

The Intrinsic Birefringence of the α , β , and γ Forms of Polyvinylidene Fluoride and the Estimation of Orientation in Fibers and Films

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INTRODUCTION

Birefringence is an important characteristic of polymeric materials and has long been known to represent a measure of molecular orientation.¹⁻⁷ With the work of Hermans and his co-workers 3, 5, 6, and others, it became clear that it could yield a quantitative measure of uniaxial orientation if the maximum or intrinsic birefringence Δ^0 were known. This has led to efforts over the past thirty years to determine Δ^0 for various polymers of interest. Values of Δ^0 for polyethylene, poly(ethylene terephthalate), and various vinyl polymers are summarized in Table I.⁸⁻¹²

The authors have been carrying out investigations of orientation and polymorphic phase development in melt spinning fibers and tapes from poly(vinylidene fluoride).¹³ It was found using wide angle X-ray diffraction that depending on the spinning conditions, α (form II) or β (form I) phases are formed. The unit cells determined for these crystalline phases and their parameters are shown in Figure 1 and Table II.¹⁴⁻¹⁸ We have measured birefringences on melt-spun fibers and tapes, but it was not possible to interpret them quantitatively. This led us to the efforts of the present paper, notably the calculation of intrinsic birefringences of various phases of poly(vinylidene fluoride).

EXPERIMENTAL ESTIMATION OF INTRINSIC BIREFRINGENCE

The simplest procedure of determining intrinsic birefringence of a two-phase polymer would be to produce uniaxially oriented filaments and measure the birefringence, crystallinity, crystalline, and amorphous orientation functions (f_{am} and f_c) using independent techniques as suggested by Samuels.¹⁹ The total birefringence of an ideal two-phase system may be expressed as

$$\Delta n = \phi \Delta_c^0 f_c + (1 - \phi) \Delta_{am}^0 f_{am} \quad (1a)$$

where Δn , ϕ (crystallinity), f_c , and f_{am} may be obtained using polarized light microscopy, differential scanning calorimetry, wide angle X-ray diffraction,

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TABLE I
 Intrinsic Birefringences of Various Polymers

Polymer	Δ^0	Reference
Poly(ethylene terephthalate)	0.220 (crystalline) 0.2755 (amorphous)	Dumbleton ⁸
Polystyrene	-0.16	Stein ⁹
Polyethylene	0.0585 (crystalline)	Nomura and Kawai ¹²
Polypropylene	0.0291 (crystalline) 0.060 (amorphous)	Samuels ¹¹
Poly(vinyl alcohol)	0.0443 (crystalline) 0.0404 (amorphous)	Hoshino et al. ¹⁰

and sonic modulus measurements.¹⁵ Rearranging eq. (1a) gives

$$\frac{\Delta n}{\phi f_c} = \Delta_c^0 + \Delta_{am}^0 \frac{1 - \phi f_{am}}{\phi f_c} \quad (1b)$$

and the plot $\Delta n/\phi f_c$ vs. $[(1 - \phi)/\phi] f_{am}/f_c$ yields Δ_c^0 from the intercept and Δ_{am}^0 from the slope. We are, however, dealing with a polymorphic crystalline material in which one may have different crystalline phases as well as amorphous polymer present at varying relative amounts. For a three-phase system, the birefringence may be expressed as

$$\Delta n = \Delta n(\alpha) + \Delta n(\beta) + \Delta n(am) \quad (2a)$$

$$\Delta n = \phi_\alpha \Delta n_\alpha + \phi_\beta \Delta n_\beta + (1 - \phi_\alpha - \phi_\beta) \Delta n_{am} \quad (2b)$$

$$\Delta n = \phi_\alpha f_\alpha \Delta_\alpha^0 + \phi_\beta f_\beta \Delta_\beta^0 + (1 - \phi_\alpha - \phi_\beta) f_{am} \Delta_{am}^0 \quad (2c)$$

Here $\Delta n(\alpha)$ is the contribution of the α - phase, $\Delta n(\beta)$ the contribution of the β -phase, and $\Delta n(am)$ the contribution of the amorphous phase. ϕ_α , ϕ_β , and $(1 - \phi_\alpha - \phi_\beta)$ are the volume fractions of the α , β , and amorphous phases and Δn_α , Δn_β , and Δn_{am} are the birefringence of the individual phases. f_α , f_β , and f_{am} are the Hermans orientation factor of the α , β , and amorphous phases, and Δ_α^0 , Δ_β^0 , and Δ_{am}^0 are the respective intrinsic birefringences.

In our earlier study¹³ of melt spinning PVF₂ fibers over a range of processing conditions, we produced fibers with birefringences ranging from 0.003 to 0.03 [see Fig. 2(a)]. These fibers possessed varying levels of the α (II) and β (I) phases and varying orientations. The fibers with low take-up speeds (and thus orientations) were predominantly α , and those with higher orientations were found to have predominantly β -phase in their crystalline structure. The most highly oriented fibers exhibited 60% β - and 40% α -phases in their crystalline regions and had an α -phase orientation factor of about 0.6 [Fig. 2(b)].

In subsequent experiments we have cold-drawn these as-spun fibers to improve the chain orientation. The fibers obtained by this cold drawing process show high chain orientation with crystal structure mainly in β form. The results are summarized in Table III. Birefringences of up to 0.04 were

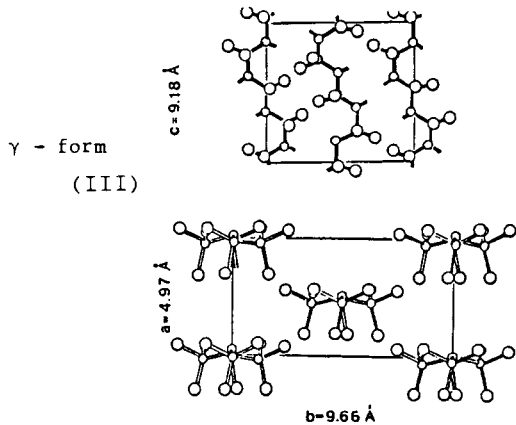
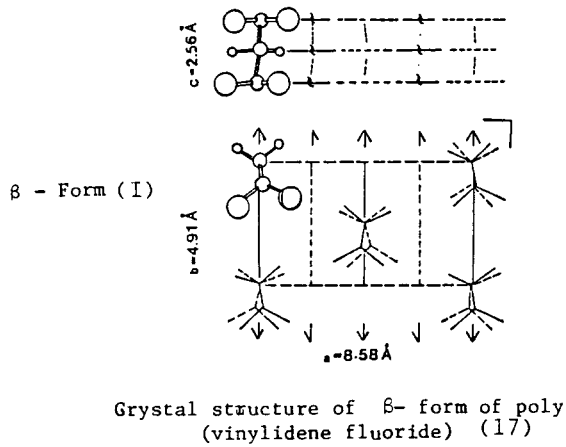
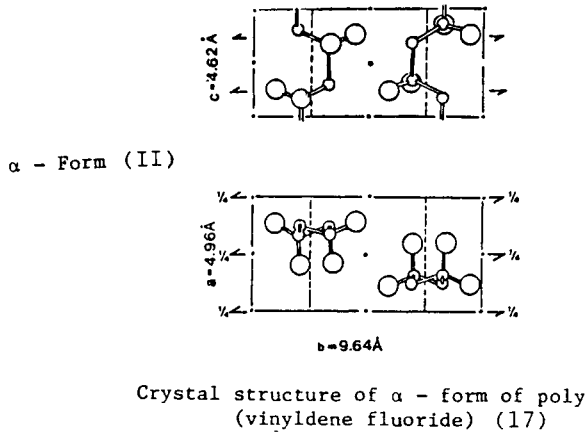


Fig. 1. Unit cells of α , β , and γ phases of poly(vinylidene fluoride) (PVF₂) (with permission).

TABLE II
Crystalline Forms of Poly(vinylidene Fluoride)

Crystalline form	Chain conformation	Unit cell type	Unit cell dimension (Å)	Reference
α , form II	TG ⁺ TG ⁻	Monoclinic	$a = 4.96$ $b = 9.64$ $c = 4.62$ $\beta = 90^0$	15-17
β , form I	TTTTT	Orthorhombic	$a = 8.58$ $b = 4.91$ $c = 2.56$	14, 16, 17
γ , form III	TTG ⁺ TTG ⁻	Orthorhombic	$a = 4.97$ $b = 9.66$ $c = 9.18$	18

determined in drawn fibers. This should be lower but approaching the value of Δ_{β}^0 .

INTRINSIC BIREFRINGENCE OF VARIOUS POLYMERS

To understand the factors influencing intrinsic birefringence, we consider the Lorentz-Lorenz equation²⁰ which relates refractive index and polarizability

$$\frac{n^2 - 1}{n^2 + 2} = \frac{N}{3} \alpha \quad (3)$$

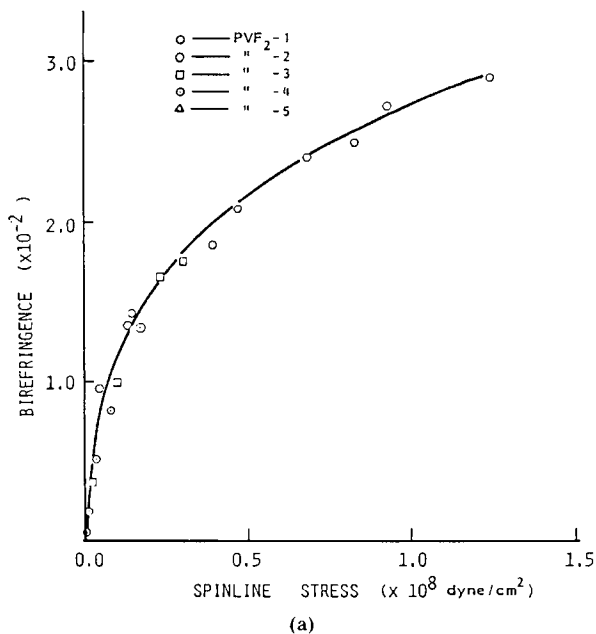
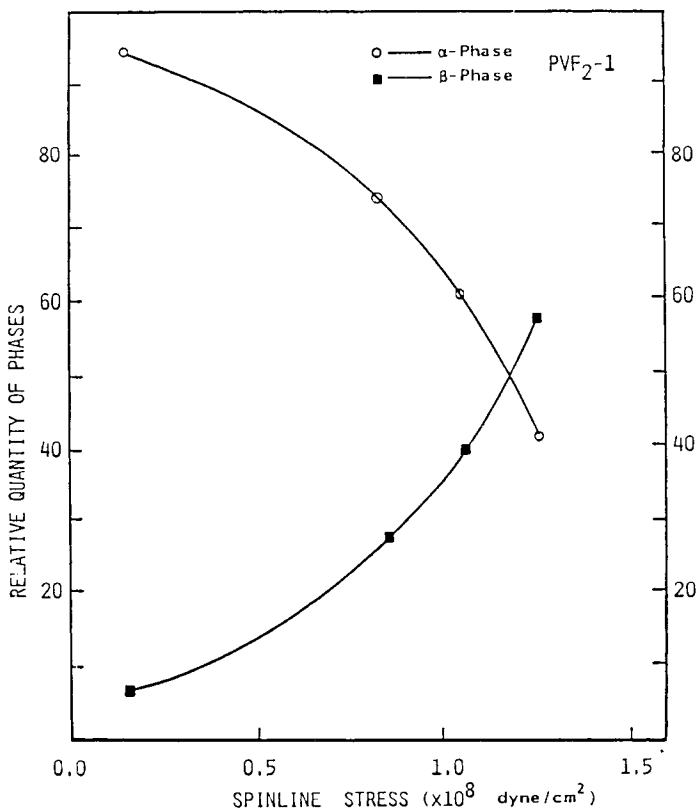


Fig. 2. (a) Birefringence of melt-spun PVF₂ fibers as a function of spinline stress. PVF₂: (○)1; (○) 2; (□) 3; (○) 4; (Δ) 5. (b) Relative amounts of α (○) and β (■) crystalline phases as a function of spinline stress.



(b)

Fig. 2. (Continued from the previous page.)

TABLE III
Birefringence of Melt-Spun PVF₂ Fibers before and after
Cold Drawing

V_1/V_0	PVF ₂ -1 ^a		PVF ₂ -2	
	141	285	141	285
Elongated (%)	40	40	400	400
Δn (before)	0.0242	0.0302	0.00364	0.00563
Δn (after)	0.0302	0.0387	0.0374	0.0382

^a Different PVF₂ samples described in our earlier paper.¹³

High refractive indices are associated with large polarizabilities. If we presume eq. (3) to be applicable to the anisotropic refractive indices of an oriented polymer, it follows that

$$\frac{n_1^2 - 1}{n_1^2 + 2} - \frac{n_2^2 - 1}{n_2^2 + 2} = \frac{2(n_1 + n_2)}{(n_1^2 + 2)(n_2^2 + 2)}(n_1 - n_2) = \frac{N}{3}\alpha \quad (4)$$

which is close to

$$n_1 - n_2 = \Delta^0 = \frac{N(\bar{n}^2 + 2)^2}{12n} (\alpha_1 - \alpha_2) \quad (5)$$

where 1 and 2 are the directions along and perpendicular to uniaxially oriented polymer chain and \bar{n} is mean refractive index. Large values of Δ^0 are associated with large $(\alpha_1 - \alpha_2)$.

We have summarized the intrinsic birefringence of various polymers in Table I. The value of Δ^0 for amorphous and crystalline phases of polymer comes with highly polarizable phenyl groups in the backbones is large and positive with values of 0.2 and above. Polystyrene which has pendant phenyl groups has its greatest polarizability perpendicular to chain axis, and this polymer has intrinsic birefringence of about -0.16 .⁹

The aliphatic polymers with various nonaromatic substituents possess low values of intrinsic birefringence. Table I shows that polyethylene with vinyl methyl substituent has a lower value of 0.031 while poly(vinyl alcohol) with a vinyl hydroxyl substituents has values of 0.040 and 0.044 for amorphous and crystalline phases, respectively.

If we consider the poly(vinylidene fluoride), the value of Δ^0 relative to polyethylene should relate to the magnitude of the polarizability of C—F relative to the C—H bond. This should be reflected in the mean refractive indices of the two polymers and similar organic compounds. Polyethylene has a mean refractive index in the range of 1.51–1.54, and poly(vinylidene fluoride) has mean refractive index of about 1.42. These values vary depending on the crystallinity as the Lorentz–Lorenz relationship implies. In small molecules, ethanol has refractive index of 1.359 and trifluoroethanol has 1.29. It appears that the replacement of hydrogen atoms with fluorine atoms in molecules reduces overall refractive index of the polymer.

ADDITIVITY OF BOND POLARIZABILITY CALCULATION OF INTRINSIC BIREFRINGENCE

We may estimate the intrinsic birefringence from the first principles using the concept of additivity of bond polarizabilities. Such calculations have a long history and were presumably applied to polymers first by Gurnee.²¹ They have now been made for various polymers.^{9, 12, 22} In this approach, anisotropic internal field effects are not taken into account in determining the principal polarizabilities. The principal polarizabilities α_n are related to bond polarizabilities with the following relationship:

$$\alpha_m = \sum_i b_{1i} \cos^2 \theta_{im} + \sum_i b_{2i} \sin^2 \theta_{im} \quad (6)$$

where b_{1i} and b_{2i} are bond polarizabilities parallel and perpendicular to the axis of the i th bond. θ_{im} is the angle between m ($= a, b,$ or c) axis of the unit cell and the i th bond.

The calculation of the intrinsic birefringence requires an exact knowledge of chain conformation and/or coordinates of the atoms relative to each other.

TABLE IV
Bond Polarizabilities

Bond polarizability ($\times 10^{25} \text{ cm}^3$)						Reference
C—C		C—H		C—F		
b_1	b_t	b_1	b_t	b_1	b_t	
18.8	0.2	7.9	5.8	9.6	5.45	Denbigh ²³
9.68	2.63	7.82	5.73	—	—	Bunn and Daubeny ²⁴
—	—	—	—	8.0	4.56	Vogel et al. ²⁵
—	—	—	—	15	4	LeFevre and LeFevre ²⁶

TABLE V
Computed Refractive Indices and Intrinsic Birefringences

	Δ^0	n_a	n_b	n_c	
(A) Calculations based on Bunn and Daubeny (C—C, C—H) and Denbigh (C—F)					
α (II)	0.01732	1.4550	1.4656	1.4753	
β (I)	0.02123	1.4620	1.4801	1.4923	
γ (III)	0.00667	1.4197	1.4679	1.4861	
(B) Calculations based on Bunn and Daubeny (C—C, C—H) and Vogel (C—F)					
α (II)	0.0236	1.4141	1.4328	1.4471	
β (I)	0.030773	1.4235	1.4450	1.4651	
γ (III)	0.001012	1.1957	1.2047	1.2103	
(C) Calculations based on Bunn and Daubeny (C—C, C—H) and LeFevre and LeFevre (C—F)					
α (II)	-0.0529	1.5199	1.4940	1.4540	
β (I)	-0.0853	1.5453	1.5216	1.4481	
γ (III)	-0.0298	1.2422	1.2343	1.2084	
(D) Calculations based on Denbigh's bond polarizabilities					
α (II)	0.1664	1.3992	1.5132	1.6227	
β (I)	0.2267	1.3924	1.5176	1.6796	
γ (III)	0.0669	1.191	1.2338	1.2815	
(E) Calculations based on Denbigh (C—C, C—H) and Vogel et al. (C—F)					
α (II)	0.1694	1.3643	1.4792	1.5912	
β (I)	0.2295	1.3558	1.4815	1.6482	
γ (III)	0.0700	1.1754	1.2235	1.2695	
(F) Calculations based on Denbigh (C—C, C—H) and LeFevre and LeFevre (C—F)					
α (II)	0.0965	1.4647	1.5413	1.6003	Ref(17)
α (II)	0.0950	1.4695	1.5420	1.6008	Ref (27)
β (I)	0.1132	1.4831	1.5480	1.6288	
γ (III)	0.0739	1.4753	1.5534	1.5883	

The α form (form II) has a glide plane chain structure (TG^+TG^-) which has been characterized by various investigators.^{15-17, 23} The β form (form I) has a zig-zag chain conformation (TTTT).^{14, 16, 17} The γ form has the $TTTG^+TTTG^-$ glide plane conformation.¹⁸ The parameters describing these crystal forms are summarized in Table II. We determined the bond angles from the structures cited above. To obtain principal polarizabilities, the bond polarizabilities along the bond axis (b_1) and perpendicular to bond axis (b_t) for all type of bonds are required. The bond polarizabilities for C—H and C—C bonds have been determined by Denbigh²⁴ and Bunn and Daubeny²⁵ and are given in Table IV. The polarizabilities of C—F bonds used were determined by LeFevre and LeFevre.²⁶

Denbigh²⁴ determined that $b_1/b_t = 0.57$ for C—Cl and C—Br bonds. Table IV also lists b_1 and b_t determined if their ratio taken to be constant for carbon halogen bonds and bond refraction of 1.72. Vogel et al.²⁷ also found bond refraction for C—F as 1.44. The b_1 and b_t values calculated using $b_1/b_t = 0.57$ and above bond refractions with the following relationship²⁴:

$$\frac{2R}{4\pi N} = \frac{b_1 + 2b_t}{3} \quad (7)$$

are given in Table IV (R = bond refraction, N = Avogadro's number). Table V summarizes the computed intrinsic birefringence and refractive indices for crystal phases determined using the bond polarizabilities listed in Table I.

DISCUSSION

The intrinsic birefringences using Bunn's values for C—C and C—H are either very small or negative (Table VA, B, C). On the other hand, C—C and C—H values of Denbigh (Table VD) and Denbigh and Vogel (Table VE) give clearly too high values especially for the β -phase. As presented earlier, the melt-spun and drawn filaments possess birefringences up to 0.04 at rough chain orientation factors of 0.6–0.7. These values suggest that the intrinsic birefringences calculated using Denbigh and LeFevre and LeFevre's (Table VF) bond polarizabilities are reasonable in magnitude. We also calculated the phase II optical properties based on Hasegawa et al.'s¹⁷ crystallographic data as well Bachman and Lando's²³ crystallographic data which involves up-down statistical packing of chains in the unit cell. Table VF shows these results, and they are slightly different. Table V also indicates that β -phase shows the highest and γ -phase shows the lowest intrinsic birefringence.

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