# Polarizability of Polyethylene

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ABSTRACT: A mutual induction polarization model is applied to the calculation of the polarizability tensor and refractive indices of polyethylene crystals. In the model, each bond contains a polarizable center that responds to the fields from other centers as well as to the applied field. The model parameters consist of the local bond polarizability tensors and their locations along the bonds. The parameters were determined by fitting the known mean molecular polarizabilities, $\langle\alpha\rangle$, and squared anisotropies, $\gamma^2$, of gaseous alkanes. The pronounced rise of $\gamma^2$ with chain length in the alkanes is well accounted for by the model. The calculation on crystalline polyethylene was then carried out in an a priori manner with no further approximations beyond those of the model. The calculated refractive index components are in reasonable agreement with experimental values although the birefringence is somewhat overestimated.

## Introduction

The optical properties of polymer crystals are important for several reasons. They are naturally birefringent and this property is much used in studying the state of orientation of deformed crystalline polymers. Polymers are finding increased use in devices where refractive indices are a key property. In spite of this interest, there has been little progress in developing ability for calculation or prediction of refractive indices of bulk polymers. For example, attempts to interpret the polarizability or refractive index of polyethylene have been confined to calculations directed toward inferring the effective molecular polarizability of a polymer chain unit from the experimental refractive indices. That this interpretation is not entirely satisfactory is attested to by the fact that there has been disagreement with respect to the inferred effective chain unit polarizability even to the extent of doubt as to whether a $CH_2$ unit is inherently more polarizable in the chain direction or normal to it. The problem with agreement on the inferred effective polarizability centers around the evaluation of the internal field acting on the polarizability centers. If there were agreement with respect to the inferred unit polarizability, there would still remain the question of its interpretation in terms of a structural model such as additive bond polarizabilities. It is well established that mean polarizabilities are adequately represented by additivity of inherent bond polarizabilities.[1,2] However, it is highly questionable that anisotropy in polarizability of individual molecules can be represented in this fashion. In the present work, the goal was to set up a model that successfully represents the mean polarizability and anisotropies of model compounds and then to apply the model to polyethylene with an accurate accounting of the internal field. The representation chosen was a mutual induction model where a polarizability center is placed in each bond. The electric field present induces a moment in each bond. The dipole field from the moment induced in a given center contributes to the total field experienced by other centers. This situation gives rise to a set of simultaneous linear algebraic equations for the electric field at each center. These are readily solved for typical model compound-sized isolated molecules.

The mutual induction scheme was first proposed many years ago by Silberstein[3] with the polarizability centers located on atoms. However, it was not implemented in a serious way until much later. Rowell and Stein[4] used bond-centered polarizability centers in an application to ethane. Applequist and co-workers[5-7] have extensively used the atom-centered version. The atom-centered model was applied to alkanes, the model compounds appropriate to the present work, by Ladanyi and Keyes.[8] We have applied the mutual induction model in the bond-centered form to calculation of inductive effects on dipole moments and to electrostatic contributions to conformational energies in haloalkanes,[9] poly(vinyl chloride,[10] and poly(vinylidene chloride).[11]

In a crystal, the mutual induction model can also be applied, since, due to the lattice periodicity, the size of the system of simultaneous equations is set by the number of polarization centers per unit cell and is quite manageable. The infinite extent of the crystal is manifested in the coefficients in the simultaneous equations by sums over the lattice points. The proper evaluation of these sums is well developed in the literature.

## Polarizabilities of Alkanes

The formulation of the model used here for isolated molecules has previously been presented.[9] Each bond, $i$, has a polarizability tensor that is cylindrically symmetric with respect to the bond direction

$$\alpha(i) = \begin{pmatrix} \alpha_{\parallel}(i) & 0 & 0 \\ 0 & \alpha_{\perp}(i) & 0 \\ 0 & 0 & \alpha_{\perp}(i) \end{pmatrix} \tag{1}$$

Required parameters for alkanes, then, are the parallel and perpendicular components $\alpha_{\parallel}$ and $\alpha_{\perp}$ for the C–C and C–H bonds. In addition, the locations of the centers along the bonds are needed. For the C–C bond, this is obviously halfway along the bond. For the C–H bond, the location is expressed as the fractional distance along the bond from C to H, $f$(C–H). We have previously reported values for these parameters in work on haloalkanes where average polarizabilities for alkanes were well represented but no attempt was made then to represent anisotropy. Here we have redetermined these parameters in an attempt to successfully represent the latter.

The data base to be used for determining the above parameters requires comment. The molecular polarizability tensor (in diagonal form)

$$\alpha_M = \begin{pmatrix} \alpha_{11} & 0 & 0 \\ 0 & \alpha_{22} & 0 \\ 0 & 0 & \alpha_{33} \end{pmatrix} \tag{2}$$

that results from application of the mutual induction model to the set of bond polarizability tensors, eq 1, representing the molecule has three invariants. One of these, the mean molecular polarizability,

$$\langle\alpha\rangle = (\alpha_{11} + \alpha_{22} + \alpha_{33})/3 \tag{3}$$

is readily available experimentally from refractive index measurements. The squared optical anisotropy,

$$\gamma^2 = \tfrac{1}{2}[(\alpha_{11} - \alpha_{22})^2 + (\alpha_{22} - \alpha_{33})^2 + (\alpha_{11} - \alpha_{33})^2] \tag{4}$$

is another, and it is available experimentally from depolarization ratios in light scattering[12-17] and also from the

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**Table I**
**Experimental Anisotropies (Å$^6$)**

| | $\gamma^2$, light scattering | $\gamma^2$, Kerr effect[a] | $\gamma^2$, selected |
|---|---|---|---|
| ethane | 1.31 (A), 1.50 (P), 0.92 (DS), 0.59 (BB) | | 1.1 ± 0.4 |
| propane | 2.7 (A), 2.9 (P), 1.6 (DS), 1.5 (G) | 0.72 | 2.2 ± 0.6 |
| butane | 5.6 (A), 5.2 (P), 3.7 (DS), 3.3 (G) | 2.3 | 4.4 ± 0.9 |
| pentane | 9.3 (P) | 5 | 9.3 |
| hexane | 18 (P) | 14 | 18 |
| heptane | 28 (P) | 10 | 28 |
| cyclohexane | 4.2 (SS) | 2.7 | 4 (4.2 calcd)[b] |

[a] Reported by Buckingham and Sutter, ref 18. [b] Calculated values for all molecules except cyclohexane are shown in Figure 1. A = Aval et al., ref 12; P = Powers et al., ref 13; DS = Dintzis and Stein, ref 14; BB = Bridge and Buckingham, ref 15; G = Gucker et al., ref 16; SS = Stuart and Schieszl, ref 17.

**Table II**
**Experimental and Calculated Mean Polarizabilities (Å$^3$)**

| | exptl[a] | calcd |
|---|---|---|
| methane | 2.60 | 2.60 |
| ethane | 4.47 | 4.46 |
| propane | 6.29 | 6.27 |
| butane | 8.12 | 8.13 |
| pentane | 10.02 | 10.02 |
| hexane | 11.84 | 11.93 |
| heptane | 13.68 | 13.83 |
| cyclohexane | 10.87 | 10.77 |

[a] From ref 19 and from refractive indices and densities reported in ref 20.

Kerr effect.[18] For some of the alkanes there have been multiple determinations of $\gamma^2$ by light scattering. Unfortunately, the agreement among the various reports for the same molecule is poor. This is probably due in part at least to the low scattering power of these molecules. As a result, the experimental values cannot be regarded as well established. As a separate issue, the Kerr effect values are significantly lower than those from light scattering. Buckingham and Sutter[18] state that the reasons for this discrepancy are unknown. We have chosen to ignore the Kerr effect values and have selected a set of values, based entirely on light-scattering results, that we believe are reliable enough to pursue the parameterization of the model. The data base for $\gamma^2$ used, the selected values, and estimated uncertainties are shown in Table I. Experimental values of mean polarizabilities[19,20] used are listed in Table II.

The determination of the bond polarizability parameters from the data base was carried out as follows. The molecular polarizabilities of each of the contributing conformers of each alkane were calculated for a set of polarizability parameters; the resulting conformer $\langle\alpha\rangle$ and $\gamma^2$ values of each alkane were Boltzmann averaged to arrive at values for each molecule. A conformational energy of 600 cal/mol for each gauche bond was used, and adjacent gauche sequences of opposite sense were excluded. In fitting the experimental values it was found that a good fit could be achieved by keeping the inherent bond polarizability tensors isotropic, that is, by setting $\alpha_{\parallel} = \alpha_{\perp}$ for both the C–C and C–H bonds. Thus, in the interest of simplicity, the parameters were reduced to three, $\alpha$(C–C), $\alpha$(C–H), and $f$(C–H). There is no fundamental molecular structural significance to the $\alpha_{\parallel} = \alpha_{\perp}$ assumption (the effective resultant polarizability in terms of induced moments is greater along bonds than transverse to them). Adopting it is satisfactory and the data base fitting does not permit discrimination between parallel and perpendicular components. The values that were found to reproduce both $\langle\alpha\rangle$ and $\gamma^2$ are listed in Table III. Within the $\alpha_{\parallel} = \alpha_{\perp}$ assumption, the fit is fairly unique but no doubt some variation of $f$(C–H) about 0.70 could be accommodated with compensating adjustments to the other parameters.

**Table III**
**Bond Polarizability Parameters (Å$^3$)**

| bond | $f$ | $\alpha_{\parallel}$ | $\alpha_{\perp}$ |
|---|---|---|---|
| C–C | 0.50 | 0.303 | 0.303 |
| C–H | 0.70 | 0.486 | 0.486 |

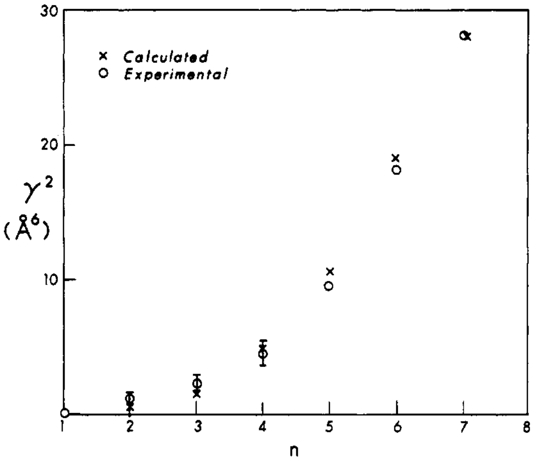

**Figure 1.** Mutual induction polarization model results. Squared optical anisotropy, $\gamma^2$, vs. carbon atom number, $n$, for linear alkanes. Circles with vertical error bars are experimental values from Table I. Crosses (×) are calculated values from mutual induction model.

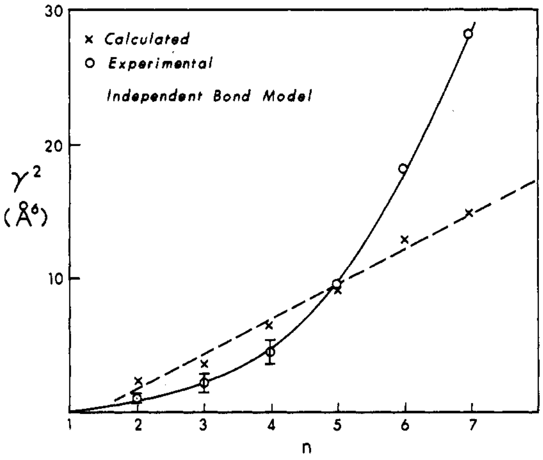

**Figure 2.** Independent bond model results. Squared optical anisotropy, $\gamma^2$, vs. carbon atom number, $n$, for linear alkanes. Circles with vertical error bars and solid curve are experimental values from Table I. Independent bond (bond additivity) model results are crosses and dashed curve. Model was parameterized for fit of calculated $\gamma^2$ to experimental value for pentane.

The fits to the experimental data achieved are displayed in Figure 1 for $\gamma^2$ and in Table II for $\langle\alpha\rangle$. The calculated value for $\gamma^2$ for cyclohexane is not conveniently displayed in Figure 1 and therefore is listed in Table I. The representation of anisotropy is quite satisfying and indicates the basic suitability of the mutual induction model.

The unsuitability of the noninteracting or independent bond model is illustrated as follows. In this model, the bond polarizability tensors are transformed to a common coordinate system and directly added to form a molecular polarizability tensor. In our work, a set of bond polarizabilities for the independent bond model was derived that fits the $\langle\alpha\rangle$ values of all of the alkanes in the data base

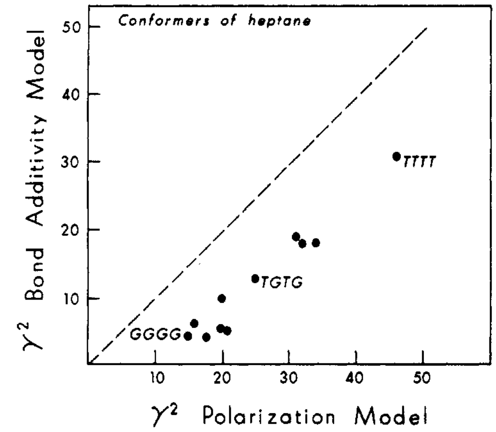

**Figure 3.** Comparison of independent bond (bond additivity) model with the mutual induction polarization model for heptane. Each point presents the results for a single conformer (several of which are labeled).

(Table II) and also arbitrarily fits the $\gamma^2$ value for pentane. The results for $\gamma^2$ are shown in Figure 2. It may be seen that the overall fit is very poor, a situation that cannot be remedied as the basic result is that $\gamma^2$ is predicted to be essentially linear in chain length. Ladanyi and Keyes[8] have pointed out this basic inadequacy of the independent bond assumption and shown that atom-centered interacting polarization centers do much better. However, they did not achieve as satisfactory a degree of fit as found here with the bond-centered approach (and with its one more parameter, the location of the C–H center).

It is important to reiterate that the anisotropy of polarizability within the mutual induction model arises largely from *interactions* between induced dipoles (and in our parameterization entirely so, since $\alpha_\parallel = \alpha_\perp$ was assumed for both C–C and C–H bonds). This was the central theme of the Silberstein calculation. It can now be adopted in practice for single molecules and crystals since the computational labor is no longer a limitation. In the independent bond model, the anisotropy has to be built into the starting bond polarizabilities.

There is great interest[21–26] in the adequacy of the independent bond model as it forms the basis for the only practical statistical mechanical calculations of the anisotropy of the polarizability of coiling macromolecules in solution, the latter quantity being connected with the molecular theory of light scattering of such systems. It is clear that the independent bond model is not satisfactory for the anisotropy of isolated molecules (vapor phase). Whether it is more satisfactory in solution is not a question addressed in the present work. However, it is of interest to make some further observations with respect to its behavior for isolated molecules. In Figure 3 we compare for heptane, conformer by conformer, the anisotropies calculated by the mutual induction polarization model with those from the independent bond model. As seen in Figure 2 when the anisotropy of pentane is fit, the conformer averaged value for heptane is seriously underestimated. In Figure 3 it is seen that the trend is strongly for all of the conformers to be underestimated by the independent bond model and by a relatively uniform factor. Thus, it appears that the increased anisotropy with chain length is a phenomenon in which the anisotropy is propagated along the chain contour and not confined to certain relatively extended conformations.

## Polarizability of PE Crystals

**Method of Calculation.** The mutual induction polarization model may be extended to crystals as follows. The electric field, $\boldsymbol{E}(m)$, at a selected bond, $m$, is related to the uniform applied field, $\boldsymbol{E}_0$, and the fields, $\boldsymbol{E}(k)$, and bond polarizabilities, $\alpha(k)$, at bonds, $k$, as

$$\boldsymbol{E}(m) = \boldsymbol{E}_0 + ... + \nabla[(\alpha(k)\boldsymbol{E}(k))\cdot\nabla(1/R_{m,k})] + ... \quad (5)$$

and when expanded into component form ($p$, $q$, $l = x, y, z$)

$$E_p(m) = E^0{}_j\delta_{p,j} + ... + \sum_l C_{m,p|k,l}\alpha_{l,q}(k)E_q(k) + ... \quad (6)$$

where the $C_{m,p|k,l}$ coefficient contains the result of applying the operators in eq 5 and depends only on the molecular geometry, the components of the bond polarizability tensor, $\alpha_{l,q}$ have been transformed into the common $x$, $y$, $z$ frame, $E^0{}_j$ is the component of the applied field in the direction $j = x, y, z$, and $\delta_{p,j}$ is the Kronecker delta. In the crystal, the terms from bonds, $k$, can be grouped as

$$E_p(m) = E^0{}_j\delta_{p,j} + ... + \sum_l C_{m,p|k,l}\alpha_{l,q}(k)E_q(k) + ... + \sum_l C_{m,p|k',l}\alpha_{l,q}(k')E_q(k') + ... \quad (7)$$

where $k'$ is a bond that differs from $k$ only by a lattice translation. Since the field at $k'$ is the same as at $k$ and the components, $\alpha_{l,q}(k')$, of the bond polarizability, $\alpha(k')$, are the same as those at $k$, the set of eq 7 reduces to

$$E(m,p) = E^0{}_j\delta_{p,j} + \sum_l\sum_q\sum_k C'_{m,p|k,l}\alpha_{l,q}(k)E_q(k) \quad (8)$$

where the sum over $k$ is over the bonds within one unit cell and

$$C'_{m,p|k,l} = \sum_{k'} C_{m,p|k',l}$$

where the sum over $k'$ is over all bonds differing from $k$ by a lattice translation (and including $k$ itself if $k \neq m$, otherwise not). The dipolar lattice sum, $C'_{m,p|k,l}$, is conditionally convergent, and if directly evaluated it will be shape dependent. This is a boundary condition problem. The dielectric constant of a polycrystalline mixture of crystals will depend on the shapes of the crystals, but the crystals themselves should not show internal dependence of the polarizability or dielectric constant on shape. These are material properties. The shape-independent lattice sums are evaluated as follows.[27–29] If the sum is extended over a finite volume, $V$, and the material outside $V$ considered from a macroscopic view, the field experienced in $V$ must have the self-field, $E_S$, of the region subtracted from the uniform macroscopic field, $E^0{}_j$.[27] Thus,

$$E_p(m) = E^0{}_j\delta_{p,j} - E_S + \sum_l\sum_q\sum_k C'(V)_{m,p|k,l}\alpha_{l,q}(k)E_q(k) \quad (9)$$

where the sum over $k'$ is restricted to the volume, $V$. The self-field due to bonds, $k$, can be regarded as related to the polarization in $V$ through a depolarization tensor, $\boldsymbol{D}_e$, as $\boldsymbol{E}_s = -4\pi\boldsymbol{D}_e\boldsymbol{P}$, or since $\boldsymbol{P} = \sum N_k\alpha(k)\boldsymbol{E}(k)$, where $N_k$ is the number of polarizability centers of type $k$ per unit volume, then

$$E_S(j) = -4\pi\sum_l\sum_k N_k D_{l,l}\alpha_{l,q}(k)E_q(k) \quad (10)$$

and

$$E_p(m) = E^0{}_j\delta_{p,j} + 4\pi\sum_l\sum_q\sum_k N_k\boldsymbol{L}_{p,l}(m,k)\alpha_{l,q}(k)E_q(k) \quad (11)$$

where

$$4\pi N_k\boldsymbol{L}_{p,l}(m,k) = C'(V)_{m,p|k,l} + 4\pi N_k D_{l,l}$$

The Lorentz tensors, $\boldsymbol{L}_{p,l}(m,k)$, can be evaluated by summation methods that have been highly developed. We have followed the description of Colpa[28,29] and used eq 2.2

**Table IV**
**Polarizabilities ($\alpha$) (per $CH_2$) and Refractive Indices ($n$) for Polyethylene**

| state | $\alpha_1$, Å$^3$ | $\alpha_2$, Å$^3$ | $\alpha_3$, Å$^3$ | $n_1$ | $n_2$ | $n_3$ | $\langle n \rangle$ |
|---|---|---|---|---|---|---|---|
| isolated planar zigzag PE chain[a] (calcd) | 1.48 | 1.42 | 3.32 | | | | |
| crystal[b] (calcd) | 2.42 | 2.40 | 3.13 | 1.51 | 1.50 | 1.68 | 1.56 |
| crystal (exptl[c]) | | | | 1.54 | 1.54 | 1.60 | 1.56 |

[a] Index 1 = transverse in-plane, 2 = out-of-plane, 3 = chain direction. [b] Index 1 = $a$, 2 = $b$, 3 = $c$. [c] From ref 30.

of the second of the two papers referenced here for the evaluation. In this equation, the notation $L_{p,q}(\mathbf{x})$ is used. If the center, $k$, is regarded as a lattice point, then $\mathbf{x}$ is the displacement of the center, $m$, from the lattice point. After the Lorentz tensor for each bond pair, $m$ and $k$, is evaluated, the set of linear algebraic equations formed from eq 11 for $m$ ranging over the number of bond centers per cell (and $p = x, y, z$) may be solved (with the applied field component, $E^0{}_j$, in a selected direction, $x$, $y$, or $z$) for the field components, $E_p(m)$, at each center, $m$. Then the three components ($p = x, y, z$) of the total induced moment per cell for the applied field in the given direction, $j$, are

$$\mu(j,p) = \sum_m \alpha_{j,p}(m) E_p(m) \qquad (12)$$

If the set of equations from eq 11 is solved 3 times, once for each of the values, $j = x, y, z$, each time with the magnitude of the applied field component, $E^0{}_j$, equal to unity, then the nine components, $\mu(j,p)$, are the components of the polarizability tensor of the cell, $\alpha_C$. In the orthorhombic system studied here for polyethylene, the polarizability tensor, $\alpha_C$, is diagonal with components, $\alpha_a$, $\alpha_b$, $\alpha_c$. The dielectric tensor of the crystal is obtained from

$$\epsilon_p - 1 = 4\pi N_C \alpha_p \qquad p = a, b, c \qquad (13)$$

where $N_C$ is the number of cells per unit volume. The refractive indices are given by $n_p = \epsilon_p{}^{1/2}$; $p = a, b, c$.

**Results for Polyethylene.** The bond polarizabilities determined for the alkanes (Table III) were used in eq 11 and 12 to obtain polarizabilities (per $CH_2$) for the polyethylene crystal. Unit cell parameters $a$ = 7.40 Å, $b$ = 4.90 Å, $c$ = 2.538 Å and setting angle = 48° were used in evaluation of the Lorentz tensor sums. The derived values for the cell polarizability are listed in Table IV. In addition, a polarizability tensor for an isolated polyethylene chain was calculated, and the results are displayed in this table also. The calculated refractive indices, from eq 13, are shown in Table IV as well.

It is, of course, of interest to compare the calculated refractive index results with experimental estimates. For the latter, we have chosen values selected by Wedgewood and Seferis.[30] Since polyethylene is both polycrystalline and semicrystalline, the experimental values require interpretation of measured values on oriented specimens of less than 100% crystallinity. The above authors have carried out such interpretation. Their values are also shown in Table IV. It may be seen that there is excellent agreement with respect to the average refractive index. The calculated birefringence is higher than the experimental value. Perhaps if the apriori nature of the calculation is considered, some measure of disagreement is to be expected. The reason for finding more anisotropy by calculation than is observed is not known. As discussed above, the gas-phase anisotropy data against which the bond polarizabilities were parameterized cannot be considered to be sell established. Especially critical are the experimental values for pentane, hexane, and heptane (see Figure 1). The experimental values are based on just one experimental study. There is no reason to doubt the methodology, but the data were taken before the advent of laser light sources and many improvements in optical detection systems. It would be beneficial if this experiment could be repeated with modern instrumentation.

It is also of interest to compare the present calculation with previous ones. As indicated in the Introduction, previous treatments have dealt with using internal field calculations to infer the effective $CH_2$ unit polarizability and its anisotropy from experimental refractive indices. In the calculation by Pietralla,[31] it was found that, in the usual convention of expressing an anisotropy of an extended chain as $\Delta\alpha = \alpha_c - (\alpha_a + \alpha_b)/2$, the inferred anisotropy was negative. This implies that although the crystal is more polarizable in the $c$ direction ($n_c > n_a, n_b$), the methylene unit is inherently more polarizable transverse to the chain direction. The reason for this unexpected result is not totally certain, but we suggest that following explanation. First, we must be precise about what is meant by the inherent polarizability components. In our calculation, these are the values in Table III. As discussed above, they are isotropic. The derived anisotropy arises from the interaction between induced moments. The inherent mean polarizability, $\langle\alpha\rangle$, calculated from Table III for a methylene unit, $CH_2$, is 1.275 (=0.303 + 2(0.486)) and $\Delta\alpha = 0$. It may be seen in Table II from increments between successive alkanes that *in the vapor* an experimental value for $\langle\alpha\rangle = \sim 1.84$ is indicated for a $CH_2$ unit. In our calculation, this $CH_2$ increment is fit well (see Table II), but this increment is a *derived* value, greatly influenced by interactions between the induced dipoles, having little direct relation with an inherent $CH_2$ group value (1.275 vs. 1.84). There is no direct relation between the inherent anisotropy $\Delta\alpha = 0$ of the bonds constituting a $CH_2$ group and the derived pronounced vapor-phase anisotropies displayed in Figure 1 that result from dipolar interaction. Similarly, in the crystal, the polarizabilities that result from the internal field calculation and are displayed in Table IV are derived results from the input inherent bond polarizabilities of Table III.

In the calculation of Pietralla, the location of the polarizability center was parameterized using the assumption of *additivity* of mean bond polarizabilities. The mean polarizability of the $CH_2$ group was found to be 1.84 Å$^3$, the same as the incremental value for the vapor. This would be appropriate if the independent bond model were used in lattice summations. However, just as in our calculation, *intra*chain mutual dipole interaction was allowed in addition to the *inter*chain induction in the internal field calculation. The close *intra*chain mutual dipolar interactions render the use of an inherent or input value equal to the vapor phase result of 1.84 inconsistent. The vapor-phase molecules already contain these close *intra*molecular interactions. The negative $\Delta\alpha$ values could well be the result of mixing the assumptions of additivity of mean bond polarizabilities (in locating the dipole) and mutual induction (in the *intra*molecular lattice sums). Certainly, the value found for $\langle\alpha\rangle$ ($CH_2$) of 1.84 is not consistent for input into a (*intra*molecular) interacting dipole model for the crystal (or as the result of an inverse calculation).

Hong et al.[32] calculated the polarizability of the $CH_2$ unit from experimental refractive index values. In their calculation, the polymer chains were regarded as continuous rods. Equation 8 was used with the sums evaluated directly. Appropriate to the continuous rod model, discrete summation along a chain was replaced by integration. Because direct evaluation of the lattice sums (eq 8) was used, the results were (nonphysically) shape dependent. No *intra*molecular summation was carried out. Under this circumstance, the polarizabilities derived would be appropriate for comparison with our results for an isolated planar zigzag (Table IV). That is, the input inherent polarizability for the rod calculation (without *intra*molecular mutual induction) should be somewhat similar to that polarizability calculated for a isolated planar zigzag. Results were reported (for a spherical sample shape) of $\alpha_a = 1.90$, $\alpha_b = 2.02$, $\alpha_c = 5.36$, and $\langle\alpha\rangle = 3.09$ Å$^3$. Both the average polarizability and the anisotropy are higher than our values for the planar zigzag. Higher anisotropy could result from the fact that in the rod calculation, the polarizability is located at the rod centers, while in our calculation the centers are distributed. However, the mean value ($\langle\alpha\rangle = 3.09$) appears to be unreasonably high compared to a vapor-phase mean polarizability increment ($\langle\alpha\rangle = 1.8$–$2.0$ Å$^3$).

Finally, it is perhaps appropriate to comment that although polarizability is not crystal size or shape dependent, there is chain length dependence. That is, the anisotropy of an extended chain (all-trans planar zigzag) continues to increase over quite long chain lengths for finite chains. For example, the calculated contribution in our model to the molecular polarizability (isolated molecule) of the center $CH_2$ group in *all-trans*-pentane is $\alpha_1 = 1.58$, $\alpha_2 = 1.50$, and $\alpha_3 = 2.42$ and for *all-trans*-heptane is $\alpha_1 = 1.55$, $\alpha_2 = 1.47$, and $\alpha_3 = 2.68$. These are still quite far from the long chain result reported in Table IV. This effect would no doubt be ameliorated in the crystalline environment (cf. the isolated chain with the crystal result in Table IV), but it probably has some effect in the chain length region of the paraffins. A paraffin crystal is probably noticeably less anisotropic than polyethylene. a chain-folded lamellar crystal probably behaves much like a finite chain length paraffin of length similar to the lamellar thickness. For the typical lamellar thickness of 100–300 Å, the finite chain length effect is probably no longer important.

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**Registry No.** Methane, 74-82-8; ethane, 74-84-0; propane, 74-98-6; butane, 106-97-8; pentane, 109-66-0; hexane, 110-54-3; heptane, 142-82-5; cyclohexane, 110-82-7; polyethylene, 9002-88-4.

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# Study of Annealing Effects on the Structure of Vinylidene Fluoride–Trifluoroethylene Copolymers Using WAXS and SAXS

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ABSTRACT: The macro- and microstructures of as-cast vinylidene fluoride–trifluoroethylene copolymers with 52/48, 54/46, and 75/25 molar compositions change remarkably with annealing temperature. The annealing effects change slightly with molar composition but may still be associated with three temperature regions: region I (cast temperatures until the ferroelectric-to-paraelectric phase transition, $T_c$); region II (beyond $T_c$ until about 120–140 °C); region III (about 120–140 °C to beyond $T_m$). The cast films have the typical lamellar structure of crystalline polymers, with pseudohexagonal packing (low-temperature phase). For the 52/48 and 54/46 films, annealing beyond $T_c$ creates disordering along the fiber axis but the pseudohexagonal packing remains. Near the melting temperature, a large morphological change in the lamellar structure occurs.

## Introduction

Vinylidene fluoride–trifluoroethylene (VDF–TrFE) copolymers show a ferroelectric phase transition. The exact nature of this transition has been the subject of numerous researches in recent years.[1-9] It is by now recognized that the ferroelectricity of VDF–TrFE copolymers is attributed

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