Macromolecules **1984**, *17*, 217–221

Dielectric Constant of Oriented Lamellar Semicrystalline Polymers

Richard H. Boyd

Department of Materials Science and Engineering and Department of Chemical Engineering, University of Utah, Salt Lake City, Utah 84112. *Received March 14, 1983*

ABSTRACT: Dielectric measurements offer in principle an attractive method for investigating phase anisotropy in oriented semicrystalling polymers since relaxations can often be directly assigned morphologically to one of the phases. However, crystal/amorphous composite or form effects, as well as inherent phase anisotropy, can contribute to measured specimen anisotropy. A recently presented theory adequately represents the composite effects on specimen anisotropy in semicrystalline polymers whose local structure is that of stacked lamellae (when the phase constants are not too disparate). In the present work that theory is extended to include the presence of anisotropy within the amorphous fraction. Under the assumption that the anisotropy in the amorphous phase is uniform through the specimen, bounds in the dielectric constant in an axially symmetric oriented specimen are derived that are functions of the amorphous-phase dielectric constants, $\epsilon_{\parallel}(1)$ and $\epsilon_{\perp}(1)$ (parallel and perpendicular to the orientation direction), the crystal-phase dielectric constant $\epsilon(2)$, the fractional crystallinity, and the orientational distribution of the lamellar surface normals about the orientation direction. When an assumed empirical distribution function for the surface normals is employed, the average angle of inclination of lamellar surfaces (tilt angle) becomes a parameter. In an application to poly(hexamethylene adipate), where measurements of specimen $\epsilon(\parallel)$ and $\epsilon(\perp)$ are available as relaxed dielectric constants for both the β (amorphous glass–rubber relaxation) and the γ (subglass amorphous relaxation) processes, the theory allows the amorphous-phase orientation function f_a to be determined from calculated values of $\epsilon_{\parallel}(1)$ and $\epsilon_{\perp}(1)$, and, in addition, the average lamellar tilt angle is also determined. This possibility arises because f_a calculated from the γ and $\gamma + \beta$ relaxation strengths have different dependences on possible average tilt angles.

The representation of the dielectric constant of a semicrystalline polymer in terms of the dielectric constants of its crystalline and amorphous phases is an important problem. For example, in determining the strength of a relaxation process occurring in one of the phases such a relation is required in order to determine the phase dielectric constant from measurements on the bulk specimen and a knowledge of the constant of the nonrelaxing phase. In oriented semicrystalline polymers dielectric measurements offer in principle an attractive method for studying phase anisotropy since a relaxation process can often be assigned to one of the phases. However, in quantifying phase anisotropy a connection between the phase dielectric constants and the bulk specimen values is necessary. Recently, we have presented a set of bounding equations for a two-phase mixture having locally lamellar morphology.[1] The bounds are tight enough to specify the mixture constant with practical accuracy for phase dielectric constant ratios that embrace a number of actual examples. The bounds included the effect of orientation of the lamellar surfaces with respect to an axially symmetric orientation direction. Anisotropy in the bulk dielectric constant occurs when the lamellar surface orientation is not random. In that treatment the separate phases were assumed to be isotropic. Thus this anisotropy is entirely due to composite effects, the analogy of "form" birefringence in optical measurements. It would be a minor extension to also allow phase anisotropy where the anisotropy is inherent in the phase structure and the phase has orthorhombic or higher symmetry (i.e., anisotropy in the crystal phase). However, an important case is an oriented semicrystalline polymer that may possess anisotropy in the amorphous phase as well as orientation of the crystals. Unlike that in the crystal phase, this anisotropy is not an inherent property of the phase but is a result of the deformation process producing specimen orientation. Its inclusion in the lamellar bounding method is not quite so straightforward, and it is the purpose of the present paper to generalize that treatment to include the presence of amorphous-phase anisotropy.

Model

As before,[1] we consider a local region in the dielectric consisting of alternating planar layers of crystal and amorphous phases. The region is of sufficient extent that a number of layers are included and a local dielectric tensor, ϵ, may be defined that represents the region as a continuous macroscopic single-phase material. The region is small enough to have uniform orientation with respect to space-fixed x,y,z coordinates in the specimen. Within the region we define a local Cartesian coordinate system that has two horizontal axes H_1 and H_2 within the plane defined by the lamellar surfaces, and a vertical axis V is normal to the surfaces (Figure 1). We further define within an amorphous layer a dielectric tensor $\epsilon(1)$ and within a crystalline layer a dielectric tensor $\epsilon(2)$. We have two problems them. First we must decide how to represent $\epsilon(1)$ and then how to combine $\epsilon(1)$ and $\epsilon(2)$ into a dielectric tensor ϵ for the local region.

Amorphous-Phase Dielectric Constant. We have already noted that for the crystal phase $\epsilon(2)$ is a property of that structure. However, for the amorphous phase $\epsilon(1)$ depends on the deformation process producing the specimen orientation. It could vary, for example, with the local orientation of a given set of lamellae containing the amorphous layer. We have assumed that the amorphous-phase dielectric tensor is affine; that is, the anisotropy is the same through all amorphous layers. In an axially symmetric sample (about z) we define $\epsilon(1)$ in terms of specimen axes x, y, and z as

$$\epsilon(1) = \begin{bmatrix} \epsilon_{\perp}(1) & 0 & 0 \\ 0 & \epsilon_{\perp}(1) & 0 \\ 0 & 0 & \epsilon_{\parallel}(1) \end{bmatrix} \qquad (1)$$

where $\epsilon_{\perp}(1)$ is the (perpendicular) component in the x,y plane and $\epsilon_{\parallel}(1)$ is the (parallel) component along the z axis. The components $\epsilon_{\perp}(1)$ and $\epsilon_{\parallel}(1)$ are to be regarded as properties of the amorphous fraction in a particular specimen and the same in all amorphous layers. In order to combine $\epsilon(1)$ and $\epsilon(2)$ we need to write both in terms

0024-9297/84/2217-0217$01.50/0

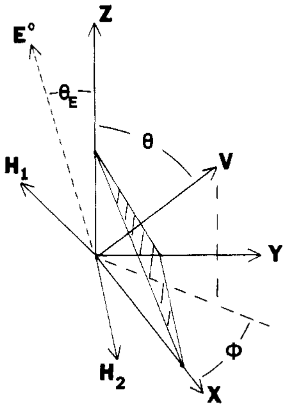

Figure 1. Local Cartesian coordinate system (H_1,H_2,V) relative to the plane defined by a lamellar surface and a specimen-fixed x,y,z Cartesian system. V is vertical to the lamellar plane, H_2 is in the x,y plant, and H_1 is normal to H_2,V; Z is the extrusion (orientation) direction in an axially symmetric specimen, θ is the angle made by V with Z, and ϕ is the angle made by the projection of V in X,Y with X. θ_E is the direction of the electric field in a measurement of the dielectric constant.

of the local coorindate system H_1,H_2,V. If H_2 is oriented to lie in the x,y plane, the orthogonal matrix $\mathbf{T}$ ($\mathbf{T}^{-1} = \mathbf{T}^{T}$), given by

$$\mathrm{T} = \begin{bmatrix} -\cos\theta\cos\phi & -\sin\phi & \sin\theta\cos\phi \\ -\cos\theta\sin\phi & \cos\phi & \sin\theta\sin\phi \\ \sin\theta & 0 & \cos\theta \end{bmatrix}$$

(where θ and ϕ are defined in Figure 1), transforms the dielectric tensor[1] via

$$\epsilon(H_1,H_2,V) = \mathbf{T}^{-1}\epsilon(x,y,z)\mathbf{T} \tag{2}$$

When applied to the amorphous-fraction tensor (eq 1) this results in

$$\epsilon(1) = \begin{bmatrix} \epsilon_\perp(1)\cos^2\theta + \epsilon_\parallel(1)\sin^2\theta & 0 & (\epsilon_\parallel(1) - \epsilon_\perp(1))\sin\theta\cos\theta \\ 0 & \epsilon_\perp(1) & 0 \\ (\epsilon_\parallel(1) - \epsilon_\perp(1))\sin\theta\cos\theta & 0 & \epsilon_\perp(1)\sin^2\theta + \epsilon_\parallel(1)\cos^2\theta \end{bmatrix} \tag{3}$$

in the H_1,H_2,V system. We will need the inverse

$$\delta(1) = \epsilon(1)^{-1} \tag{4}$$

which is given in the same system by

$$\delta_{11}(1) = 1/\epsilon_\parallel(1)\sin^2\theta + 1/\epsilon_\perp(1)\cos^2\theta$$

$$\delta_{22}(1) = 1/\epsilon_\perp(1)$$

$$\delta_{33}(1) = 1/\epsilon_\parallel(1)\cos^2\theta + 1/\epsilon_\perp(1)\sin^2\theta$$

$$\delta_{13}(1) = \delta_{31}(1) = (1/\epsilon_\parallel(1) - 1/\epsilon_\perp(1))\sin\theta\cos\theta$$

$$\delta_{12}(1) = \delta_{21}(1) = \delta_{23}(1) = \delta_{32}(1) = 0$$

Local Dielectric Constant. Writing the displacement field, $\mathbf{D}$, in each phase in terms of the electric field $\mathbf{E}$, $\mathbf{D}(1) = \epsilon(1)\mathbf{E}(1)$, $\mathbf{D}(2) = \epsilon(2)\mathbf{E}(2)$, we see that electric fields within the lamellar planes (H_1 and H_2 directions) must be continuous across the phase interface ($E_1(1) = E_1(2)$, $E_2(1) = E_2(2)$) and that we can write the local displacement field $\mathbf{D}$ in the lamellar planes as $\mathbf{D} = \bar{\sigma} = (A_1\sigma_1 + A_2\sigma_2)/A = \upsilon_1\mathbf{D}(1) + \upsilon_2\mathbf{D}(2)$ (where $\bar{\sigma}$ is the average surface charge density acting as a source of $\mathbf{D}$, σ_1 and σ_2 are the surface charge densities in each phase 1 and 2, and A_1 and A_2 are the surface areas presented by each phase in a plane normal to H_1 and H_2). Therefore the local dielectric tensor ϵ must have the structure (1 corresponding to H_1, 2 to H_2, and 3 to V)

$$\epsilon = \begin{bmatrix} \epsilon_{11} & \epsilon_{12} & \mathrm{X} \\ \epsilon_{21} & \epsilon_{22} & \mathrm{X} \\ \mathrm{X} & \mathrm{X} & \mathrm{X} \end{bmatrix} \tag{5}$$

where

$$\epsilon_{11} = \upsilon_1\epsilon_{11}(1) + \upsilon_2\epsilon_{11}(2)$$

$$\epsilon_{12} = \epsilon_{21} = \upsilon_1\epsilon_{12}(1) + \upsilon_2\epsilon_{12}(2)$$

$$\epsilon_{22} = \upsilon_1\epsilon_{22}(1) + \upsilon_2\epsilon_{22}(2)$$

and the elements denoted by X are to be determined. υ_1 and υ_2 are the volume fractions of the amorphous and crystalline phases, respectively, $\epsilon_{11}(1)$, $\epsilon_{22}(1)$, and $\epsilon_{12}(1)$ are the elements of $\epsilon(1)$, the amorphous-phase dielectric tensor given by eq 3, and $\epsilon_{11}(1)$, $\epsilon_{22}(2)$, and $\epsilon_{12}(2)$ are the elements of the crystal-phase dielectric tensor, which we write as

$$\epsilon(2) = \begin{bmatrix} \epsilon_1(2) & 0 & 0 \\ 0 & \epsilon_2(2) & 0 \\ 0 & 0 & \epsilon_3(2) \end{bmatrix} \tag{6}$$

The inverse of $\epsilon(2)$ is $\delta(2)$, where

$$\delta(2) = \begin{bmatrix} 1/\epsilon_1(2) & 0 & 0 \\ 0 & 1/\epsilon_2(2) & 0 \\ 0 & 0 & 1/\epsilon_3(2) \end{bmatrix} \tag{7}$$

Since $\epsilon_{12}(1)$ and $\epsilon_{12}(2) = 0$, $\epsilon_{12} = \epsilon_{21} = 0$. Continuity of displacement field normal to lamellar surfaces across the phase interface and additivity of work in carrying a test charge in the V direction require that the inverse of the local dielectric constant $\delta = \epsilon^{-1}$ have the structure

$$\delta = \begin{bmatrix} \mathrm{X} & \mathrm{X} & \delta_{13} \\ \mathrm{X} & \mathrm{X} & \delta_{23} \\ \delta_{31} & \delta_{32} & \delta_{33} \end{bmatrix} \tag{8}$$

where

$$\delta_{13} = \upsilon_1\delta_{13}(1) + \upsilon_2\delta_{13}(2) = \delta_{31}$$

$$\delta_{23} = \upsilon_1\delta_{23}(1) + \upsilon_2\delta_{23}(2) = \delta_{32}$$

$$\delta_{33} = \upsilon_1\delta_{33}(1) + \upsilon_2\delta_{33}(2)$$

and the elements denoted by X are to be determined. $\delta_{13}(1)$, $\delta_{23}(1)$, and $\delta_{33}(1)$ are elements of $\delta(1)$ (eq 4), and $\delta_{13}(2)$, $\delta_{23}(2)$, and $\delta_{33}(2)$ are elements of $\delta(2) = \epsilon(2)^{-1}$ (eq 7). From eq 7, $\delta_{13}(2) = \delta_{31}(2) = \delta_{23}(2) = \delta_{32}(2) = 0$ and

$$\delta_{33}(2) = 1/\epsilon_3(2)$$

Since $\delta_{23}(1) = \delta_{32}(1) = 0$ (eq 4), $\delta_{23} = \delta_{32} = 0$. The undetermined elements of ϵ (eq 5) and δ (eq 8) can be constructed from the relation $\delta = \epsilon^{-1}$ and are found to be[2]

$$\epsilon_{13} = -\delta_{13}\epsilon_{11}/\delta_{33} \tag{9a}$$

$$\epsilon_{33} = 1/\delta_{33} + \epsilon_{11}\delta_{13}^{2}/\delta_{33}^{2} \tag{9b}$$

$$\delta_{11} = 1/\epsilon_{11} + \delta_{13}^{2}/\delta_{33} \tag{9c}$$

$$\delta_{22} = 1/\epsilon_{22} \tag{9d}$$

$$\delta_{12} = 0 \tag{9e}$$

We now know the local dielectric tensor and its inverse in terms of the separate phase constants $\epsilon_\parallel(1)$, $\epsilon_\perp(1)$, $\epsilon_1(2)$, $\epsilon_2(2)$, and $\epsilon_3(2)$ as

$$\epsilon = \begin{bmatrix} \epsilon_{11} & 0 & \epsilon_{13} \\ 0 & \epsilon_{22} & 0 \\ \epsilon_{13} & 0 & \epsilon_{33} \end{bmatrix} \tag{10}$$

and

$$\delta = \begin{bmatrix} \delta_{11} & 0 & \delta_{13} \\ 0 & \delta_{22} & 0 \\ \delta_{13} & 0 & \delta_{33} \end{bmatrix} \tag{11}$$

where ϵ_{11} and ϵ_{22} are given by eq 5, 3, and 6, δ_{33} and δ_{13} by eq 8, 4, and 7, and ϵ_{13}, ϵ_{33}, δ_{11}, and δ_{22} by eq 9a–d.

Specimen Dielectric Constants. For a specimen of uniform orientation of lamellae, the dielectric constant, ϵ_m, measured in response to an applied electric field $\mathbf{E}^0$ (with components $E_x{}^0$, $E_y{}^0$, and $E_z{}^0$ and magnitude E^0) is[1]

$$\epsilon_m = (\mathbf{E}^0)^T\epsilon(x,y,z)\mathbf{E}^0/(E^0)^2 \tag{12}$$

Since the dielectric tensor (ϵ, eq 10) was formulated in terms of the H_1,H_2, V system, we must use the inverted analogue of eq 2 and write

$$\epsilon_m = (\mathbf{E}^0)^T\mathbf{T}\epsilon\mathbf{T}^{-1}\mathbf{E}^0/(E^0)^2 \tag{13}$$

In a specimen of various local orientations of lamellae, spatially averaging eq 13 under uniform $\mathbf{E}^0$ leads to an upper bound, U, on ϵ_m, which reads, when expanded, as

$$\epsilon_U = \langle\epsilon_m\rangle = [\langle\epsilon_{11}\cos^2\theta\rangle + \epsilon_{22} - 2\langle\epsilon_{13}\sin\theta\cos\theta\rangle + \langle\epsilon_{33}\sin^2\theta\rangle]\sin^2\theta_E/2 + [\langle\epsilon_{11}\sin^2\theta\rangle + 2\langle\epsilon_{13}\sin\theta\cos\theta\rangle + \langle\epsilon_{33}\cos^2\theta\rangle]\cos^2\theta_E \tag{14}$$

where θ_E is the angle made by the electric field (measuring direction) with the orientation direction (z axis) and where $\langle\ \rangle$ means an average over θ and the brackets must include ϵ_{11}, ϵ_{13}, and ϵ_{33} since they are functions of θ themselves. Explicitly, from eq 3, 5, 6, 7, 8, and 9

$$\epsilon_{11} = \upsilon_1(\epsilon_\perp(1)\cos^2\theta + \epsilon_\parallel(1)\sin^2\theta) + \upsilon_2\epsilon_1(2) \tag{15a}$$

$$\epsilon_{22} = \upsilon_1\epsilon_\perp(1) + \upsilon_2\epsilon_2(2) \tag{15b}$$

$$\epsilon_{13} = -\upsilon_1(1/\epsilon_\parallel(1) - 1/\epsilon_\perp(1))\sin\theta\cos\theta\epsilon_{11}/[\mathrm{A}] \tag{15c}$$

$$\epsilon_{33} = 1/[\mathrm{A}] + \epsilon_{11}[\upsilon_1(1/\epsilon_\parallel(1) - 1/\epsilon_\perp(1))\sin\theta\cos\theta/[\mathrm{A}]]^2 \tag{15d}$$

where

$$[\mathrm{A}] = \upsilon_1[(1/\epsilon_\parallel(1))\cos^2\theta + (1/\epsilon_\perp(1))\sin^2\theta] + \upsilon_2/\epsilon_3(2) = \delta_{33} \tag{15e}$$

and $\epsilon_\parallel(1)$ and $\epsilon_\perp(1)$ are the amorphous-phase (of volume fraction υ_1) dielectric constants in the specimen-fixed parallel and perpendicular directions and $\epsilon_1(2)$, $\epsilon_2(2)$, and $\epsilon_3(2)$ are the components of the crystalline-phase (of volume fraction υ_2) dielectric tensor (in crystal-fixed axes).

Spatial averaging of δ, the inverse of ϵ through

$$1/\epsilon_m = (\mathbf{D}^0)^T\mathbf{T}\delta\mathbf{T}^{-1}\mathbf{D}^0/(D^0)^2 \tag{16}$$

where $\mathbf{D}^0$ is the displacement field in a uniformly oriented specimen, leads to a lower bound on the dielectric constant as

$$1/\epsilon_L = \langle 1/\epsilon_m\rangle = [\langle\delta_{11}\cos^2\theta\rangle + \delta_{22} - 2\langle\delta_{13}\sin\theta\cos\theta\rangle + \langle\delta_{33}\sin^2\theta\rangle]\sin^2\theta_E/2 + [\langle\delta_{11}\sin^2\theta\rangle + 2\langle\delta_{13}\sin\theta\cos\theta\rangle + \langle\delta_{33}\cos^2\theta\rangle]\cos^2\theta_E \tag{17}$$

and

$$\delta_{11} = 1/\epsilon_{11} + \delta_{13}{}^2\delta_{33} \tag{18a}$$

$$\delta_{22} = \upsilon_1/\epsilon_\perp(1) + \upsilon_2/\epsilon_2(2) \tag{18b}$$

$$\delta_{13} = \upsilon_1(1/\epsilon_\parallel(1) - 1/\epsilon_\perp(1))\sin\theta\cos\theta \tag{18c}$$

$$\delta_{33} = \upsilon_1(1/\epsilon_\parallel(1)\cos^2\theta + 1/\epsilon_\perp(1)\sin^2\theta) + \upsilon_2/\epsilon_3(2) \tag{18d}$$

and ϵ_{11} is given by eq 15a.

Determination of $\epsilon_\parallel(1)$ and $\epsilon_\perp(1)$ from Specimen Dielectric Constants. One of the applications of the theory developed above is to use measured values of the specimen dielectric constant to determine the components $\epsilon_\parallel(1)$ and $\epsilon_\perp(1)$ and thereby investigate the anisotropy in the amorphous phase. This would involve, for example, measuring the dielectric constant at at least two angles (θ_E), 0° (‖) and 90° (⊥) say. For an upper bound equation estimate this would require simultaneously solving the set of equations resulting from eq 14 (one for each measurement and θ_E) for $\epsilon_\parallel(1)$ and $\epsilon_\perp(1)$. Since eq 14, through eq 15a–e, is a complicated function of $\epsilon_\parallel(1)$ and $\epsilon_\perp(1)$, direct solution is not possible. The spatial averaging $\langle\ \rangle$ is specific to the distribution of lamellar normals in a particular system. For the moment we assume the integrations can be performed, thus providing $\epsilon(\parallel)$ and $\epsilon(\perp)$ as functions of $\epsilon_\parallel(1)$ and $\epsilon_\perp(1)$. Then numerical solution by Newton–Raphson iteration is very straightforward and rapid. If we let $F(0°)$ represent the right-hand side in eq 14 at 0° (‖ measurement) and $F(90°)$ the value at 90° (⊥ measurement) and expand F about estimates $F_0(0°)$ and F_0-(90°)

$$F(0°) = F_0(0°) + F_1(0°)\Delta X_1 + F_2(0°)\Delta X_2$$

$$F(90°) = F_0(90°) + F_1(90°)\Delta X_1 + F_2(90°)\Delta X_2$$

where F_1 and F_2 are partial derivatives of F with respect to X_1 ($=\epsilon_\parallel(1)$) and X_2 ($=\epsilon_\perp(1)$), then updates ΔX_1 and ΔX_2 to X_1 and X_2 are

$$\Delta X_1 = (\Delta F_0(0°)F_2(90°) - \Delta F(90°)F_2(0°))/D \tag{19a}$$

$$\Delta X_2 = (\Delta F_0(90°)F_1(0°) - \Delta F_0(0°)F_1(90°))/D \tag{19b}$$

where

$$D = F_1(0°)F_2(90°) - F_1(90°)F_2(0°)$$

$$\Delta F_0(0°) = F_0(0°) - \epsilon_m(\parallel)$$

$$\Delta F_0(90°) = F_0(90°) - \epsilon_m(\perp)$$

and $\epsilon_m(\parallel)$ and $\epsilon_m(\perp)$ are the experimentally measured values. We have found this procedure to converge very rapidly when the derivatives are calculated numerically and the initial estimates X_1 and X_2 made in the following way. If we find $\epsilon_U(0°) + 2\epsilon_U(90°)$ from eq 14 and then impose $X_1 = X_2$, the result can be solved and initial estimates are

$$\epsilon_\parallel{}^0(1) = \epsilon_\perp{}^0(1) = [-b + (b^2 - 4ac)^{1/2}]/2a \tag{20a}$$

where $a = 2\upsilon_1\upsilon_2$, $b = -\langle\epsilon\rangle\upsilon_2 + (2\upsilon_1{}^2 + 2\upsilon_2{}^2 + 1)\epsilon(2)$, $c = -\langle\epsilon\rangle\upsilon_1\epsilon(2) + 2\upsilon_1\upsilon_2\epsilon(2)^2$, and $\langle\epsilon\rangle = \epsilon_m(0°) + 2\epsilon_m(90°)$, if $\epsilon_1(2) = \epsilon_2(2) = \epsilon_3(2) = \epsilon(2)$.

A similar procedure allows rapid solution of eq 17 to provide a lower bound equation calculation of $\epsilon_\parallel(1)$ and $\epsilon_\perp(1)$ from the starting approximation

$$\epsilon_\parallel{}^0(1) = \epsilon_\perp{}^0(1) = [-b - (b^2 - 4ac)^{1/2}]/2a \tag{20b}$$

where $a = -\langle\epsilon\rangle\upsilon_1 + \upsilon_1\upsilon_2/\epsilon(2)$, $b = -\langle\epsilon\rangle\upsilon_2\epsilon(2) + \upsilon_1{}^2 + \upsilon_2{}^2 + 2$, and $c = \upsilon_1\upsilon_1\epsilon(2)$.

An Application

As an example we consider the experimental data[3,4] for semicrystalline poly(hexamethylene adipate) in Table I. It represents the specimen dielectric constant measured parallel (‖) and perpendicular (⊥) to the extrusion direction in a rod oriented by diameter reduction from 1 to 0.5 in. by solid-state extrusion through a tapered die. The Hermans orientation function

$$f_c = \tfrac{1}{2}(3\langle\cos^2\theta_c\rangle - 1) \tag{21}$$

for the crystal c axes was measured by X-ray diffraction and was found to be 0.58. The fractional crystallinity, υ_2, from heat of fusion was measured to be 0.52. The polymer has two relaxation processes: the β is the glass–rubber relaxation process in the amorphous fraction and γ is a

Table I
Dielectric Constants of Oriented Poly(hexamethylene adipate): Experimental Bulk Specimen Values and Calculated Amorphous-Phase Values

					calcd[b]				
	exptl[a]				$\epsilon_{\parallel}(1)$		$\epsilon_{\perp}(1)$		
relaxation	$\epsilon(\parallel)$	$\epsilon(\perp)$	$\epsilon_{\infty}(1)$	$\epsilon(2)$	U	L	U	L	f_a
γ (−100 °C)	3.01	3.07	2.56	2.85	3.187	3.187	3.313	3.313	0.118
$\gamma + \beta$ (0 °C)	3.51	3.67	2.49	2.76	4.418	4.426	4.803	4.813	0.118

[a] The measured values are parallel ($\epsilon(\parallel)$) and perpendicular ($\epsilon(\perp)$) to the extrusion direction in an extruded rod; $\epsilon_{\infty}(1)$ and $\epsilon(2)$ are the unrelaxed amorphous-phase and crystal-phase constants obtained from the specimen low-temperature value by a Clausius-Mosotti density correction. [b] $\epsilon_{\parallel}(1)$ and $\epsilon_{\perp}(1)$ are the amorphous-phase constants in the parallel and perpendicular directions respectively; two values, U and L, are listed for each: U is obtained from the upper bound eq 14 and L from the lower bound eq 17 of the text. f_a is the amorphous-phase orientation function (eq 25 of text) calculated from $\epsilon_{\parallel}(1)$, $\epsilon_{\perp}(1)$, and $\epsilon_{\infty}(1)$; all calculations are for average lamellar tilt angle = 45° (for this tilt angle, f_a is the same for the γ and $\gamma + \beta$ processes).

subglass relaxation also assigned to the amorphous fraction. The specimen dielectric constants $\epsilon(\parallel)$ and $\epsilon(\perp)$ for each process represent relaxed values obtained from Cole–Cole plots for $\parallel$ and $\perp$ specimens. The quantities $\epsilon_{\infty}(1)$ and $\epsilon(2)$ are the unrelaxed dielectric constant of the amorphous phase and the dielectric constant of the nonrelaxing crystal phase (assumed to be isotropic) and were obtained from Clausius–Mosotti density corrections on the low-temperature specimen unrelaxed dielectric constant.

In using eq 14 or 17 to deduce the amorphous-phase dielectric constant components $\epsilon_{\parallel}(1)$ and $\epsilon_{\perp}(1)$, we must now consider the integration process implied in the averaging, $\langle\ \rangle$. Although the crystal c axis orientation function (eq 21) was measured, we must recognize that θ in eq 14 and 17 is defined by the normal to the lamellar surface (Figure 1). The latter is not necessarily perpendicular to the crystal c axis. As c axes line up along the extrusion direction as orientation develops, the lamellar surfaces can and probably do line up with an average inclination or tilt with respect to the extrusion direction. In addition, the averages $\langle\ \rangle$ in eq 14 and 17 require the distribution function for θ, and not just the second moment $\langle\cos^2\theta\rangle$, since ϵ_{11}, ϵ_{13}, and ϵ_{33} or δ_{11}, δ_{13}, and δ_{33} are functions of θ. We have adopted the following expedient to handle these questions. A convenient empirical distribution function that has been used for the c-axis orientation is[5]

$$n'(\theta_c) = (1 + \alpha)\cos^{\alpha}\theta_c \qquad (22)$$

The distribution parameter α ($\alpha = 0$, isotropic; $\rightarrow \infty$ narrowly distributed about extrusion axis) gives $\langle\cos^2\theta_c\rangle = (\alpha + 1)/(\alpha + 3)$. We assume that the lamellar surfaces follow a similar distribution but about an average tilt angle, θ_0, and use

$$n(\theta) = C\cos^{\alpha}(\theta - \theta_0) \qquad (23)$$

where α is taken to have the same value as in eq 22. Thus α is known from the measured f_c ($\alpha = 4.14$ for $f_c = 0.58$). Then eq 23 was used to calculate the averages as functions of average tilt angle from

$$\langle\epsilon_{ij}\rangle = \int_0^{\pi/2}\epsilon_{ij}n(\theta)\sin\theta\,d\theta \Big/ \int_0^{\pi/2}n(\theta)\sin\theta\,d\theta \qquad (24)$$

by means of numerical integration. For a given value of lamellar tilt angle, θ_0, both eq 14 and 17 were solved for $\epsilon_{\parallel}(1)$ and $\epsilon_{\perp}(1)$ by the Newton–Raphson method described above. For the data in Table I for both the γ and $\gamma + \beta$ processes the values of $\epsilon_{\parallel}(1)$ and $\epsilon_{\perp}(1)$ from eq 14 do not differ significantly from those from eq 17, and the bounding approach successfully serves to define them closely (see Table I).

Although the average tilt angle was not available from other means, the data in Table I permit its determination, within the validity of the model, along with $\epsilon_{\parallel}(1)$ and $\epsilon_{\perp}(1)$. To demonstrate this we use an amorphous-phase orientation function f_a defined as

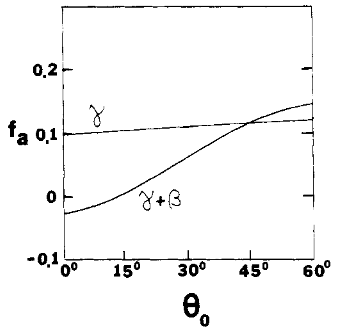

Figure 2. Amorphous-phase orientation function derived from γ-process $\parallel$ and $\perp$ relaxation strengths compared with that from $\gamma + \beta$ relaxation strengths as a function of possible average lamellar tilt angles.

$$f_a = 2(3\Delta\epsilon_{\perp}(1)/(2\Delta\epsilon_{\perp}(1) + \Delta\epsilon_{\parallel}(1)) - 1) \qquad (25)$$

where

$$\Delta\epsilon_{\perp}(1) = \epsilon_{\perp}(1) - \epsilon_{\infty}(1)$$

$$\Delta\epsilon_{\parallel}(1) = \epsilon_{\parallel}(1) - \epsilon_{\infty}(1)$$

In a system where direct dipole–dipole correlation vanishes, f_a is an orientation function for chain direction when the dipole direction is normal to the chain.[6-9] This point is elaborated on in the Appendix. For the polyester considered here the dipoles are fairly widely spaced along the chain and no evidence of intramolecular dipole–dipole correlation was evident in other work[10] and the dipole direction is nearly normal to the chain in the planar-zigzag conformation.

In Figure 2 values of f_a as a function of possible average lamellar tilt angle calculated from $\epsilon_{\parallel}(1)$ and $\epsilon_{\perp}(1)$ derived from the γ-process relaxed $\epsilon(\parallel)$ and $\epsilon(\perp)$ data are compared with values derived from the $\gamma + \beta$ data. It is seen that $f_a(\gamma)$ is only slightly dependent on possible average tilt angles, rising from 0.10 to 0.12 as the latter increases from 0 to 60°. In contrast, $f_a(\gamma + \beta)$ is strongly dependent on possible average tilt angle values. Since we have every reason to believe the f_a from both the γ and $\gamma + \beta$ process is a good approximation to an amorphous chain direction orientation function, both processes should lead to the same value. Thus the crossover point in Figure 2 serves to define both f_a and average tilt angle (at 0.12 and 45°, respectively).

The reasons for the different sensitivity of $f_a(\gamma)$ and $f_a(\gamma + \beta)$ to possible average tilt angles are physically easy to see. In a sample where the lamellar surfaces are completely oriented normal to the extrusion direction, as may be easily written directly or as eq 14 and 17 reduce to, the specimen dielectric constants are

$$1/\epsilon(\parallel) = v_1/\epsilon_\parallel(1) + v_2/\epsilon(2) \qquad (26)$$

$$\epsilon(\perp) = v_1\epsilon_\perp(1) + v_2\epsilon(2) \qquad (27)$$

Even if the amorphous phase is isotropic ($\epsilon_\parallel(1) = \epsilon_\perp(1)$), the specimen dielectric constant will be anisotropic, with $\epsilon(\parallel) < \epsilon(\perp)$. This is composite or form anisotropy. However, the more similar $\epsilon(1)$ and $\epsilon(2)$ are, the smaller this effect is. These equations are extremes as far as differences in $\parallel$ and $\perp$ specimen constants due to composite effects are concerned. Incomplete orientation or tilting of lamellar surfaces in a highly oriented specimen produces intermediate results (rotation of the surfaces by 90° of course would interchange eq 26 and 27). For the γ-process dielectric constants treated above, the amorphous- and crystal-phase constants are similar enough that the $\parallel$ and $\perp$ specimen constants are dominated not by the difference in form between eq 26 and 27 but by the differences with constants $\epsilon_\parallel(1)$ and $\epsilon_\perp(1)$ in them. For the $\gamma + \beta$ process the amorphous-phase relaxation strength is higher and the amorphous- and crystal-phase constants are more dissimilar. The differences due to the structure of the extrema eq 26 and 27 are more important and therefore the specimen constants more sensitive to producing an intermediate result by tilting of the lamellar surfaces. A significant tilt angle is indicated because for the $\gamma + \beta$ process the measured specimen anisotropy is not great enough, for the degree of crystal orientation present, to admit the maximum composite anisotropy demanded by the lamellae being normal to the c axis. There is no guarantee at all that an arbitrary set of data would have to lead to a crossover of the curves like that in Figure 2. The fact that reasonable values of both f_a and average tilt angle are obtained lends credence to the model presented and its underlying assumptions.

Acknowledgment. The author is indebted to the National Science Foundation, Division of Materials Research, Polymers Program (Grant DMR 18326), for financial support of this work.

Appendix

An argument that the amorphous-phase orientation function f_a defined by eq 25 is an orientation function for chain direction is made as follows. A chain locally has a direction specified by a vector **R**, and normal to **R** is a dipole with moment μ. Let **R** be expressed in a spherical polar coordinate system θ,ϕ relative to specimen-fixed axes (x,y,z) (i.e., as an illustration the system is the same as that for V in Figure 1). Then the dipole moment μ in this system is[7]

$$\mu = \mu[(-\cos\theta\cos\phi\cos\omega - \sin\omega\sin\phi)\mathbf{i} + (-\cos\theta\sin\phi\cos\omega + \cos\phi\sin\omega)\mathbf{j} + (\sin\theta\cos\omega)\mathbf{k}] \qquad \text{(A-1)}$$

where ω is the angle of rotation of a perpendicular dipole about the axis defined by **R**. Phillips et al.[7] have shown (under some simplifying assumptions concerning the internal field) that such a dipole, when completely free to relax about ϕ and ω and restricted only in reorientational ability about the θ coordinate (thus leading to anisotropy), leads to the relation

$$f = 2(\Delta\epsilon_\perp/\Delta\epsilon_0 - 1) \qquad \text{(A-2)}$$

where f is defined by the usual Hermans relation $f = {}^1/_2(3\langle\cos^2\theta\rangle - 1)$, $\Delta\epsilon_\perp$ is the relaxation strength measured in the $\perp$ direction, and $\Delta\epsilon_0$ is the relaxation strength of an unoriented specimen. Since $2\Delta\epsilon_\perp + \Delta\epsilon_\parallel = 3\Delta\epsilon_0$ is an invariant, eq A-2 is the same as eq 25. We need to show that it is plausible that eq A-2 or 25 is still valid when dipole reorientation is restricted, leading to reduction in relaxation strengths compared to the freely reorienting case (e.g., the γ process vs. the β process). For a restricted-relaxation case we suppose that the principal mode of relaxation is hindered rotation of ω about R and that an individual dipole does not relax about θ,ϕ. In such a case

$$\Delta\epsilon = \bar{N}B(kT)^{-1}\langle\overline{(\mu\cdot\mathbf{E}^0/E^0)^2} - (\overline{\mu\cdot\mathbf{E}^0/E^0})^2\rangle \qquad \text{(A-3)}$$

where $\bar{N}$ is the number density of dipoles, $B = \mathbf{E}/\mathbf{E}^0$, the ratio of internal field **E** to macroscopic field $\mathbf{E}^0$, the superscript bar denotes a Boltzmann average over ω, and the brackets $\langle\ \rangle$ denote a spatial average over the θ,ϕ coordinates of the collection of individual dipoles. For a measurement in the $\perp$ direction ($\mathbf{E}/E^0 = \mathbf{i}$), $\mu\cdot\mathbf{E}/E^0 = -\mu(\cos\theta\cos\phi\cos\omega + \sin\omega\sin\phi)$ and eq A-3 reduces to

$$\Delta\epsilon_\perp = {}^1\!/_2\bar{N}B(kT)^{-1}[\langle\cos^2\theta\rangle \times (\overline{\cos^2\omega} - (\overline{\cos\omega})^2) + \overline{\sin^2\omega} - (\overline{\sin\omega})^2] \qquad \text{(A-4)}$$

where under axial symmetry $\langle\cos^2\phi\rangle = \langle\sin^2\phi\rangle = {}^1/_2$, $\langle\cos\phi\sin\phi\rangle = 0$, and, following Phillips et al.,[7] we assume B independent of orientation. We now consider that the hindering potential acting on ω is measured relative to ω_0 and is a function of $\gamma = \omega - \omega_0$. We assume that for the collection of dipoles ω_0 is distributed randomly. In this case $\overline{\cos^2\omega} = \overline{\sin^2\omega} = {}^1/_2$ and $(\overline{\cos\omega})^2 = (\overline{\sin\omega})^2 = {}^1/_2 (\overline{\cos\gamma})^2 + {}^1/_2(\overline{\sin\gamma})^2$ when averaged over ω_0. Then we may write

$$\Delta\epsilon_\perp = {}^1\!/_4\bar{N}B(kT)^{-1}[1 - (\overline{\cos\gamma})^2 - (\overline{\sin\gamma})^2](1 + \langle\cos^2\theta\rangle) \qquad \text{(A-5)}$$

and for random θ distribution ($\langle\cos^2\theta\rangle = {}^1/_3$)

$$\Delta\epsilon_0 = {}^1\!/_3\bar{N}B(kT)^{-1}[1 - (\overline{\cos\gamma})^2 - (\overline{\sin\gamma})^2] \qquad \text{(A-6)}$$

For our purposes, the significance of this result is that the ratio $\Delta\epsilon_\perp/\Delta\epsilon_0$ is independent of the degree of hindrance of ω expressed by $\overline{\cos\gamma}$ and $\overline{\sin\gamma}$ and that eq A-5 and A-6 when substituted into eq A-2 (or eq 25) give

$$f = {}^1\!/_2(3\langle\cos^2\theta\rangle - 1)$$

a Hermans orientation function.

Registry No. Poly(hexamethylene adipate) (SRU), 24937-10-8; adipic acid–1,6-hexanediol copolymer, 25212-06-0.

References and Notes

(1) R. H. Boyd, *J. Polym. Sci., Polym. Phys. Ed.*, 21, 505 (1983).
(2) R. H. Boyd, *J. Polym. Sci., Polym. Phys. Ed.*, 21, 493 (1983).
(3) A. A. Hasan, Ph.D. Dissertation, University of Utah, 1982.
(4) R. H. Boyd and A. A. Hasan, *Polymer*, in press.
(5) R. L. McCullough, *Treatise Mater. Sci. Technol.*, **10B** (1977).
(6) J. Bares, *Kolloid Z. Z. Polym.*, **239**, 552 (1970).
(7) P. J. Phillips, G. Kleinheins, and R. S. Stein, *J. Polym. Sci., Part A-2*, **10**, 1593 (1972).
(8) K. H. Lau and K. Young, *Polymer*, **16**, 477 (1975).
(9) K. H. Lau and K. Young, *Polymer*, 17, 7 (1976).
(10) R. H. Boyd and P. A. Aylwin, *Polymer*, in press.