^{\mathrm{II}} + S_{33}^{\mathrm{II}}\sigma_{33}^{\mathrm{II}} + \alpha_{33}^{\mathrm{II}}\Delta T\end{aligned} \tag{19}$$

and

$$\begin{aligned}\epsilon_{11}^{\mathrm{a}} &= S_{11}^{\mathrm{av}}\sigma_{11}^{\mathrm{a}} + S_{13}^{\mathrm{av}}\sigma_{33}^{\mathrm{a}} + \alpha_{11}^{\mathrm{av}}\Delta T\\ \epsilon_{22}^{\mathrm{a}} &= S_{12}^{\mathrm{av}}\sigma_{11}^{\mathrm{a}} + S_{13}^{\mathrm{av}}\sigma_{33}^{\mathrm{a}} + \alpha_{22}^{\mathrm{av}}\Delta T\\ \epsilon_{33}^{\mathrm{a}} &= S_{13}^{\mathrm{av}}\sigma_{11}^{\mathrm{a}} + S_{33}^{\mathrm{av}}\sigma_{33}^{\mathrm{a}} + \alpha_{33}^{\mathrm{av}}\Delta T\end{aligned} \tag{20}$$

The elastic compliances S_{ij}^{II} of phase II can be formulated as a function of S_{ij}^{I}, S_{ij}^{av}, and μ according to the model of Hibi et al.,[9,10] and the thermal expansion coefficients $\alpha_{ii}^{\mathrm{II}}$ are also written in the Appendix. The uniaxial stress condition with respect to the X_3 axis leads to the relations

$$\begin{aligned}\sigma_{11}^{\mathrm{III}} &= \mu\sigma_{11}^{\mathrm{II}} + (1-\mu)\sigma_{11}^{\mathrm{a}} = 0\\ \sigma_{22}^{\mathrm{III}} &= 0\\ \sigma_{33}^{\mathrm{III}} &= \mu\sigma_{33}^{\mathrm{II}} + (1-\mu)\sigma_{33}^{\mathrm{a}} = \sigma_{33}\end{aligned} \tag{21}$$

For the above restriction upon the strains, one has

$$\begin{aligned}\epsilon_{11}^{\mathrm{III}} &= \epsilon_{11}^{\mathrm{II}} = \epsilon_{11}^{\mathrm{a}}\\ \epsilon_{22}^{\mathrm{III}} &= \mu\epsilon_{22}^{\mathrm{II}} + (1-\mu)\epsilon_{22}^{\mathrm{a}}\\ \epsilon_{33}^{\mathrm{III}} &= \epsilon_{33}^{\mathrm{a}} = \epsilon_{33}^{\mathrm{II}}\\ \epsilon_{12}^{\mathrm{III}} &= \epsilon_{13}^{\mathrm{III}} = 0\end{aligned} \tag{22}$$

where $\epsilon_{33}^{\mathrm{III}}$ and $\sigma_{33}^{\mathrm{III}}$ correspond to the strain of the bulk specimen and the applied external stress, respectively. Therefore we replace $\epsilon_{33}^{\mathrm{III}}$ and $\sigma_{33}^{\mathrm{III}}$ as ϵ_{33} and σ_{33}, respectively.

By use of eqs 1–4 and eqs 15–22, the bulk strain ϵ_{uv} can be separated into two components: one is ϵ_{ii}^{σ}, associated with the external applied stress, and the other is $\epsilon_{ii}^{\mathrm{T}}$, associated with the thermal expansion effect. That is

$$\epsilon_{33} = \epsilon_{33}^{\sigma} + \epsilon_{33}^{\mathrm{T}} \tag{23}$$

where

$$\epsilon_{33}^{\sigma} = \left[\frac{(S_{13}^{\mathrm{II}})^2(S_{33}^{\mathrm{av}} - S_{33}^{\mathrm{II}})}{\left(S_{13}^{\mathrm{II}} + \dfrac{\mu S_{13}^{\mathrm{av}}}{1-\mu}\right)S_{13}^{\mathrm{av}} - \left(S_{11}^{\mathrm{II}} + \dfrac{\mu S_{11}^{\mathrm{av}}}{1-\mu}\right)S_{33}^{\mathrm{av}}} + S_{33}^{\mathrm{II}}\right]\sigma_{33} \tag{23a}$$

$$\epsilon_{33}^{\mathrm{T}} = \left[\frac{S_{13}^{\mathrm{II}}[S_{13}^{\mathrm{av}}(\alpha_{33}^{\mathrm{av}} - \alpha_{33}^{\mathrm{II}}) - S_{33}^{\mathrm{av}}(\alpha_{11}^{\mathrm{av}} - \alpha_{11}^{\mathrm{II}})]}{\left(S_{13}^{\mathrm{II}} + \dfrac{\mu S_{13}^{\mathrm{av}}}{1-\mu}\right)S_{13}^{\mathrm{av}} - \left(S_{11}^{\mathrm{II}} + \dfrac{\mu S_{11}^{\mathrm{av}}}{1-\mu}\right)S_{33}^{\mathrm{av}}} + \alpha_{33}^{\mathrm{II}}\right]\Delta T \tag{23b}$$

Thus, Young's modulus E is given by

$$E = \frac{\sigma_{33}}{\epsilon_{33}^{\sigma}} = S_{33}^{\mathrm{II}} + \frac{(S_{13}^{\mathrm{II}})^2(S_{33}^{\mathrm{av}} - S_{33}^{\mathrm{II}})}{\left(S_{13}^{\mathrm{II}} + \dfrac{\mu S_{13}^{\mathrm{av}}}{1-\mu}\right)S_{13}^{\mathrm{av}} - \left(S_{11}^{\mathrm{II}} + \dfrac{\mu S_{11}^{\mathrm{av}}}{1-\mu}\right)S_{33}^{\mathrm{av}}} \tag{24}$$

and the thermal expansion coefficient in the bulk in the X_3 direction is given by

$$\alpha_{ij} = \frac{\epsilon_{33}^{\mathrm{T}}}{\Delta T} = \alpha_{33}^{\mathrm{II}} + \frac{S_{13}^{\mathrm{II}}[S_{13}^{\mathrm{av}}(\alpha_{33}^{\mathrm{av}} - \alpha_{33}^{\mathrm{II}}) - S_{33}^{\mathrm{av}}(\alpha_{11}^{\mathrm{av}} - \alpha_{11}^{\mathrm{II}})]}{\left(S_{13}^{\mathrm{II}} + \dfrac{\mu S_{13}^{\mathrm{av}}}{1-\mu}\right)S_{13}^{\mathrm{av}} - \left(S_{11}^{\mathrm{II}} + \dfrac{\mu S_{11}^{\mathrm{av}}}{1-\mu}\right)S_{33}^{\mathrm{av}}} \tag{25}$$

Returning to Figure 2, we now shall discuss the crystal strain detected by X-ray diffraction. First, the crystal strains of the structural units of crystalline phase in the three principal direction must be formulated. In this model system, they are as follows:

$$\begin{aligned}\epsilon_{11}^{\mathrm{co}} &= S_{11}^{\mathrm{co}}\sigma_{11}^{\mathrm{c}} + S_{12}^{\mathrm{co}}\sigma_{22}^{\mathrm{c}} + S_{13}^{\mathrm{co}}\sigma_{33}^{\mathrm{c}} + \alpha_{11}^{\mathrm{co}}\Delta T\\ \epsilon_{22}^{\mathrm{co}} &= S_{12}^{\mathrm{co}}\sigma_{11}^{\mathrm{c}} + S_{11}^{\mathrm{co}}\sigma_{22}^{\mathrm{c}} + S_{13}^{\mathrm{co}}\sigma_{33}^{\mathrm{c}} + \alpha_{22}^{\mathrm{co}}\Delta T\\ \epsilon_{33}^{\mathrm{co}} &= S_{13}^{\mathrm{co}}\sigma_{11}^{\mathrm{c}} + S_{23}^{\mathrm{co}}\sigma_{22}^{\mathrm{c}} + S_{33}^{\mathrm{co}}\sigma_{33}^{\mathrm{c}} + \alpha_{33}^{\mathrm{co}}\Delta T\\ \epsilon_{12}^{\mathrm{co}} &= \epsilon_{23}^{\mathrm{co}} = \epsilon_{13}^{\mathrm{co}} = 0\end{aligned} \tag{26}$$

The crystal strain $\epsilon_{11}^{\mathrm{co}}$, $\epsilon_{22}^{\mathrm{co}}$, and $\epsilon_{33}^{\mathrm{co}}$ may be represented by the external applied stress σ_{33} and by ΔT. That is

$$\begin{aligned}\epsilon_{11}^{\mathrm{co}} &= U_1\sigma_{33} + V_1\Delta T\\ \epsilon_{22}^{\mathrm{co}} &= U_2\sigma_{33} + V_2\Delta T\\ \epsilon_{33}^{\mathrm{co}} &= U_3\sigma_{33} + V_3\Delta T\end{aligned} \tag{27}$$

where the coefficients U_i ($i = 1\sim3$) and V_i (i = 1, 3) are written in the Appendix.

In the geometrical arrangement shown in Figure 1c, the crystal lattice strain in the direction of the reciprocal lattice vector of the jth crystal plane may be given by using the formula of transformation of strain components:

$$\epsilon_{r_j}^{\mathrm{app\,co}} = \cos^2\Theta_j\epsilon_{33}^{\mathrm{co}} + \sin^2\Theta_j\sin^2\Phi_j\epsilon_{22}^{\mathrm{co}} + \sin^2\Theta_j\cos^2\Phi_j\epsilon_{11}^{\mathrm{co}} \tag{28a}$$

$$= (U_3\cos^2\Theta_j + U_2\sin^2\Theta_j\sin^2\Phi_j + U_1\sin^2\Theta_j\cos^2\Phi_j)\sigma_{33} + (V_3\cos^2\Theta_j + V_2\sin^2\Theta_j\sin^2\Phi_j + V_1\sin^2\Theta_j\cos^2\Phi_j)\Delta T \tag{28b}$$

$$= S_{r_j}^{\mathrm{co}}\sigma_{33} + \alpha_{r_j}^{\mathrm{co}}\Delta T = \epsilon_{r_j}^{\mathrm{co}}(\sigma) + \epsilon_{r_j}^{\mathrm{co}}(\Delta T) \tag{28c}$$

Thus, the apparent crystal lattice modulus of the jth plane may be defined as

$$E_{r_j}^{\mathrm{co}} = 1/S_{r_j}^{\mathrm{co}} \tag{29}$$

where

$$S_{r_j}^{\mathrm{co}} = U_3\cos^2\Theta_j + U_2\sin^2\Theta_j\cos^2\Phi_j + U_1\sin^2\Theta_j\cos^2\Phi_j \tag{30}$$

The apparent thermal expansion coefficient of the jth plane is defined as

$$\alpha_{r_j}^{\mathrm{co}} = V_3\cos^2\Theta_j + V_2\sin^2\Theta_j\cos^2\Phi_j + V_1\sin^2\Theta_j\cos^2\Phi_j \tag{31}$$

Here we must emphasize that $E_{r_j}^{\mathrm{co}}$ and $\alpha_{r_j}^{\mathrm{co}}$ are the constants obtained by X-ray diffraction when the external stress is parallel to the X_3 axis, but they are different from the intrinsic value. The values of $E_{r_j}^{\mathrm{co}}$ and $\alpha_{r_j}^{\mathrm{co}}$ can be estimated experimentally from the measurement of the X-ray intensity distribution by using an ordinary horizontal scanning type goniometer over a desirable range of twice the Bragg angle, $2\theta_{\mathrm{B}}$.[1-5] In this case, the specimen must be mounted horizontally in the stretching clamps of a constant-tension stretching apparatus in such a way that the tilting angle between the film normal direction (the X_1 axis) and the direction of the incident beam is Θ_j. When there exists a crystal plane perpendicular to the chain direction detectable by X-ray diffraction ($\Theta_j = 0$), $\epsilon_{r_j}^{\mathrm{app\,co}}$ is equivalent to $\epsilon_{33}^{\mathrm{co}}$. Thus, the crystal lattice modulus and thermal expansion coefficient in the chain direction reduct to E_{33}^{co} ($=1/U_3$) and $\alpha_{33}^{\mathrm{co}}$ ($=V_3$), respectively.

III. Discussion

Equations 29 and 31 should be used to estimate the crystal lattice modulus and thermal expansion coefficient for polymeric systems like poly(ethylene terephthalate), whose crystal unit cell is triclinic and has no plane perpendicular to the chain axis detected by X-ray diffraction. For a monoclinic system such as isotactic polypropylene, one should estimate the crystal lattice modulus and thermal expansion coefficient of the ($\bar{1}13$) plane using eqs 29 and 31, respectively. In this case, orientation factors G_{l0n} in eq 10 become zero.

For nylon 6, poly(vinyl alcohol), and cellulose, one can estimate the crystal lattice modulus E_{33}^{co} from $1/U_3$, directly. In this case, orientation factors in eqs 9 and 10 become

$$F_{l0n} = 0 \quad (n \text{ is odd})$$

$$G_{l0n} = 0 \quad (n \text{ is odd}) \tag{32}$$

For orthorhombic systems, like polyethylene, we have

$$F_{l0n} = 0 \quad (n \text{ is odd})$$

$$G_{l0n} = 0 \tag{33}$$

IV. Concluding Remark

In this paper, we presented a treatment that may be useful for the estimation of the effects of crystallinity ($\delta\mu^2$ in our model) and chain orientation in the determination of the crystal lattice modulus of semicrystalline polymers. In the following paper in this issue,[1] we will illustrate, through numerical calculations, the application of the present theory to X-ray measurements of the lattice moduli of cellulose I and II. In a future publication,[8] we will discuss the crystal lattice moduli of nylon 6, poly(vinyl alcohol), and poly(ethylene terephthalate) derived from X-ray measurements.

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Appendix

The average thermal coefficient can be obtained by representing all strains $\epsilon_{ij}^{\mathrm{I}}$ and $\epsilon_{ij}^{\mathrm{II}}$ as functions of σ_{33}. For example

$$\epsilon_{33}^{\mathrm{I}} = \left[\frac{2X_{\mathrm{c}}(S_{13}^{\mathrm{cv}} - S_{13}^{\mathrm{av}})(S_{13}^{\mathrm{av}} - S_{13}^{\mathrm{cv}})}{S_{11}^{\mathrm{av}} + S_{12}^{\mathrm{cv}} + \frac{\delta}{1-\delta}(S_{11}^{\mathrm{av}} + S_{12}^{\mathrm{av}})} + \delta S_{33}^{\mathrm{cv}} + (1-\delta)S_{33}^{\mathrm{av}}\right]\sigma_{33} + \left[\frac{2X_{\mathrm{c}}(S_{13}^{\mathrm{cv}} - S_{13}^{\mathrm{av}})(\alpha_{11}^{\mathrm{av}} - \alpha_{11}^{\mathrm{cv}})}{S_{11}^{\mathrm{cv}} + S_{12}^{\mathrm{cv}} + \frac{\delta}{1-\delta}(S_{11}^{\mathrm{av}} + S_{12}^{\mathrm{av}})} + \delta\alpha_{33}^{\mathrm{cv}} + (1-\delta)\alpha_{33}^{\mathrm{av}}\right]\Delta T$$

Therefore α_{33}^{I} becomes

$$\alpha_{33}^{\mathrm{I}} = \delta\alpha_{33}^{\mathrm{cv}} + (1-\delta)\alpha_{33}^{\mathrm{av}} + \frac{2X_{\mathrm{c}}(S_{13}^{\mathrm{cv}} - S_{13}^{\mathrm{av}})(\alpha_{11}^{\mathrm{av}} - \alpha_{11}^{\mathrm{cv}})}{S_{11}^{\mathrm{cv}} + S_{12}^{\mathrm{cv}} + \frac{\delta}{1-\delta}(S_{11}^{\mathrm{av}} + S_{12}^{\mathrm{av}})} \tag{A1}$$

Using the same procedure, one has

$$\alpha_{11}^{\mathrm{I}} = \alpha_{22}^{\mathrm{I}} = \alpha_{11}^{\mathrm{cv}} + \frac{(S_{11}^{\mathrm{cv}} + S_{12}^{\mathrm{cv}})(\alpha_{11}^{\mathrm{av}} - \alpha_{11}^{\mathrm{cv}})}{S_{11}^{\mathrm{cv}} + S_{12}^{\mathrm{cv}} + \frac{\delta}{1-\delta}(S_{11}^{\mathrm{av}} + S_{12}^{\mathrm{av}})} \tag{A2}$$

$$\alpha_{33}^{\mathrm{II}} = \alpha_{33}^{\mathrm{I}} + \frac{S_{13}^{\mathrm{I}}[S_{13}^{\mathrm{av}}(\alpha_{33}^{\mathrm{av}} - \alpha_{33}^{\mathrm{I}}) - S_{33}^{\mathrm{av}}(\alpha_{11}^{\mathrm{av}} - \alpha_{11}^{\mathrm{I}})]}{\left(S_{13}^{\mathrm{I}} + \frac{\mu}{1-\mu}S_{13}^{\mathrm{av}}\right)S_{13}^{\mathrm{av}} - \left(S_{11}^{\mathrm{I}} + \frac{\mu}{1-\mu}S_{11}^{\mathrm{av}}\right)S_{33}^{\mathrm{av}}} \tag{A3}$$

$$\alpha_{22}^{\mathrm{II}} = \alpha_{11}^{\mathrm{I}} + \frac{S_{11}^{\mathrm{I}}[S_{13}^{\mathrm{av}}(\alpha_{33}^{\mathrm{av}} - \alpha_{33}^{\mathrm{I}}) - S_{33}^{\mathrm{av}}(\alpha_{11}^{\mathrm{av}} - \alpha_{11}^{\mathrm{I}})]}{\left(S_{13}^{\mathrm{I}} + \frac{\mu}{1-\mu}S_{13}^{\mathrm{av}}\right)S_{13}^{\mathrm{av}} - \left(S_{11}^{\mathrm{I}} + \frac{\mu}{1-\mu}S_{11}^{\mathrm{av}}\right)S_{33}^{\mathrm{av}}} \tag{A4}$$

$$\alpha_{11}^{\mathrm{II}} = \mu\alpha_{11}^{\mathrm{I}} + (1-\mu)\alpha_{11}^{\mathrm{av}} + \left[\left(S_{13}^{\mathrm{I}} + \frac{\mu}{1-\mu}S_{13}^{\mathrm{av}}\right)S_{13}^{\mathrm{av}} - \left(S_{11}^{\mathrm{I}} + \frac{\mu}{1-\mu}S_{11}^{\mathrm{cv}}\right)S_{33}^{\mathrm{av}}\right]^{-1}\left[(\alpha_{33}^{\mathrm{av}} - \alpha_{33}^{\mathrm{I}})S_{13}^{\mathrm{av}}\left[\mu(S_{12}^{\mathrm{I}} - S_{12}^{\mathrm{av}}) + (1-\mu)\left(S_{11}^{\mathrm{I}} + \frac{\mu}{1-\mu}S_{11}^{\mathrm{av}}\right)\right] - (\alpha_{11}^{\mathrm{av}} - \alpha_{11}^{\mathrm{I}})\left[\mu S_{33}^{\mathrm{av}}(S_{12}^{\mathrm{I}} - S_{12}^{\mathrm{av}}) + (1-\mu)S_{13}^{\mathrm{av}}\left(S_{13}^{\mathrm{I}} + \frac{\mu}{1-\mu}S_{13}^{\mathrm{av}}\right)\right]\right] \tag{A5}$$

The coefficients U_i ($i = 1 \sim 3$) and V_i ($i = 1 \sim 3$) in eq 28b are given by

$$U_1 = (-\mathrm{FA1} + S_{13}^{\mathrm{co}})/C[\mu + (1-\mu)A] \tag{A6}$$

$$V_1 = -(-\mathrm{FA1} + S_{13}^{\mathrm{co}})[BC(1-\mu) + D]/[\mu + (1-\mu)A]C - \mathrm{FA2} + \alpha_{11}^{\mathrm{co}} \tag{A7}$$

$$U_2 = (-\mathrm{FB1} + S_{23}^{\mathrm{co}})/[\mu + (1-\mu)A]C \tag{A8}$$

$$V_2 = -(-\mathrm{FB1} + S_{23}^{\mathrm{co}})[BC(1-\mu) + D]/[\mu + (1-\mu)A]C - \mathrm{FB2} + \alpha_{22}^{\mathrm{co}} \tag{A9}$$

$$U_3 = (-\mathrm{FC1} + S_{33}^{\mathrm{co}})/[\mu + (1-\mu)A]C \tag{A10}$$

$$V_3 = -(\mathrm{FC1} + S_{33}^{\mathrm{co}})[BC(1-\mu) + D]/[\mu + (1-\mu)A]C - \mathrm{FC2} + \alpha_{33}^{\mathrm{co}} \tag{A11}$$

where

$$\mathrm{FA1} = \frac{(S_{13}^{\mathrm{cv}} - S_{13}^{\mathrm{av}})(S_{11}^{\mathrm{co}} + S_{12}^{\mathrm{co}})}{S_{11}^{\mathrm{cv}} + S_{12}^{\mathrm{cv}} + \frac{\delta}{1-\delta}(S_{11}^{\mathrm{av}} + S_{12}^{\mathrm{av}})} \tag{A12}$$

$$\mathrm{FA2} = \frac{(\alpha_{11}^{\mathrm{cv}} - \alpha_{11}^{\mathrm{av}})(S_{11}^{\mathrm{co}} + S_{12}^{\mathrm{co}})}{S_{11}^{\mathrm{cv}} + S_{12}^{\mathrm{cv}} + \frac{\delta}{1-\delta}(S_{11}^{\mathrm{av}} + S_{12}^{\mathrm{av}})} \tag{A13}$$

$$\mathrm{FB1} = \frac{(S_{13}^{\mathrm{cv}} - S_{13}^{\mathrm{av}})(S_{12}^{\mathrm{co}} + S_{22}^{\mathrm{co}})}{S_{11}^{\mathrm{cv}} + S_{12}^{\mathrm{cv}} + \frac{\delta}{1-\delta}(S_{11}^{\mathrm{av}} + S_{12}^{\mathrm{av}})} \tag{A14}$$

$$\mathrm{FB2} = \frac{(\alpha_{11}^{\mathrm{cv}} - \alpha_{11}^{\mathrm{av}})(S_{12}^{\mathrm{co}} + S_{22}^{\mathrm{co}})}{S_{11}^{\mathrm{cv}} + S_{12}^{\mathrm{cv}} + \frac{\delta}{1-\delta}(S_{11}^{\mathrm{av}} + S_{12}^{\mathrm{av}})} \tag{A15}$$

$$\mathrm{FC1} = \frac{(S_{13}^{\mathrm{cv}} - S_{13}^{\mathrm{av}})(S_{13}^{\mathrm{co}} + S_{23}^{\mathrm{co}})}{S_{11}^{\mathrm{cv}} + S_{12}^{\mathrm{cv}} + \frac{\delta}{1-\delta}(S_{11}^{\mathrm{av}} + S_{12}^{\mathrm{av}})} \tag{A16}$$

$$\mathrm{FC2} = \frac{(\alpha_{11}^{\mathrm{cv}} - \alpha_{11}^{\mathrm{av}})(S_{13}^{\mathrm{co}} + S_{23}^{\mathrm{co}})}{S_{11}^{\mathrm{cv}} + S_{12}^{\mathrm{cv}} + \frac{\delta}{1-\delta}(S_{11}^{\mathrm{av}} + S_{12}^{\mathrm{av}})} \tag{A17}$$

$$C = \mu + \frac{(1-\mu)\left[\left(S_{13}^{\mathrm{II}} + \frac{\mu S_{13}^{\mathrm{av}}}{1-\mu}\right)S_{13}^{\mathrm{II}} - \left(S_{11}^{\mathrm{II}} + \frac{\mu S_{13}^{\mathrm{av}}}{1-\mu}\right)S_{33}^{\mathrm{II}}\right]}{\left(S_{13}^{\mathrm{II}} + \frac{\mu S_{13}^{\mathrm{av}}}{1-\mu}\right)S_{13}^{\mathrm{av}} - \left(S_{11}^{\mathrm{II}} + \frac{\mu S_{13}^{\mathrm{av}}}{1-\mu}\right)S_{33}^{\mathrm{av}}} \tag{A18}$$

$$D = \frac{(1-\mu)\left[\left(S_{11}^{\mathrm{II}} + \frac{\mu S_{11}^{\mathrm{av}}}{1-\mu}\right)(\alpha_{33}^{\mathrm{av}} - \alpha_{33}^{\mathrm{I}}) - \left(S_{13}^{\mathrm{II}} + \frac{\mu S_{13}^{\mathrm{av}}}{1-\mu}\right)(\alpha_{11}^{\mathrm{av}} - \alpha_{11}^{\mathrm{II}})\right]}{\left(S_{13}^{\mathrm{II}} + \frac{\mu S_{13}^{\mathrm{av}}}{1-\mu}\right)S_{13}^{\mathrm{av}} - \left(S_{11}^{\mathrm{II}} + \frac{\mu S_{13}^{\mathrm{av}}}{1-\mu}\right)S_{33}^{\mathrm{av}}} \tag{A19}$$

$$A = \frac{\left(S_{13}^{\mathrm{I}} + \frac{\mu}{1-\mu}S_{13}^{\mathrm{av}}\right)S_{13}^{\mathrm{I}} - \left(S_{11}^{\mathrm{I}} + \frac{\mu}{1-\mu}S_{11}^{\mathrm{av}}\right)S_{33}^{\mathrm{I}}}{\left(S_{13}^{\mathrm{I}} + \frac{\mu}{1-\mu}S_{13}^{\mathrm{av}}\right)S_{13}^{\mathrm{av}} - \left(S_{11}^{\mathrm{I}} + \frac{\mu}{1-\mu}S_{11}^{\mathrm{av}}\right)S_{33}^{\mathrm{av}}} \tag{A20}$$

$$B = \frac{(\alpha_{33}^{\mathrm{av}} - \alpha_{33}^{\mathrm{I}})\left(S_{11}^{\mathrm{I}} + \frac{\mu}{1-\mu}S_{11}^{\mathrm{av}}\right) - (\alpha_{11}^{\mathrm{av}} - \alpha_{11}^{\mathrm{I}})\left(S_{13}^{\mathrm{I}} + \frac{\mu}{1-\mu}S_{13}^{\mathrm{av}}\right)}{\left(S_{13}^{\mathrm{I}} + \frac{\mu}{1-\mu}S_{13}^{\mathrm{av}}\right)S_{13}^{\mathrm{av}} - \left(S_{11}^{\mathrm{I}} + \frac{\mu}{1-\mu}S_{11}^{\mathrm{av}}\right)S_{33}^{\mathrm{av}}} \tag{A21}$$

References and Notes

(1) Sakurada, I.; Nukushina, Y.; Ito, T. *J. Polym. Sci.* **1962**, *57*, 651.

(2) Sakurada, I.; Ito, T.; Nakamae, K. *Macromol. Chem.* **1964**, *75*, 1.

(3) Sakurada, I.; Kaji, K. *J. Polym. Sci., Part C: Polym. Symp.* **1970**, *31*, 57.

(4) Matsuo, M.; Sawatari, C. *Macromolecules* **1986**, *19*, 2036.

(5) Sawatari, C.; Matsuo, M. *Macromolecules* **1986**, *19*, 2653.

(6) Sawatari, C.; Matsuo, M. *Macromolecules* **1986**, *19*, 2726.

(7) Matsuo, M.; Sawatari, C.; Iwai, Y.; Ozaki, F. *Macromolecules.* Following paper in this issue.

(8) Matsuo, M.; Sato, R. In preparation.

(9) Hibi, S.; Maeda, M.; Makino, S.; Nomura, S.; Kawai, H. *Sen-i-Gakkaishi* **1973**, *29*, 79.

(10) Maeda, M.; Hibi, S.; Itoh, F.; Nomura, S.; Kawaguchi, T.; Kawai, H. *J. Polym. Sci., Polym. Phys. Ed.* **1970**, *8*, 1303.

(11) Takayanagi, M.; Imada, K.; Kajiyama, T. *J. Polym. Sci., Part C: Polym. Symp.* **1966**, *15*, 263.

(12) Roe, R. J.; Krigbaum, W. R. *J. Chem. Phys.* **1964**, *40*, 2608.

(13) Krigbaum, W. R.; Roe, R. J. *J. Chem. Phys.* **1964**, *41*, 737.

Effect of Orientation Distribution and Crystallinity on the Measurement by X-ray Diffraction of the Crystal Lattice Moduli of Cellulose I and II

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ABSTRACT: The crystal lattice moduli of cellulose I and II were measured by X-ray diffraction using ramie and mercerized ramie. The measured crystal lattice moduli were in the range from 120 to 135 GPa and from 106 to 112 GPa for cellulose I and II, respectively. These values were different from recent theoretical estimates of 167 and 163 GPa for cellulose I and II, respectively, reported by Tashiro and Kobayashi. To study the origin of this difference, a numerical calculation of the crystal lattice modulus, as measured by X-ray diffraction, was carried out by considering effects of the orientation factors of crystal and amorphous chains and crystallinity. In this calculation, a previously introduced model was employed, in which oriented crystalline layers are surrounded by oriented amorphous phases and the strains of the two phases at the boundary are identical. The theoretical results indicate that the crystal lattice modulus measured by X-ray diffraction is different from the intrinsic lattice modulus when a parallel coupling between amorphous and crystalline phases is predominant, while the values of both moduli are almost equal when a series coupling is predominant. Thus, the crystal lattice moduli of cellulose I and II measured by X-ray diffraction are predicted to be dependent upon the morphological properties of the bulk specimens. The numerical calculations, however, indicate that the morphological dependence is less pronounced with increasing degree of molecular orientation and crystallinity. Thus, it is concluded that fibers and films with a high degree of molecular orientation and a high crystallinity should be used as test specimens for measuring crystal lattice moduli by X-ray diffraction.

I. Introduction

In previous papers, the crystal lattice moduli of polyethylene[1] and isotactic polypropylene[2] were studied by X-ray diffraction using ultradrawn specimens. The results obtained suggest that the stress in a ultradrawn specimen is almost equal to the external applied stress and that the homogeneous stress hypothesis commonly used to derive the crystal lattice modulus from X-ray measurement is valid. In related work,[3] a mathematical representation based on a linear elastic theory was proposed to account for the dependence of the measured crystal lattice modulus in the chain direction on molecular orientation and crystallinity.[3] This description indicated that the crystal lattice modulus as measured by X-ray diffraction is different from the intrinsic crystal lattice modulus, but the calculated value is almost independent of the molecular orientation and crystallinity, except in the case of a low degree of molecular orientation and low crystallinity.

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