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Applicability of light depolarization technique to crystallization studies

Andrzej Ziabicki*, Beata Misztal-Faraj

Institute of Fundamental Technological Research, Polish Academy of Sciences, ul. Świetokrzyska 21, 00-049 Warsaw, Poland

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Abstract

Critical analysis of light depolarization technique (LDT) widely used in polymer crystallization kinetics is presented. It is demonstrated, that intensity of light depolarized on a system of birefringent crystals cannot be treated as a measure of volume fraction of crystalline phase (degree of crystallinity). Intensity of light depolarized in a polycrystalline system is a non-linear function of the product of the degree of crystallinity and function of average crystal dimensions. Closed-form expression for depolarization ratio is derived and the range of conditions where linear approximation is acceptable is discussed.

In spite of interpretational weaknesses, further development of light depolarization technique seems to be justified by potentially short response time. LDT may appear useful for studying rapid crystallization processes (above 1 kHz sampling frequency), which cannot be followed by measurements of density, X-ray diffraction or calorimetry. However, the LDT data either have to be combined with independent measurements of crystal thickness, or treated as a 'crystallization characteristic' per se, quantitatively inconsistent with calorimetric, volumetric or X-ray diffraction data.

Keywords: Crystallization; Crystallinity; Optical retardation

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1. Introduction

Crystallization plays essential role in determining physical properties of various materials, in particular organic polymers. In industrial processing, crystalline structure of the polymer and its morphology is developed in complex conditions including rapidly changing deformation, stress and temperature which calls for rapid measurement of the degree of crystallinity. Experimental techniques of crystallization kinetics based on calorimetry (DSC) density (dilatometry, density-gradient column) or X-ray diffraction (WAXSSAXS) offer reliable information limited, however, to slow processes. Maximum sampling frequency available does not exceed 1–10 Hz, while non-isothermal and stress-induced crystallization processes may require sampling frequency in excess of 1 kHz. In these circumstances, measurement of light depolarization seems a promising solution.

First attempts of following polymer crystallization by light depolarization technique (LDT) were made in 50s and early 60s of the XX century [1–5]; the method is currently in use in a slightly modified form [6–10]. Theoretical background provided by the theory of compensators [11,12] considers stack of optically anisotropic plates parallel to the polarizer plane. This assumption, natural for compensators, has been adopted to polycrystalline systems where individual crystals may be inclined to the polarizer plane. Inclination of crystal plates affects average optical retardation and absolute intensity of the depolarized light. Relative variations of depolarization ratio (and the relative changes of crystallinity) would not be affected, though. Analyzing the LDT as it is currently applied we will keep the assumption of parallelity unchanged. More general model admitting tilting of crystal plates and non-uniform orientation distribution will be published separately.

In spite of the fact that many experimental data have been accumulated, very little reflection was devoted to their interpretation. We are going to reconsider the problem. Following the theory of compensators [11], we will analyze light depolarization in a statistical system of birefringent

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* Corresponding author. Tel.: +48 228 278 182; fax: +48 228 269 815.
E-mail addresses: aziab@ippt.gov.pl (A. Ziabicki), bfaraj@ippt.gov.pl (B. Misztal-Faraj).

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crystal plates parallel to the plane of polarizer (Fig. 1). The polarizer (P), analyzer (A) and crystal plate (CR) all lie in the plane *XY*. Optical axes of individual plates are oriented with respect to polarizer by angles α_i (Fig. 2).

2. Review of the earlier work

2.1. Experimental setup

First experiments using light depolarization to study crystallization of polymers were made by Fischer and Schram [1]. Parallel light beam traveling along the *Z* axis passes polarizer, P, sample, S, and analyzer, A, all placed on planes normal to *Z* (Fig. 3). The analyzer is rotated in the *XY* plane with respect to the polarizer, and intensity of the transmitted light, *I*, is recorded as a function of the analyzer rotation angle ϕ (Fig. 2). On the other hand, Magill [2–5] replaced one eyepiece of the polarizing microscope with a photosensor and measured light intensity transmitted through crossed polarizers ($\phi = (1/2)\pi$).

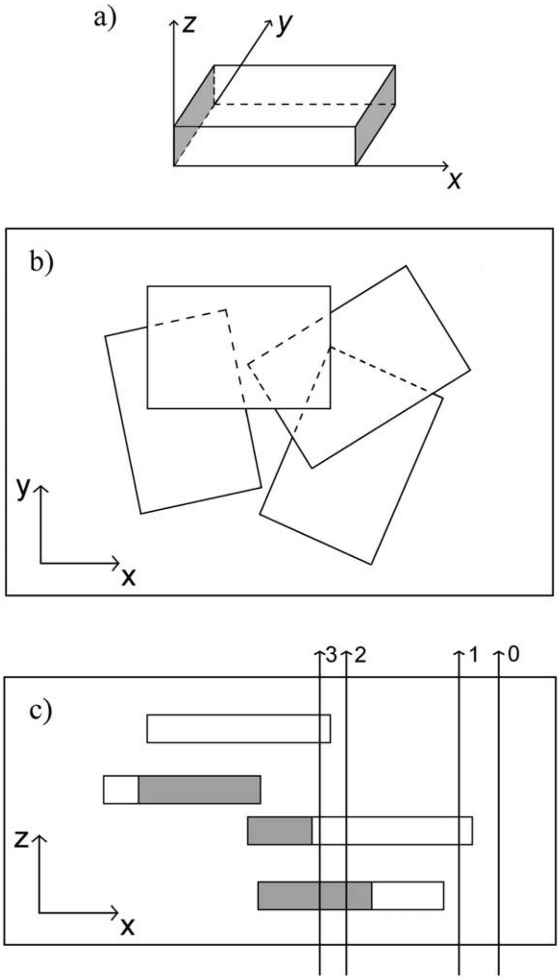

Fig. 1. Parallel crystal plates in a polycrystalline system (a) film sample in the coordinate system, (b) projection on the *XY* plane, (c) projection on the *XZ* plane. *Z*, direction of the light beam.

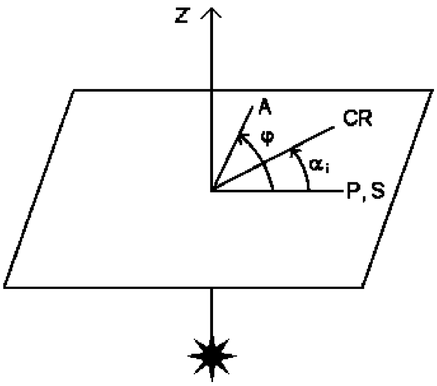

Fig. 2. Orientation of optical axes with respect to polarizer in the plane normal to light beam. Sample axis (S) parallel to polarizer (P); ϕ, orientation of the analyzer (A), α_i, orientation of the axis of an *i*-th crystal (CR).

Consider a single birefringent plate placed between polarizer and analyzer. Optical axis of the plate is oriented at the angle α with respect to the polarizer and the analyzer is oriented at the angle ϕ vs. polarizer (Fig. 2). According to the theory of compensators [11,12] intensity of the incident (linearly polarized) light, I_0, after passing through the plate is changed to

$$I(\varphi) = I_0\left[\cos^2\varphi + \sin 2\alpha \sin 2(\varphi - \alpha)\sin^2\frac{\delta}{2}\right] \quad (1)$$

Relative optical retardation of the plate, δ, is a function of optical birefringence, Δn, thickness of the plate, *d*, and wavelength of the incident light, λ

$$\delta = \frac{2\pi\Delta nd}{\lambda}; \quad D = \sin^2\frac{\delta}{2} \quad (2)$$

When measurements are made with crossed polarizers, $\phi = (1/2)\pi$

$$\frac{I_\perp}{I_0} = \sin^2 2\alpha D \quad (3)$$

In the absence of scattering and absorption, the reference

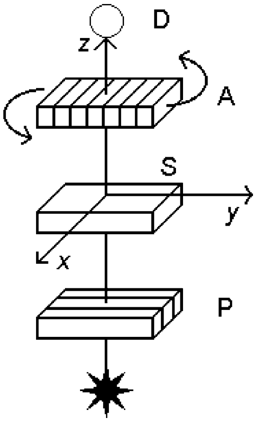

Fig. 3. Light depolarization setup with one detector. P, polarizer; S, sample; A, analyzer; D, detector.

intensity, I_0, is that of the incident light. Larger crystallites and crystalline superstructures (spherulites) embedded in an amorphous matrix may scatter light. The corrections for scattering were discussed in Refs. [1,6–9]. To take scattering into account, Ding and Spruiell [8] replaced eyepieces of the polarizing microscope with two photosensors. Light leaving the sample was split into two beams (Fig. 4). One of the beams passed analyzer and its intensity, I_1, was measured by the detector D1; the other beam, I_2, was deflected and measured by another detector (D2) without passing through the analyzer. Scattering reduces intensity of the transmitted light. Therefore, depolarized intensity leaving the analyzer, I_1, should be compared with incident intensity reduced for scattering, $I_0 - I_S$

$$
\begin{gathered}
I_\perp = I_1 \\
I_2 = I_0 - I_S \\
\frac{I_1}{I_2} \equiv \frac{I_\perp}{I_0 - I_S} = \sin^2 2\alpha D
\end{gathered}
\tag{4}
$$

Fischer and Schram [1] who recorded intensity transmitted through the analyzer at various angles ϕ, made use of the fact that the sum of intensities transmitted through the analyzer parallel and perpendicular to the polarizer is a constant and presented reference intensity corrected for scattering as

$$
\begin{gathered}
I_\parallel + I_\perp = I_0 - I_S \\
\frac{I_\perp}{I_0 - I_S} \equiv \frac{I_\perp}{I_\parallel + I_\perp} = \sin^2 2\alpha D
\end{gathered}
\tag{5}
$$

Determination of the depolarization ratio requires two measurements: either I_1 and I_2 (in the Ding and Spruiell setup), or $I_\perp$ and $I_\parallel$ (according to Fischer and Schram). The ratio

$$
\frac{2I_\perp}{I_\parallel + I_\perp} = \frac{2I_\perp}{I_0 - I_S}
\tag{6}
$$

is a measure of the degree of depolarization. Degree of depolarization reduces to zero in the absence of birefringent elements between the polarizer and analyzer and asymptotically approaches unity in a system of many randomly oriented birefringent objects, when polarization of the transmitted light is changed from elliptic to circular.

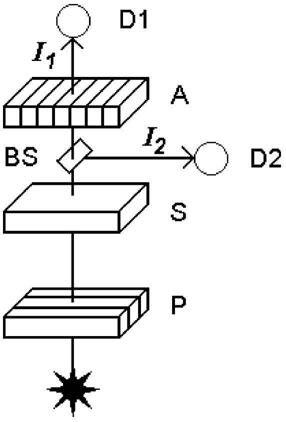

Fig. 4. Light depolarization setup with two detectors. P, polarizer; S, sample; A, analyzer; BS, beam splitter. D1 and D2, detectors.

2.2. Interpretation of light depolarization experiments

Except Fischer and Schram [1] who studied phase transitions (crystallization and melting) as a function of temperature, light depolarization technique was used to following crystallization kinetics [2–10,16]. All authors assumed (explicitly, or implicitly) that depolarization intensity expressed by the single crystal formula (Eqs. (1) and (3)) provides a measure of the degree of crystallinity. There are some controversial problems associated with such interpretation.

The first controversy, raised by one of us a few decades ago [13], concerned optical interaction of many crystals appearing in the light path. Crystallizing systems consist of many birefringent plates, arranged in the light path either side-by-side or in series. Fig. 1 illustrates possible arrangements of parallel plates. For a stack of parallel plates the theory [11,12] predicts non-additive light intensity. Ziabicki [13] argued that single-crystal formula, Eq. (3), should be applied only to very dilute systems, and/or very thin samples, in which probability of the appearance of more than one crystal in the light path is negligible. On the other hand, Binsbergen [14] developed a model of stacks of plates with small optical retardation ($D \ll 1$), claiming applicability of the single-crystal formula to non-dilute systems. We will show that neither the condition of low concentration (Ziabicki) nor thin-plate requirement (Binsbergen) is sufficient for quantitative description of depolarization in terms of the single-crystal formula. We will define the range of conditions in which linear approximation is acceptable, and present a general formula applicable in the entire range of conditions.

Another controversial point is proportionality of depolarization ratio to volume fraction of birefringent elements (degree of crystallinity, x). We will show that depolarization ratio is not proportional to crystallinity alone, but to crystallinity multiplied by a function of average plate dimensions. Binsbergen [14] did notice this problem, but circumvented it assuming constant crystal thickness. Also in the Ding thesis [6] there appears depolarization intensity proportional to the product of crystallinity and lamellar thickness, but in the final publications [7–9] the thickness has been incorporated in a constant. We will discuss several special situations when development of crystallinity can be estimated from variation of the depolarization ratio, but there is hardly a way of knowing a priori which specific situation can be expected.

All authors studying polymer crystallization via light depolarization required crystals to be randomly oriented in the sample and the amorphous matrix to be optically isotropic. The problem is not purely academic: the main motivation for following high-speed crystallization using light depolarization concerns oriented systems in which crystal orientation is not random and the amorphous matrix is anisotropic. Extension of the theory onto systems with arbitrarily oriented crystals will be presented in a separate paper.

3. Theory of light depolarization in a statistical system of parallel crystal plates

3.1. Description of the system

Consider a flat film with thickness, B, and surface area, F, containing N birefringent crystal plates parallel to the sample plane, each with surface area f_i, and thickness d_i. The degree of crystallinity, x, defined as volume fraction of the crystalline phase reads

$$x = \frac{1}{FB}\sum_{i=1}^{N} f_i d_i = \frac{N\langle fd\rangle}{FB} \tag{7}$$

Naturally, x is limited to unity. On the other hand, depolarization ratio is controlled by the number of plates appearing in the light path and their optical anisotropy. The average number of plates appearing in the light path in series is

$$E = \langle n\rangle = \frac{1}{F}\sum_{i=1}^{N} f_i = \frac{N\langle f\rangle}{F} \tag{8}$$

E is the sum of projections of all plates on the base of the sample divided by surface area of the sample, F. Comparison of Eqs. (7) and (8) yields relation between crystallinity, x, and the parameter E

$$E = x\frac{B\langle f\rangle}{\langle fd\rangle} = B\frac{x}{\langle d\rangle}\Xi[w(f,d)] \tag{9}$$

Ξ is a functional of the plate size distribution function, $w(f,d)$ which reduces to unity when the distribution $w(f,d)$ is infinitely narrow.

The probability $P(n)$ that there appear exactly n plates in the light path, can be obtained from the Poisson distribution

$$P(n) = \text{const.}\frac{E^n}{n!} \tag{10}$$

The above distribution normalized in the final range $0 \le n \le E_{\max}$ reads

$$P(n) = \frac{E^n}{n!}\left(\sum_{k=0}^{E_{\max}}\frac{E^k}{k!}\right)^{-1} \tag{11}$$

but $E_{\max}$ being very large (cf. Fig. 5 below), Eq. (11) can be replaced with standard Poisson distribution normalized in the infinite range of n

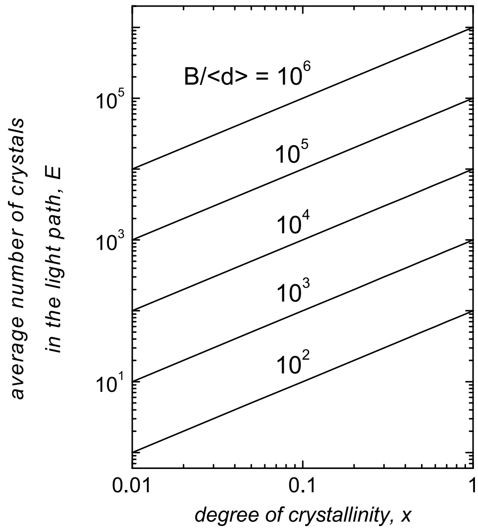

Fig. 5. Average number of crystals in the light path, E, vs. degree of crystallinity, x. Sample-to-crystal thickness ratio, $B/\langle d\rangle$ indicated.

$$P(n) \cong \frac{e^{-E}E^n}{n!} \tag{12}$$

3.2. Depolarization of light in a stack of parallel plates

General expressions for light intensity transmitted through a stack of exactly n birefringent elements has been derived by Hsü, Richartz and Liang [11]. Their result averaged over orientation angles α_i and retardation functions D_i yields [15]

$$\begin{aligned}\left\langle\frac{I_n(\varphi)}{I_0 - I_S}\right\rangle &= \cos^2\varphi \\ &\quad -\frac{1}{2}\cos 2\varphi\left[2\binom{n}{1}DS - 4\binom{n}{2}D^2S^2\right. \\ &\quad \left. + 8\binom{n}{3}D^3S^3 - \ldots + (-2)^n\binom{n}{n}D^nS^n\right]\end{aligned} \tag{13}$$

where $S = \langle\sin^2 2\alpha_i\rangle$ and $D = \langle D_i\rangle$. It is evident that Eq. (13) can be presented in a compact form

$$\begin{aligned}\left\langle\frac{I_n(\varphi)}{I_0 - I_S}\right\rangle &= \cos^2\varphi \\ &\quad -\frac{1}{2}\cos 2\varphi\sum_{k=1}^{n}(-1)^{k-1}\binom{n}{k}(2DS)^k \\ &= \frac{1}{2} + \frac{1}{2}\cos 2\varphi(1 - 2DS)^n\end{aligned} \tag{14}$$

The intensity of light transmitted through the polycrystalline sample, $I_{\text{trans}}(\phi)$ is a sum of average contributions, $\langle I_n(\phi)\rangle$, weighted with the appropriate probabilities $P(n)$

$$\frac{I_{\mathrm{trans}}(\varphi)}{I_0 - I_{\mathrm{S}}} = \sum_{n=0}^{\infty}\left\langle\frac{I_n(\varphi)}{I_0 - I_{\mathrm{S}}}\right\rangle P(n) = \mathrm{e}^{-E}\left[\cos^2\varphi + \left\langle\frac{I_1(\varphi)}{I_0 - I_{\mathrm{S}}}\right\rangle\frac{E}{1!} + \left\langle\frac{I_2(\varphi)}{I_0 - I_{\mathrm{S}}}\right\rangle\frac{E^2}{2!} + \dots\right] \tag{15}$$

Combination of Eqs. (14) and (15) yields function of the single variable, (DES)

$$\frac{I_{\mathrm{trans}}(\varphi)}{I_0 - I_{\mathrm{S}}} = \mathrm{e}^{-E}\sum_{n=0}^{\infty}\frac{E^n}{n!}\left[\frac{1}{2} + \frac{1}{2}\cos 2\varphi(1 - 2DS)^n\right] = \cos^2\varphi - \frac{1}{2}\cos 2\varphi[1 - \mathrm{e}^{-2DES}] \tag{16}$$

In the case of random crystal orientation ($S = 1/2$)

$$\frac{I_{\mathrm{trans}}(\varphi)}{I_0 - I_{\mathrm{S}}} = \cos^2\varphi - \frac{1}{2}\cos 2\varphi[1 - \mathrm{e}^{-DE}] = \cos^2\varphi - \frac{1}{2}\cos 2\varphi\left[DE - \frac{1}{2}(DE)^2 + \frac{1}{6}(DE)^3 - \dots\right] = \cos^2\varphi - \frac{1}{2}\cos 2\varphi\Phi(DE) \tag{17}$$

In all experimental studies [2–10,16] only the first, linear term of the expansion (17) was used

$$\frac{I_{\mathrm{trans}}(\varphi)}{I_0 - I_{\mathrm{S}}} \cong \cos^2\varphi - \frac{1}{2}\cos 2\varphi DE \tag{18}$$

Eq. (18) is equivalent to single crystal formula (Eq. (1)) averaged over distribution of orientation angles, α and retardation functions D.

It is evident that neither small surface concentration of crystals E (claimed in Ref. [13]) nor small optical retardation of a single plate, D (Ref. [14]) does provide correct criterion of linearization. It is the combined variable, (DE), which should be small to justify replacement of the non-linear function Φ (Eq. (17)) with the single-crystal formula, Eq. (18). Before analyzing the range of conditions in which linear approximation of the function $\Phi(DE)$ is acceptable, we will briefly review another model [14] claimed to describe multiple depolarization in a concentrated system of thin plates.

Binsbergen [14] considered a stack of k thin, birefringent plates in the light path. Optical retardation of each plate was assumed small ($\delta_i \ll 1$), and orientation distribution of plates within the stack-random. Each k-element stack was treated as a single birefringent object

$$\left\langle\sin^2 2\alpha\,\sin^2\frac{\delta}{2}\right\rangle_{k-\mathrm{stack}} = \left\langle\left[\sum_{i=1}^{k}\sin 2\alpha_i\,\sin\frac{\delta_i}{2}\right]^2\right\rangle = \sum_{i=1}^{k}\left(\langle\sin^2 2\alpha_i\rangle\left\langle\sin^2\frac{\delta_i}{2}\right\rangle\right) \tag{19}$$

which, after averaging over random orientation distribution $W(\alpha_i) = \mathrm{const.}$ yields

$$\left(\frac{I_k(\varphi = 1/2\pi)}{I_0 - I_{\mathrm{S}}}\right)_{k-\mathrm{stack}} = \langle\sin^2 2\alpha\rangle kD \to 1/2kD \tag{20}$$

In the process of averaging, mixed sine products $\langle\sin 2\alpha_i$ - $\sin 2\alpha_j\rangle$ in Eq. (19) disappear for symmetry reasons. After summation with the Poisson distribution the stack model reduces to the first term of the expanded function $\Phi(DE)$

$$\frac{I_\perp}{I_0 - I_{\mathrm{S}}} = \sum_{k=0}^{\infty}\left\langle\frac{I_k(\varphi = 1/2\pi)}{I_0 - I_{\mathrm{S}}}\right\rangle P(k) = 1/2D\sum_{k=0}^{\infty}kP(k) = 1/2\langle k\rangle D \equiv 1/2DE \tag{21}$$

Can the stack of k thin plates be treated as a single object? Yes, provided that what is small, is average retardation of the entire stack, (kD), rather than that of the single plate, D. Binsbergen model is equivalent to the first term of the general expression (Eq. (17)), or Eq. (18). Binsbergen and de Lange [16] who tested their model numerically, considered relatively small number of plates within a stack (up to $k = 20$) and assumed rather low intrinsic birefringence ($\Delta n < 0.007$) which naturally did fit the linear range. We will show that the number of plates within the stack may be as high as 10^3–10^5 and well outside the linear region.

4. Polynomial approximation of the depolarization function $\Phi(DE)$

We will analyze approximation of the depolarization function $\Phi(DE)$ using m-degree polynomials, Φ_m

$$\Phi(DE) = \frac{1}{2}[1 - \mathrm{e}^{-DE}] \tag{22}$$

$$\Phi_m(DE) = \frac{1}{2}DE - \frac{1}{4}(DE)^2 + \frac{1}{12}(DE)^3 - \dots + \frac{(-1)^{m-1}(DE)^m}{2m!}$$

We are looking for the range of the variable DE in which truncation of the infinite series on the m-th term ($m = 2, 3, \dots$) creates error smaller than 1%. Critical DE values, C_m found from the condition

$$\left|\frac{\Phi(C_m) - \Phi_m(C_m)}{\Phi(C_m)}\right| = 0.01 \qquad (23)$$

are listed in Table 1.

C_1 provides upper limit of the variable DE when single-crystal formula (linear approximation, $m=1$) can be applied. With $C_1=0.02$ up to 2000 plates in stack can be accommodated provided that retardation function of a single plate, D, does not exceed 10^{-5}. Alternatively, when average retardation function is $D=0.1$, linear approximation requires that the system is very dilute ($E<0.2$). Two-term approximation, Φ_2, can accommodate systems characterized by $DE \leq 0.238$, etc.

We will analyze the range of the parameters E and D in polycrystalline systems. For this purpose we will assume infinitely narrow distribution of crystal sizes, $\Xi=1$ leading to

$$\Xi[w(f,d)] = 1 \qquad (24)$$

$$E \cong B\frac{x}{\langle d\rangle}$$

The average number of crystal plates in the light path, E, is roughly proportional to the degree of crystallinity, x, sample thickness, B, and inversely proportional to average crystal thickness, $\langle d\rangle$. Thickness of polymer samples used for optical measurements lies within the range of 10–200 μm and the average thickness of polymer crystals ranges from 1 to 100 nm. Consequently, the ratio $B/\langle d\rangle$ appearing in the approximate formula (24) varies from 10^2 to 2×10^5.

Fig. 5 presents E calculated from the approximate formula Eq. (24) plotted vs. degree of crystallinity, x, at constant thickness ratios. It is evident that, except for very low crystallinities ($x<0.01$) and/or extremely thin samples ($B/\langle d\rangle<100$) there appear in the light path many crystals in series.

The effect of large E may be compensated by small values of optical retardation, D.

To estimate optical retardation function for a single plate, we assume wavelength $\lambda=650$ nm and birefringence ranging from $\Delta n=0.02$ to 0.70. This covers majority of polymers, from cellulose acetate ($\Delta n=0.02$), through polyethylene ($\Delta n=0.044$) [17] and polyethylene terephthalate ($\Delta n=0.118$) [18] up to aramide ($\Delta n=0.662$) [17]. Fig. 6 presents average retardation function, D, as a function of crystal thickness, $\langle d\rangle$. The range of $\langle d\rangle$ considered starts with 1 nm (crystallites with a few lattice distances) and reaches 100 nm (polymer crystals slowly grown under high pressure [19]). It is evident that in the entire range of $\langle d\rangle$, retardation function is much smaller than unity, which justifies approximation of the retardation function D suggested by Binsbergen [14]

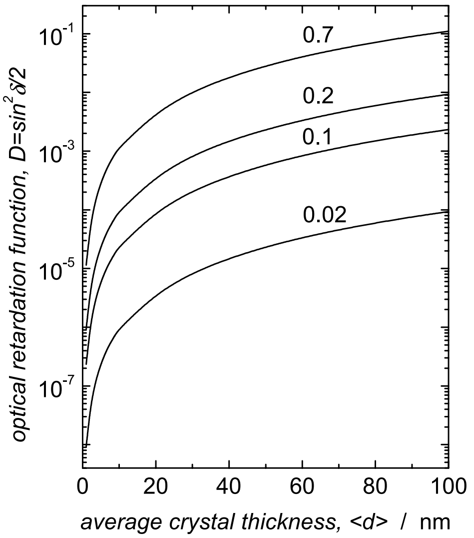

Fig. 6. Optical retardation function, $D=\sin^2((1/2)\delta)$, vs. average crystal thickness, $\langle d\rangle$. Birefringence, Δn, indicated. Wavelength, $\lambda=650$ nm.

$$D \cong \frac{\langle\delta^2\rangle}{4} = \left(\frac{\pi\Delta n}{\lambda}\right)^2\langle d^2\rangle = \left(\frac{\pi\Delta n}{\lambda}\right)^2\langle d\rangle^2\Theta[w(d,f)] \qquad (25)$$

where Θ is another functional of the size distribution function, w. Using the approximation (25) the variable DE

$$DE \cong B\left(\frac{\pi\Delta n}{\lambda}\right)^2\left(\frac{x\langle f\rangle\langle d^2\rangle}{\langle fd\rangle}\right)$$

$$= B\left(\frac{\pi\Delta n}{\lambda}\right)^2 x\langle d\rangle\Xi(w)\Theta(w) \qquad (26)$$

appears to be proportional to the product of crystallinity and a functional of crystal size distribution, $w(f,d)$. For very narrow distribution ($\Xi=\Theta=1$) DE reduces to

$$DE \cong B\left(\frac{\pi\Delta n}{\lambda}\right)^2 x\langle d\rangle \qquad (27)$$

Approximations Eqs. (24) and (27) are being used as a rough, but transparent estimate of the relationship between the depolarized light intensity and structure of the system. Fig. 7 presents values of DE estimated from Eq. (27) and plotted vs. degree of crystallinity, x, for various products of sample and crystal thickness, ($B\langle d\rangle$).

For reasonably thin crystals ($\langle d\rangle=1$–10 nm) and thin samples ($B<100$ μm) the variable DE lies in the range of 0.002–0.2. At the lower DE end application of the linear (single-crystal formula), or the Binsbergen stack model

Table 1
Critical values of the variable DE

Number of terms, m	1	2	3	4	5
$C_m=(DE)_{\text{crit}}$	0.020	0.238	0.588	0.974	1.364

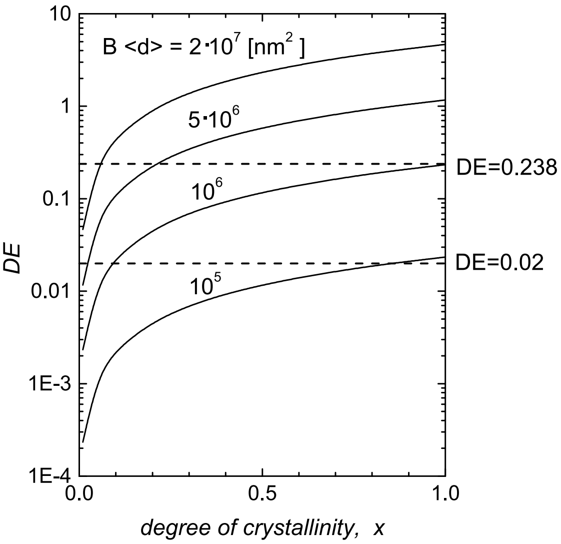

Fig. 7. The combined variable *DE* vs. degree of crystallinity, *x*. The product of crystal and sample thickness, ($\langle d\rangle B$) (nm^2), indicated. $\Delta n = 0.1$, $\lambda = 650$ nm.

seems justified. On the other hand, crystals with average thickness 100 nm even in reasonably thin samples, $B = 20$ μm, yield *DE* values too high for linear approximation, which calls for using several terms in Eq. (20). When the subject of interest is onset of crystallization (i.e. crystallinity is smaller than 0.05), *DE* does not exceed 0.02 and linear approximation can still be used. Application of thinner samples (smaller *B*) expands the range of admissible characteristics $\langle d\rangle$ and *x*.

Linearity of depolarization intensity vs. variable *DE* can also be checked experimentally. Since *E* is proportional to *B*, doubling film thickness should result in doubling depolarization ratio if the argument *DE* lies in the linear range

$$B \to 2B,\ E \to 2E; \qquad \frac{I_\perp}{I_0 - I_S}(2DE) = 2\frac{I_\perp}{I_0 - I_S}(DE) \tag{28}$$

Whenever the above test fails, more terms of the expansion should be used. Ding and Spruiell [6,8] demonstrated proportionality of depolarization intensity to sample thickness, *B*, in agreement with the condition (28).

5. Depolarization ratio and the degree of crystallinity

In the linear approximation of the theory, combination of Eqs. (21) and (27) yields approximate relationship between depolarization ratio and the degree of crystallinity

$$\frac{I_\perp}{I_0 - I_S} \cong \frac{1}{2}\left(\frac{\pi\Delta n}{\lambda}\right)^2 xB\langle d\rangle \tag{29}$$

It is evident that depolarization ratio is proportional to the product of crystallinity and crystal thickness, rather than crystallinity alone. Both characteristics may change independently in the course of crystallization.

Consider a process of crystallization followed by measurement of depolarization ratio. Relative variation of crystallinity, $\dot{x}/x = \mathrm{d}\ln x/\mathrm{d}t$, may result from different mechanisms:

$$\frac{\mathrm{d}\ln x}{\mathrm{d}t} = \frac{\mathrm{d}\ln N}{\mathrm{d}t} + \frac{\mathrm{d}\ln\langle fd\rangle}{\mathrm{d}t} \tag{30}$$

Nucleation changes number of crystals, *N*. Lateral and thickness growth rates affect average crystal volume, $\langle fd\rangle$. At the same time, relative variation of depolarized light intensity depends on the number of crystal plates, *N*, their average surface, $\langle f\rangle$, and average square of thickness, $\langle d^2\rangle$

$$\frac{\mathrm{d}\ln[I_\perp/(I_0 - I_S)]}{\mathrm{d}t} = \frac{\mathrm{d}\ln N}{\mathrm{d}t} + \frac{\mathrm{d}\ln\langle f\rangle}{\mathrm{d}t} + \frac{\mathrm{d}\ln\langle d^2\rangle}{\mathrm{d}t} \tag{31}$$

Combination of Eqs. (30) and (31) yields relationship between the relative rates of depolarization and crystallization

$$\begin{aligned}\frac{\mathrm{d}\ln[I_\perp/(I_0 - I_S)]}{\mathrm{d}t} &= \frac{\mathrm{d}\ln x}{\mathrm{d}t} + \frac{\mathrm{d}\ln\langle f\rangle}{\mathrm{d}t} + \frac{\mathrm{d}\ln\langle d^2\rangle}{\mathrm{d}t} - \frac{\mathrm{d}\ln\langle fd\rangle}{\mathrm{d}t} \\ &= \frac{\mathrm{d}\ln x}{\mathrm{d}t} + \frac{\mathrm{d}\ln\langle d\rangle}{\mathrm{d}t} + \frac{\mathrm{d}\ln(\Xi\Theta)}{\mathrm{d}t}\end{aligned} \tag{32}$$

is controlled not only by the overall degree of crystallinity, *x*, but also on the distribution of crystal sizes (functionals Ξ and Θ). With the narrow distribution approximation, $\Xi = \Theta = 1$, Eq. (32) reduces to

$$\frac{\mathrm{d}\ln[I_\perp/(I_0 - I_S)]}{\mathrm{d}t} \cong \frac{\mathrm{d}\ln x}{\mathrm{d}t} + \frac{\mathrm{d}\ln\langle d\rangle}{\mathrm{d}t} \tag{33}$$

Relative depolarization rate is equal to the sum of relative crystallization rate and relative rate of variation of crystal thickness.

The fact that depolarized light intensity is proportional to the product of crystallinity and crystal thickness, rather then crystallinity alone, has been noticed by Binsbergen [14]. Assuming predetermined nucleation ($\dot{N} = 0$) and identical linear growth rate in all crystal dimensions

$$\langle \mathrm{d}(t)\rangle \propto \dot{R}t; \quad \langle f(t)\rangle \propto (\dot{R}t)^2; \quad \dot{R} = \text{const.} \tag{34}$$

Binsbergen arrived at the degree of crystallinity, *x*, proportional to the third power of time and depolarization intensity proportional to the fourth power, in accordance with Eq. (33). Binsbergen tried to explain this discrepancy by assuming constant plate thickness ($\mathrm{d}\langle d\rangle/\mathrm{d}t = 0$) and/or change of the intrinsic birefringence in the course of crystallization.

6. Some special cases

We will discuss development of depolarization ratio and crystallinity in special conditions. For the sake of simplicity our discussion will be based on the narrow distribution of crystal dimensions, leading to approximation Eq. (33).

(i) Crystal thickness does not change in time. Crystallization rate is controlled by nucleation and lateral crystal growth $\langle \dot{f} \rangle$. Consequently, relative crystallization rate is equal to relative variation of depolarization ratio

$$\frac{\mathrm{d}\langle d \rangle}{\mathrm{d}t} = 0 \Rightarrow \frac{\mathrm{d}\ln[I_\perp/(I_0 - I_\mathrm{S})]}{\mathrm{d}t} = \frac{\mathrm{d}\ln x}{\mathrm{d}t} \tag{35}$$

(ii) The number of crystals is constant and their linear growth rate is the same in all directions

$$\left(\dot{N} = 0 \wedge \frac{\mathrm{d}\ln\langle f \rangle}{\mathrm{d}t} = 2\frac{\mathrm{d}\ln\langle d \rangle}{\mathrm{d}t}\right) \Rightarrow \frac{\mathrm{d}\ln[I_\perp/(I_0 - I_\mathrm{S})]}{\mathrm{d}t} = \frac{4}{3}\frac{\mathrm{d}\ln x}{\mathrm{d}t} \tag{36}$$

which yields situation described by Binsbergen [14,16].

(iii) The number of crystals, N, and their lateral dimensions $\langle f \rangle$ are constants. Crystallization rate and variation of depolarization intensity are both controlled by the variation of thickness.

$$(\dot{N} = \langle \dot{f} \rangle = 0) \Rightarrow \frac{\mathrm{d}\ln[I_\perp/(I_0 - I_\mathrm{S})]}{\mathrm{d}t} = 2\frac{\mathrm{d}\ln x}{\mathrm{d}t} \tag{37}$$

Unfortunately, there is no way to predict a priori which case we are actually facing. To quantitatively interpret light depolarization intensity in terms of crystallinity, an independent measurement of crystal thickness (or optical retardation function, D) is required.

7. Discussion

Theoretical analysis reveals two features of light depolarization technique (LDT) when applied to crystallization studies. Unlike calorimetry, dilatometry, or X-ray diffraction, light depolarization alone does not provide a direct measure of the degree of crystallinity.

Depolarization ratio is a non-linear function of the single variable DE

$$\frac{I_\perp}{I_0 - I_\mathrm{S}} = \frac{1}{2}[1 - \exp(-DE)] = \frac{1}{2}DE - \frac{1}{4}(DE)^2 + \dots \tag{38}$$

proportional to the degree of crystallinity, x, and a functional of the distribution of crystal plate dimensions, d and f

$$DE = \ln\left[\frac{I_\parallel + I_\perp}{I_\parallel - I_\perp}\right] = B\left\langle \sin^2\left(\frac{\pi\Delta n d}{\lambda}\right)\right\rangle \frac{x\langle f \rangle}{\langle fd \rangle} \tag{39}$$

which, in the approximation of thin crystals (Eq. (25)) and narrow dimension distribution (Eq. (27)) reduces to the product of crystallinity and average crystal thickness

$$DE \cong B\left(\frac{\pi\Delta n}{\lambda}\right)^2 x\langle d \rangle \tag{40}$$

Depolarization experiments yield the variable DE. Determination of the degree of crystallinity, x, requires decoupling of DE and independent determination of the average crystal thickness, $\langle d \rangle$.

An alternative to decoupling is resignation from interpreting light depolarization data as a conventional measure of the degree of crystallinity, quantitatively comparable with calorimetric, density or X-ray diffraction data. Assuming directly observable quantity DE (Eq. (39)) as a crystallization characteristic per se, comparative information about structure and structural changes can be obtained. The variable DE could be used for correlation with other physical properties. For example light depolarization data converted into the variable DE could be correlated with rheological characteristics of a polymer melt and might provide valuable information about structural effects in polymer processing.

An important outcome of our analysis is closed-form, non-linear expression for depolarization ratio valid for the entire range of the argument DE which should replace the single-crystal formula (Eqs. (1) and (21)). All experiments involving LDT took only first, linear term in the power expansion of the general intensity function. We have discussed conditions where such an approximation can be used and demonstrated the necessity of using the non-linear formula.

In spite of the controversial interpretation, further development of light depolarization technique seems to be justified, especially so, when polycrystalline structure is changing too rapidly to be followed by other experimental techniques. LDT may appear to be the only method of studying rapid crystallization above 1 kHz sampling frequency. This concerns non-isothermal processes with fast cooling and/or orientation-induced crystallization. The present model does not describe oriented systems. It will be extended to accommodate inclined crystal plates and non-random orientation distribution of their optical axes.

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