Materials Science-Poland, Vol. 24, No. 2/2, 2006

Interpretation of light depolarization data in terms of polymer crystallinity

A. ZIABICKI[*], B. MISZTAL-FARAJ

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

Theoretical principles of light depolarization technique (LDT) have been analysed. It has been shown that the traditional way of interpretation assuming a linear relationship between depolarization ratio, average optical retardation of a single birefringent plate, D, and volume fraction of crystalline material (crystallinity) is incorrect. An exact non-linear relationship between depolarization ratio and the product DE (E is average number of plates in the light path) has been derived. The parameter DE has been shown to be proportional not to the crystallinity alone but to the product of crystallinity and average crystal thickness, ($x\langle d\rangle$). A method of decoupling light depolarization data, based on measurements at different sample orientations and different wavelengths, has been outlined.

Key words: *optical retardation; theory of compensators; depolarization; depolarization ratio; polymer crystallization; degree of crystallinity; degree of crystal orientation*

1. Introduction

Physical properties of polymer materials are very sensitive to their supramolecular structure. Two chemically identical polymer samples can exhibit very different properties depending on the fraction of crystalline phase, composition of crystal modifications, etc. Different crystallographic structures and textures can be developed by varying processing conditions [1]. Variation of temperature, cooling rate, stress or flow fields can result in a change of crystallization rate by many orders of magnitude affecting final structure and properties of the material.

Traditional techniques used for measuring the polymer crystallinity – DSC, dilatometry, WAXS – are all limited to slow processes (sampling frequency less than 1 Hz), whereas in industrial conditions the crystallization proceeds in a fraction of a second, when a stress or flow is applied. When cooling rates are very high as is the

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[*] Corresponding author, e-mail: andrzej.ziabicki@ippt.gov.pl

case in fibre spinning or film formation, the entire process is completed in milliseconds. Application of an optical method seems a natural solution. Light depolarization technique (LDT) has been introduced for studying crystallization and melting of polymers by Fischer and Schram [2] and Magill [3–6] in late fifties and sixties. In spite of its controversial interpretation [7–9], the method is widely used at present [10–13]. An experimental setup for LDT measurements is presented in Figure 1. A parallel light beam is passed through a polarizer (P), film sample containing anisotropic crystals (S), analyser (A) and its intensity is measured by a detector (D).

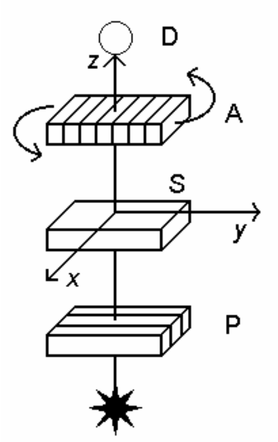

Fig. 1. Light depolarization setup:
P – polarizer, S – sample, A – analyser, D – detector

A theoretical basis for interpretation of light intensity data is based on the Fresnel formula [14] describing intensity of polarized light transmitted through an optically retardant (birefringent) object

$$\frac{I(\varphi)}{I_0} = \cos^2\varphi + \sin 2\alpha \sin 2(\varphi - \alpha)\, D \tag{1}$$

where I_0 is incident intensity, φ – the angle between optical axes of the polarizer and analyser, $D = \sin^2(\delta/2)$ – optical retardation function, and α – the angle between the optical axis of the birefringent plate and the polarizer. The relative retardation is proportional to the plate thickness, d, and birefringence, Δn, and inversely proportional to the wavelength, λ

$$\delta = \frac{2\pi\Delta n\, d}{\lambda} \tag{2}$$

The presence of a retardant element converts a linearly polarized light beam into elliptically polarized one. A quantitative characterization of the depolarization effect requires that scattering and absorption effects leading to intensity loss, I_S, be taken into account. This can be done by replacing the incident intensity I_0 in Eq. (1) by a sum of intensities at parallel and crossed polarizers [2]

$$I_0 \quad \rightarrow \quad I_0 - I_S = I(\varphi = \frac{1}{2}\pi) + I(\varphi = 0) = I_\perp + I_\parallel \tag{3}$$

The ratio of intensity transmitted through the system with crossed polarizers, $I_\perp$, to the incident intensity corrected for scattering, is a quantitative measure of the depolarization effect

$$\frac{2I_\perp}{I_\perp + I_\parallel} = 2\sin^2 2\alpha\, D \in (0,1) \tag{4}$$

In the absence of any retardant elements between the polarizer and analyser no light is transmitted through crossed polarizers

$$2\sin^2 2\alpha\, D = 0: \quad \frac{2I_\perp}{I_\perp + I_\parallel} = 0 \tag{5}$$

while an anisotropic element with maximum retardation effect yields a complete depolarization, i.e. a conversion into the state of circular polarization

$$2\sin^2 2\alpha\, D \rightarrow 1: \quad \frac{2I_\perp}{I_\perp + I_\parallel} \rightarrow 1 \tag{6}$$

The single-plate formula (Eq. (1)), yielding linear relation between the plate retardation and the depolarization ratio, has been used in experimental studies [2–6, 9–13]. The depolarization ratio and the average plate retardation have been (explicitly or implicitly) identified with the degree of crystallinity, x

$$\frac{2I_\perp}{I_\perp + I_\parallel} = \text{const}D = \text{const}'x \tag{7}$$

In real crystallizing systems, there appear many birefringent plates. It is natural to expect that the higher degree of crystallinity the higher will be the degree of depolarization. This does not imply a linear relationship between the depolarization ratio and the retardation function D. A proportionality between these two parameters seems reasonable only in very dilute systems in which the light beam does not meet more than one plate on its path (Fig. 2). Analysing structure of crystallizing polymers [15], we found the number of plates in the light path to be rather high (10^2–10^4) making inapplicable the single-plate formula (Eq. (1)). One has to analyse optical behaviour of many-plate “stacks” appearing in the light path (Fig. 3), the intensity of depolarized light being affected by optical interactions within the stack.

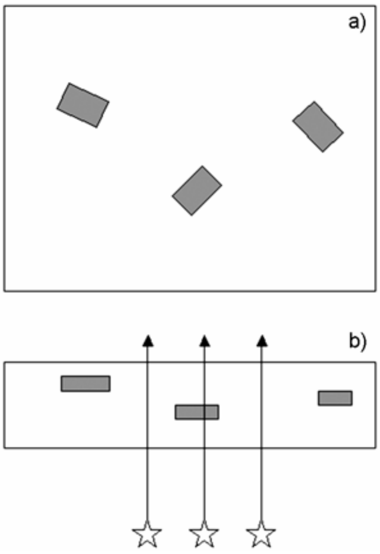

Fig. 2. Distribution of birefringent plates in a dilute system: a) projection on the *XY* plane normal to the light beam, b) projection on the *ZX* plane

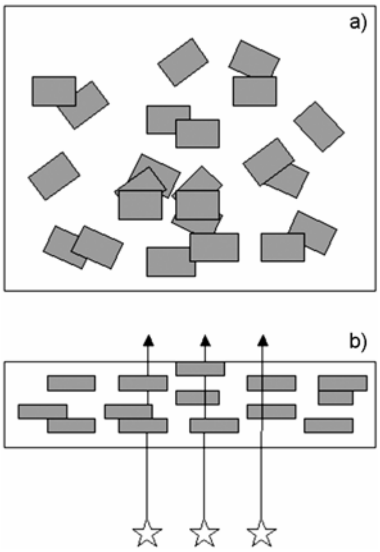

Fig. 3. Distribution of birefringent plates in a concentrated system: a) projection on the *XY* plane normal to the light beam, b) projection on the *ZX* plane

There is also no obvious reason to assume that relation between the retardation and crystallinity should be unique or (the more so) linear. A more thorough theoretical analysis is needed.

2. Depolarization of light on a statistical system of birefringent plates

Optical behaviour of a stack of parallel birefringent elements is described by the theory of compensators [16–18]. Hsü, Richartz and Liang [17] arrived at the expression of light intensity transmitted through a stack of exactly *n* birefringent elements

$$\frac{I_n(\varphi)}{I_{\parallel}+I_{\perp}} = F\left[D_1, D_2, ..., D_n, \beta_1, \beta_2, ..., \beta_n\right] \tag{8}$$

where D_1, D_2, ..., D_n are optical retardation functions of individual elements and β_1, β_2,..., β_n – orientations of optical axes with respect to the sample axis.

In the situation of interest for polymer crystallization, the number of plates appearing serially in a stack is large which justifies averaging over the variables D_i and β_i. The averaging described in detail elsewhere [19] takes into account two properties of the function $F(D_i, \beta_i)$: linearity with respect to each variable D_i, and symmetry of the orientation distribution, eliminating all odd moments of $\sin 2\beta_i$. Consequently, the average intensity ratio reduces to a function of two moments of the function $F(D_i, \beta_i)$

$$\left\langle \frac{I_n}{I_\parallel + I_\perp}(\varphi,\vartheta)\right\rangle = \Phi\left[D,\, S;\, \varphi, \vartheta\right] \tag{9}$$

$$D = < D_i >; \quad S = < \sin^2 2\beta_i > \tag{10}$$

where φ is an angle between the polarizer and analyser, and ϑ – angle between the sample axis and the polarizer. It can be shown [19] that averaging of the expressions given by Hsü, Richartz and Liang [17] yields

$$\begin{aligned}\left\langle \frac{I_n}{I_\parallel + I_\perp}(\varphi;\vartheta)\right\rangle &= \cos^2\varphi - \frac{1}{2}\cos 2\varphi + ½\cos 2\varphi\left(1-2DS\right)^n \\ &\quad -\frac{1}{2}\sin 2\vartheta \sin 2(\vartheta-\varphi)\left[\left(1-2DS\right)^n - \left(1-2D+2DS\right)^n\right]\end{aligned} \tag{11}$$

It is evident that the average intensity transmitted through an *s*-plate stack is an *n*-degree polynomial of the two averaged material variables – *D* and *S*. In the field of view, many stacks appear in parallel. We assume that the distribution of stack sizes is random and can be described with the Poisson distribution

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

where *n* is the number of plates in the light path.

The intensity of light transmitted through a statistical system of many parallel stacks is given by the equation [19]

$$\begin{aligned}\left\langle \frac{I_{\mathrm{trans}}(\varphi;\vartheta)}{I_\parallel + I_\perp}\right\rangle &= \sum_{n=0}^{\infty} P(n)\left\langle \frac{I_n(\varphi;\vartheta)}{I_\parallel + I_\perp}\right\rangle = \cos^2\varphi - \frac{1}{2}\cos 2\varphi + \frac{1}{2}\cos 2\varphi\, \mathrm{e}^{-2DES} \\ &\quad -\frac{1}{2}\sin 2\vartheta \sin 2(\vartheta-\varphi)\left[\mathrm{e}^{-2DES} - \mathrm{e}^{-2DE(1-S)}\right]\left\langle \frac{2I_\perp}{I_\parallel + I_\perp}\right\rangle \\ &= (1-\mathrm{e}^{-2DES}) - \sin^2 2\vartheta\left[\mathrm{e}^{-2DES} - \mathrm{e}^{-2DE(1-S)}\right]\end{aligned} \tag{13}$$

In the case of a random distribution of plate orientations, the transmitted intensity reduces to a function of a single variable *DE*

$$\left\langle \frac{I_{\mathrm{trans}}(\varphi)}{I_\parallel + I_\perp}\right\rangle = \cos^2\varphi - \frac{1}{2}\cos 2\varphi\left[1-\mathrm{e}^{-DE}\right], \qquad \left\langle \frac{2I_\perp}{I_\parallel + I_\perp}\right\rangle = 1-\mathrm{e}^{-DE} \tag{14}$$

In the range of infinitely small values of *DE*, the single-plate (linear) formula is returned

$$DE \to 0: \quad \left\langle \frac{I_{\text{trans}}(\varphi;\vartheta)}{I_{\parallel}+I_{\perp}} \right\rangle \to \cos^2\varphi - \frac{1}{2}\cos 2\varphi\, DE, \qquad \left\langle \frac{2I_{\perp}}{I_{\parallel}+I_{\perp}} \right\rangle \to DE \tag{15}$$

On the other hand, in the range of very large *DE*, the depolarization ratio asymptotically approaches unity

$$DE \to \infty: \quad \left\langle \frac{I_{\text{trans}}(\varphi;\vartheta)}{I_{\parallel}+I_{\perp}} \right\rangle \to \cos^2\varphi - \frac{1}{2}\cos 2\varphi, \qquad \left\langle \frac{2I_{\perp}}{I_{\parallel}+I_{\perp}} \right\rangle \to 1 \tag{16}$$

which corresponds to a complete depolarization of the transmitted light (cf. Fig. 4). Obviously, depolarization ratios larger than unity lack physical sense.

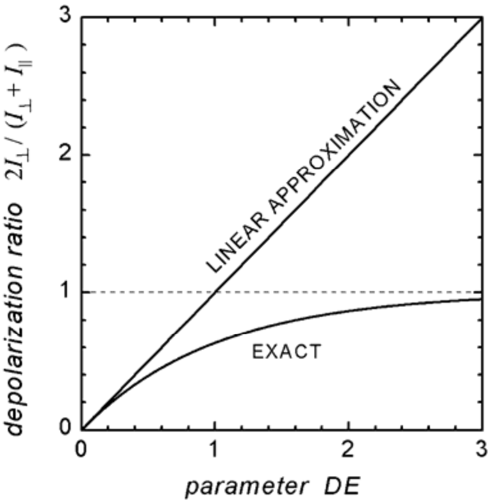

Fig. 4. Depolarization ratio 2 $I_{\perp}/(I_{\perp}+I_{\parallel})$ calculated from Eq. (14). Linear approximation corresponds to single-plate formula

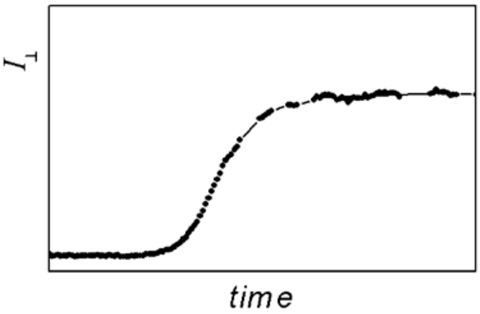

Fig. 5. Light intensity for crystallizing polyethylene transmitted through crossed polarizers, $I_{\perp}$

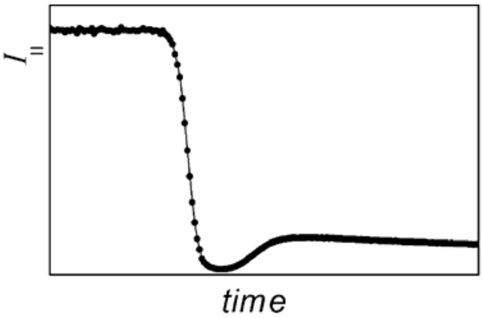

Fig. 6. Light intensity for crystallizing polyethylene transmitted through parallel polarizers, $I_{\parallel}$

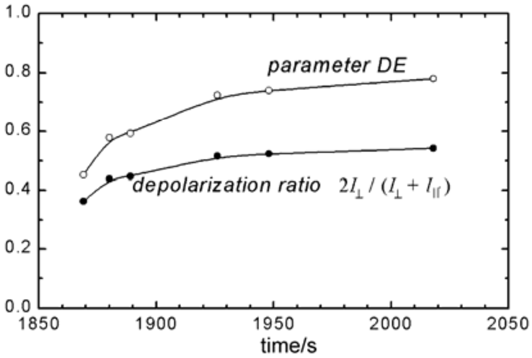

Fig. 7. Depolarization ratio 2 $I_\perp/(I_\perp + I_\parallel)$ and the variable *DE* for crystallizing polyethylene obtained from intensity measurements switched from $\varphi = 0$ to $\varphi = \pi/2$ (Fig. 4)

To check the magnitude of depolarization effects during crystallization of polyethylene, we recorded intensities of light transmitted through crossed ($I_\perp$, Fig. 5) and parallel polarizers ($I_\parallel$, Fig. 6). The depolarization ratio, $2I_\perp/(I_\perp + I_\parallel)$ was calculated from a separate experiment in which the analyser was switched from $\varphi = 0$ to $\varphi = \pi/2$ and back (Fig. 7). The intensity of light transmitted through crossed polarizers, $I_\perp$, monotonically increases with crystallization time while the parallel component, $I_\parallel$, decreases, reaches a minimum and then increases. A similar behaviour of the total transmitted intensity, I_0, observed by Ding and Spruiell [11] seems to be result of scattering on isotropic objects formed at the beginning of crystallization. The depolarization effect corrected for scattering, $2I_\perp/(I_\perp + I_\parallel)$, monotonically increases with time, its magnitude extending far beyond the linear region (*DE* = 0.4–0.8).

3. Degree of crystallinity

To analyse the relationship between the depolarization ratio and crystallinity, let us consider a plane-parallel sample of thickness *B* and surface area *F*, containing *N* birefringent crystal plates. The face area of a single plate is f_i, and its thickness – d_i. The volume fraction of the crystalline material, i.e. degree of crystallinity reads

$$x = \frac{\sum_{i=1}^{N} f_i d_i}{FB} = \frac{N < fd >}{FB} \tag{17}$$

and the average number of plates in a stack *E*

$$E = < n > = \frac{\sum_{i=1}^{N} f_i}{F} = \frac{N < f >}{F} \tag{18}$$

representing ratio of the total area of plate faces to the area of the sample, appears as a parameter in the Poisson distribution (Eq. (12)). In contrast to the volume fraction, E can be much larger than unity: many-plate stacks may appear in the light path. At full crystallinity, the maximum number of plates in a stack is equal to the ratio of sample-to-crystal thicknesses

$$E_{\max} = \frac{B}{< d >} >> 1 \tag{19}$$

Comparing Eqs. (17) and (18) one finds relationship between the crystallinity, x, and the parameter E

$$E = \frac{B < f >}{< fd >} x = B \frac{x}{< d >} \Xi \left[w(f,d) \right] \tag{20}$$

where

$$\Xi \left[w(f,d) \right] = \frac{< f >< d >}{< f \cdot d >} \tag{21}$$

is a functional of crystal size distribution function. In the case of a monodisperse distribution, Ξ reduces to unity. Consequently, the light depolarization parameter DE

$$DE = \ln \frac{I_{\parallel} + I_{\perp}}{I_{\parallel} - I_{\perp}} \cong \left(\frac{\pi \, \Delta n < d >}{\lambda} \right)^2 B \frac{x}{< d >} = \text{const } x < d > \tag{22}$$

is proportional to the crystallinity but also to the average plate thickness, <*d*>. The crystallization involves nucleation and growth, crystal growth rates being (in general), different in different crystallographic directions. Thus, the interpretation of light depolarization as a measure of volume fraction of crystalline phase is incorrect. Following the crystallization with LDT is justified only when an independent measurement of the crystal thickness is performed. A possible decoupling procedure will be discussed in Section 6.

4. Degree of crystal orientation, *S*

Basic assumptions underlying the original light depolarization technique required that optical axes of crystal plates be oriented randomly and no axis of the entire system (sample) could be specified. Analysis of systems with a non-random orientation distribution requires a more general description. Orientation of sample axis is defined and the intensity of the transmitted light becomes a function of the orientation of the sample with respect to the polarizer, ϑ (Eqs. (13)). On changing the sample orientation, one can obtain two independent equations for *DE* and *DES*. Putting $\vartheta = 0$ (the sample axis parallel to the polarizer) results in

$$J_0 \equiv \left\langle \frac{2I_\perp(\vartheta=0)}{I_\| + I_\perp} \right\rangle = 1 - \mathrm{e}^{-2DES}, \qquad DES = -\frac{1}{2}\ln\left[1 - \left\langle \frac{2I_\perp(\vartheta=0)}{I_\| + I_\perp} \right\rangle\right] = \frac{1}{2}\ln\frac{1}{1-J_0} \tag{23}$$

J_0 is depolarization ratio identical with that used for a characterization of unoriented systems (Eq. (14)). Another measurement made on the sample oriented at the angle $\vartheta = \pi/4$ with respect to the polarizer yields

$$\begin{aligned} J_{\pi/4} &\equiv \left\langle \frac{2I_\perp(\vartheta=\pi/4)}{I_\| + I_\perp} \right\rangle = 1 - \mathrm{e}^{-2DE(1-S)} \\ DE(1-S) &= -\frac{1}{2}\ln\left[1 - \left\langle \frac{2I_\perp(\vartheta=\pi/4)}{I_\| + I_\perp} \right\rangle\right] = ½\ln\frac{1}{1-J_{\pi/4}} \end{aligned} \tag{24}$$

A combination of Eqs. (23) and (24) yields a partial decoupling of the variable *DES*

$$\begin{aligned} S &\equiv <\sin^2 2\beta> = \frac{\ln(1-J_{\pi/4})}{\ln(1-J_{\pi/4}) + \ln(1-J_0)} \\ DE &= \frac{½\ln\frac{1}{1-J_{\pi/4}}\left[\ln(1-J_{\pi/4}) + \ln(1-J_0)\right]}{\ln(1-J_0)} \end{aligned} \tag{25}$$

and can be used for determining the crystal orientation characteristic, S.

5. Decoupling of the characteristic *DE*. Independent characterization of crystallinity and crystal thickness

We will present the way of decoupling the product *DE* into *D* and *E* based on application of two different wavelengths, λ_1 and λ_2. Consider three depolarization ratios. The first two, $J_0(\lambda_1)$ and $J_{\pi/4}(\lambda_1)$ defined by Eqs. (23), (24) use monochromatic light of the wavelength λ_1. The third one, $J_0(\lambda_2)$, an analogue to $J_0(\lambda_1)$, is measured at a wavelength λ_2 different from λ_1. From Eq. (23) we obtain

$$\begin{aligned} DES(\lambda_1) &= -\frac{1}{2}\ln[1-J_0(\lambda_1)] \\ DES(\lambda_2) &= -\frac{1}{2}\ln[1-J_0(\lambda_2)] \\ \frac{DES(\lambda_1)}{DES(\lambda_2)} &= \frac{D(\lambda_1)}{D(\lambda_2)} = \frac{\ln[1-J_0(\lambda_1)]}{\ln[1-J_0(\lambda_2)]} \end{aligned} \tag{26}$$

Neither the number of plates in the light path, *E*, nor the orientation characteristic, *S*, are affected by the wavelength. What changes is the optical retardation of individual plates, δ_i, and the average retardation characteristic, *D*

$$\delta(\lambda) = 2\Lambda(\lambda)d$$
$$D(\lambda) \equiv < \sin^2 \frac{1}{2}\delta(\lambda) > = < \sin^2(\Lambda d) > \tag{27}$$
$$\Lambda(\lambda) = \frac{\pi\, \Delta n(\lambda)}{\lambda}$$

D can be expanded in power series with respect to the plate thickness, *d*. Averaging of the sine-square function introduces various moments of the plate thickness distribution. For the sake of simplicity, we will consider a monodisperse distribution leading to

$$< d^{2n} > = \left(< d^2 >\right)^n \tag{28}$$

which yields

$$D(\lambda_i) = < \sin^2(\Lambda_i d) > = \mathit{\Delta}^2 - \frac{1}{3}\mathit{\Delta}^4 + \frac{2}{45}\mathit{\Delta}^6 - \frac{1}{315}\mathit{\Delta}^8 + \frac{2}{14175}\mathit{\Delta}^{10} - \ldots$$
$$\mathit{\Delta}^2 \equiv \Lambda_1^2 < d^2 > \tag{29}$$

where $\mathit{\Delta}$ is a reduced plate thickness. Introducing the ratio of optical coefficients

$$\xi \equiv \frac{\Lambda_1^2}{\Lambda_2^2} = \frac{\Lambda^2(\lambda_1)}{\Lambda^2(\lambda_2)}$$

we obtain

$$\frac{D(\lambda_1)}{D(\lambda_2)} = \xi \left[1 - \frac{1-\xi}{3}\mathit{\Delta}^2 + \frac{2\left(1-\xi^2\right) - 5\xi\,(1-\xi)}{45}\mathit{\Delta}^4 \right.$$
$$- \frac{3\left(1-\xi^3\right) - 14\,\xi\left(1-\xi^2\right) + 21\,\xi^2\,(1-\xi)}{945}\mathit{\Delta}^6 \tag{30}$$
$$\left. + \frac{2\left(1-\xi^4\right) - 15\,\xi\left(1-\xi^3\right) + 42\xi^2\left(1-\xi^2\right) - 50\xi^3\,(1-\xi)}{14175}\mathit{\Delta}^8 + \ldots \right]$$

We also introduce a new variable, *Z*, obtainable directly from depolarization ratios measured at two different wavelengths λ_1 and λ_2

$$Z \equiv \frac{3\Lambda_1^2}{\Lambda_1^2 - \Lambda_2^2}\left[1 - \frac{\Lambda_2^2}{\Lambda_1^2}\frac{D(\lambda_1)}{D(\lambda_2)}\right] = \frac{3}{1-\xi}\left[1 - \xi\frac{\ln[1-J_0(\lambda_1)]}{\ln[1-J_0(\lambda_2)]}\right] \tag{31}$$

The details of calculations are described elsewhere [19]. Z can be expressed as a power series of the reduced thickness Δ

$$Z = \Delta^2 - \left(\frac{2-3\xi}{15}\right)\Delta^4 + \left(\frac{3-11\xi+10\xi^2}{315}\right)\Delta^6 - \left(\frac{2-13\xi+29\xi^2-21\xi^3}{4725}\right)\Delta^8 + \ldots \quad (32)$$

and, after inversion

$$\begin{aligned}\Delta^2 \equiv \Lambda_1^2 < d^2 > = Z + \left(\frac{2-3\xi}{15}\right)Z^2 + \left(\frac{41-113\xi+76\xi^2}{1575}\right)Z^3 \\ + \left(\frac{28-110\xi+142\xi^2-60\xi^3}{4725}\right)Z^4 + \ldots\end{aligned} \quad (33)$$

Now, all physical characteristics of the system are expressed as functions of Z and the parameter ξ. The retardation characteristic D_1 is obtained in the form

$$D_1 = D(\lambda_1) = Z\left[1 - \frac{1+\xi}{5}Z - \frac{29-97\xi-76\xi^2}{1575}Z^2 + \frac{4+87\xi+3\xi^2-60\xi^3}{4725}Z^3 + \ldots\right] \quad (34)$$

To calculate the average number of plates in the light path, E, we go back to Eqs. (25) and obtain

$$\begin{aligned}E = \frac{DE(\lambda_1)}{D(\lambda_1)} = \frac{1}{2\mathrm{Z}}\ln\left(\frac{1}{1-J_0(\lambda_1)}\right)\left[1 + \frac{\ln[1-J_0(\lambda_1)]}{\ln[1-J_{\pi/4}(\lambda_1)]}\right] \\ \times\left[1 + \frac{1+\xi}{5}Z + \frac{92+29\xi-13\xi^2}{1575}Z^2 - \frac{35+1410\xi+1620\xi^2+345\xi^2}{23625}Z^3 + \ldots\right]\end{aligned} \quad (35)$$

Equations. (25), (34) and (35) present solutions for three basic characteristics derivable from the light depolarization: average plate orientation, $S = <\sin^2 2\beta>$, average retardation function of a single plate, $D(\lambda_1)$, and average number of plates in the light path, E. These three characteristics, combined with reduced plate thickness Δ, and parameters ξ, Λ_1, Λ_2 , may be used for estimation of other material characteristics. In the range of a monodisperse distribution of plate dimensions and not too thick plates, average plate thickness is found in the form

$$\begin{aligned}< d > \cong \sqrt{< d^2 >} = \sqrt{\frac{\Delta^2}{\Lambda_1^2}} = \frac{\sqrt{Z}}{\Lambda_1}\left[1 + \left(\frac{2-3\xi}{30}\right)Z + \left(\frac{136-368\xi+24\xi^2}{12600}\right)Z^2\right. \\ \left. + \left(\frac{1012-3954\xi+5076\xi^2-2133\xi^3}{378000}\right)Z^3 + \ldots\right]\end{aligned} \quad (36)$$

and the degree of crystallinity

$$x \cong \frac{E < d >}{B} = \frac{\ln\left(\dfrac{1}{1 - J_0(\lambda_1)}\right)\left[1 + \dfrac{\ln[1 - J_0(\lambda_1)]}{\ln[1 - J_{\pi/4}(\lambda_1)]}\right]}{2\,\Lambda_1\, B\sqrt{\dfrac{3}{1-\xi}\left[1 - \dfrac{\xi \ln[1 - J_0(\lambda_1)]}{\ln[1 - J_0(\lambda_2)]}\right]}}$$
$$\times\left[1 + \frac{8 + 3\,\xi}{30} Z + \frac{1040 - 220\,\xi - 332\,\xi^2}{12600} Z^2 + \ldots\right] \tag{37}$$

7. Final remarks

It has been demonstrated that the light depolarization technique, as it is currently used for following polymer crystallization, does not yield reliable information about the degree of crystallinity or crystallization rate. First, the depolarization ratio is not proportional to the average retardation function of a single crystal plate, *D*. An exact non-linear relation derived in ref. [19]

$$J_0 = \left\langle \frac{2I_\perp}{I_\| + I_\perp} \right\rangle = 1 - \mathrm{e}^{-DE} = DE - \frac{1}{2}(DE)^2 + \ldots. \tag{38}$$

reduces to the linear expression only in the limit of infinitely small *DE*. There is enough experimental evidence (see Figs, 5–7) proving that actually observed depolarization ratios often exceed the linear range. Second, depolarization variable, *DE*, is not a unique function of the crystallinity but depends also on the average crystal thickness and crystal size distribution. In the limit of monodisperse plate size distribution and thin enough plates, *DE* reduces to the product of crystallinity and average plate thickness

$$DE \to 0 : DE \cong \text{const } x < d > \tag{39}$$

Table 1. Measurement conditions and structural characteristics

Angle φ	Angle ϑ	Wave-length λ	Intensity measurement	Depolarization ratio	Structural characteristics
π/2	0	λ_1	$I_\perp(0, \lambda_1)$	$J_0(\lambda_1) = \dfrac{2I_\perp(0,\lambda_1)}{I_\perp(0,\lambda_1) + I_\|(0,\lambda_1)}$	$DES(\lambda_1)$
0	0	λ_1	$I_\|(0, \lambda_1)$		
π/2	π/4	λ_1	$I_\perp(\pi/4, \lambda_1)$	$J_{\pi/4}(\lambda_1) = \dfrac{2I_\perp(\pi/4,\lambda_1)}{I_\perp(\pi/4,\lambda_1) + I_\|(\pi/4,\lambda_1)}$	*DE*, *S*
0	π/4	λ_1	$I_\|(\pi/4, \lambda_1)$		
π/2	0	λ_2	$I_\perp(0, \lambda_2)$	$J_0(\lambda_2) = \dfrac{2I_\perp(0,\lambda_2)}{I_\perp(0,\lambda_2) + I_\|(0,\lambda_2)}$	$DES(\lambda_2)$, *D*, *E*, <*d*>, x
0	0	λ_2	$I_\|(0, \lambda_2)$		

An extension of the theory of compensators onto statistical systems [19] provides a tool for studying the material structure. Variation of sample orientation with respect to the axis of the polarizer (angle ϑ) makes possible analysing samples with non-random crystal orientation distribution. Depolarization measurements performed at two different wavelengths may be used for decoupling of the variable *DE* and obtaining independent information about the average retardation function, $D(\lambda_1)$, average number of plates in the light path, *E*, average plate thickness, $<d>$, and the degree of crystallinity, x.

Six intensities presented in Table 1 enable a complete decoupling of the characteristic *DES*. The measurements require application of two different wavelengths and two different sample orientations.

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Received 13 May 2005
Revised 16 December 2005