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Optical birefringence and molecular orientation of electrospun polycaprolactone fibers by polarizing-interference microscopy

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ABSTRACT

The potential of polarizing-interference Pluta microscope for determination of optical birefringence of individual nanofibers formed by electrospinning was shown. This technique can be applied for measurements of fiber birefringence, practically at diameter above 300 nm. The molecular orientation of individual polycaprolactone (PCL) nanofibers was determined from birefringence assuming the same orientation of both phases, crystal and amorphous. The molecular orientation was determined using DSC crystallinity, crystal intrinsic birefringence calculated for the first time for PCL from bond polarizabilities as well as estimated value of amorphous intrinsic birefringence. Our results indicate that the birefringence and thus molecular orientation are strongly inhomogeneous along the nanofibers, reflecting a complex nature of forces acting during electrospinning process. The average molecular orientation is weak if any, being dependent together with fiber thickness and crystallinity on electrospinning parameters, like applied voltage, concentration and type of solvent. The obtained results indicate that the average molecular orientation displays similar dependence on applied voltage as fiber diameter. Relatively low melting temperature of electrospun nanofibers suggests low crystal size and/or high concentration of defects in crystals. This observation corresponds with low crystallinity and molecular orientation, indicating together relatively low degree of crystal ordering due to high rate of cooling and solvent evaporation during electrospinning, limiting thus crystallization process.

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1. Introduction

Formation of nanofibers by electrospinning is an exciting challenge both from fundamental and practical point of view. One of the important fields of application of nanofibers is tissue engineering. It is known that electrospinning and the resulting structure of fibers are very sensitive to various parameters both related to the material and the process. Up to date major attention was focused on the external structure of nanofibers like diameter, beads etc. Analysis of internal structure of nanofibers like crystallinity or molecular orientation was usually performed by various methods (e.g. WAXS, DSC) using large bundles of

nanofibers providing information on the average structure being under investigations. The results indicate usually that crystallinity of electrospun fibers is lower than for raw polymer [1,2], most probably because of high rate of solvent evaporation. Molecular orientation of electrospun nanofibers tends to be rather weak, or even there is no preferred orientation in such nanofibers [1,3]. There are only few papers trying to analyze the internal structure of individual nanofibers [e.g. [4,5]]. They indicate that the internal structure changes significantly along the nanofibers. According to Dersch et al. [5] orientation of the crystals along the fiber axis is strongly inhomogeneous. This kind of information could be very important not only for better understanding of the complex nature of electrospinning but could be also relevant for applications.

In this paper, we show the capability of determination of optical birefringence of individual nanofibers using the

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polarizing-interference Pluta microscope [6]. This microscope, designed and developed by Pluta is suitable for analysis of birefringence changes along individual fibers. Additional analysis of crystallinity by DSC together with calculation of intrinsic birefringence of investigated polymer allows estimation of molecular orientation of nanofibers.

For the one phase material, birefringence $\Delta n = (n_e - n_o)$, where n_o and n_e are the refractive indices for polarizations perpendicular (ordinary) and parallel (extraordinary) to the axis of anisotropy of material, respectively, is a direct measure of orientation:

$$\Delta n = f \cdot \Delta n^0 \quad (1)$$

where Δn^0 is intrinsic birefringence (difference between refractive indices parallel and perpendicular to the axis of unit structure of material), and f is Herman's orientation function given by

$$f = (3\langle \cos^2 \phi \rangle - 1)/2 \quad (2)$$

where Φ is an angle between the fiber axis and the polymer chain axis, and the averaging occurs over all molecules,

In the case of two phase system, for instance crystalline-amorphous polymer, the birefringence depends not only on the internal orientation of both phases, f_c, f_a , but also on phase content, $x_c, (1 - x_c)$. Neglecting form birefringence:

$$\Delta n = x_c \cdot f_c \cdot \Delta n_c^0 + (1 - x_c) \cdot f_a \cdot \Delta n_a^0 \quad (3)$$

where $\Delta n_c^0, \Delta n_a^0$ are intrinsic birefringence for ideally oriented crystal and amorphous phases, respectively.

For two phase system, determination of birefringence allows estimation of molecular orientation of one of the phase, providing additional information on molecular orientation of second phase, phase content as well as intrinsic birefringence of both phases. At this stage of work we illustrate the possibility of estimation of molecular orientation of individual fibers assuming the same degree of orientation within both phases, $f_c = f_a = f$, providing supplementary information on crystallinity from DSC measurements and calculating intrinsic birefringence of crystal, Δn_c^0 , and amorphous phases, Δn_a^0 . In the case of PCL, there is no data available on intrinsic birefringence of crystal and amorphous phases.

2. Experimental

2.1. Materials and method

2.1.1. Electrospinning

Polycaprolactone (PCL) with $M_w = 80,000$ g/mole from Aldrich Chemical Co. was used. Electrospinning was performed from solutions using two solvent mixtures, chloroform/*N,N*-dimethylformamide (DMF) and chloroform/methanol, containing 7–14%(w/w) of PCL. The applied voltage was in a range between 7.5 and 15 kV. The needle tip was connected to a high voltage power source. Polymer solution was feed into 1 ml syringe with 2 mm long and 0.35 mm internal diameter needle. The constant flow rate was controlled by a syringe pump NE-1000 New Era Pump Systems at the rate 0.2 ml/h. Nanofibers were collected on microscope cover glass slides, being 15 cm far from the needle tip.

2.1.2. Optical microscopy

The direct measurements of birefringence was performed using Pluta polarizing-interference microscope (Biolar PI) produced by Polish Optical Works (PZO). This microscope is equipped with Wollstone birefringent prisms, allowing a quantitative determination of the optical path difference caused by investigated object, which in turn is proportional to the birefringence. Quantitative measurements of birefringence were performed using interference fringed field method. Ordinary and extraordinary waves, polarized versus each other in perpendicular planes can interfere so that after their superposition in the image plane, interference is obtained in the form of interference fringes. Direct determination of fiber birefringence is performed at crossed polaroids, putting a fiber at 45° to the planes of polarization in both polarizer and analyzer (perpendicular to the direction of fringes). In such a case the deviation of fringes inside the fibers, d , is a measure of optical path difference, Φ , caused by birefringence, Δn :

Table 1
Parameters used for calculation of crystal intrinsic birefringence.

Bond	Polarizability $b_{ii} \times 10^{-25} [\text{cm}^{-3}]$ [10]	Polarizability $b_{ij} \times 10^{-25} [\text{cm}^{-3}]$ [10]	Angle, $\theta_{ia} [\text{deg}]$ calc. from [7]	Angle, $\theta_{ib} [\text{deg}]$ calc. from [7]	Angle, $\theta_{ic} [\text{deg}]$ calc. from [7]
C-C	9.7	2.5			
C-H	8.2	6			
C-O	14.6	1.7			
C=O	20	10			
C1-O			-10.42	3.30	60.03
C2-C1			-9.94	176.61	120.61
H-C1			30.53	52.53	90.00
H-C1			-7.81	82.19	90.00
C3-C2			77.90	115.42	120.67
H-C2			34.96	56.96	90.00
H-C2			77.75	12.25	90.00
C4-C2			-9.94	176.61	120.61
H-C3			30.53	52.53	90.00
H-C3			-7.81	82.19	90.00
C5-C4			77.90	115.42	120.67
H-C4			34.96	56.96	90.00
H-C4			77.75	12.25	90.00
C6-C5			-9.94	176.61	120.61
H-C5			34.96	56.96	90.00
H-C5			77.75	12.25	90.00
C6=O			87.80	70.20	90.00
C6-O			-10.42	78.42	60.03
C7-O			-10.42	78.42	60.03
H-C7			34.96	56.96	90.00
H-C7			77.75	12.25	90.00
C7-C8			77.90	115.42	120.67
H-C8			30.53	52.53	90.00
H-C8			-7.81	82.19	90.00
C8-C9			-9.94	176.61	120.61
H-C9			34.96	56.96	90.00
H-C9			77.75	12.25	90.00
C9-			77.90	115.42	120.67
C10					
H-C10			30.53	52.53	90.00
H-C10			-7.81	82.19	90.00
C10-			-9.94	176.61	120.61
C11					
H-C11			34.96	56.96	90.00
H-C11			77.75	12.25	90.00
C12=O			87.80	70.20	90.00

$$\phi = \Delta n \cdot t = \frac{d}{h} \cdot \lambda \quad (4)$$

where t is fiber thickness, h is the interference fringe spacing and λ is the wavelength (550 nm for the applied white light). The birefringence, Δn , is determined from:

$$\Delta n = \frac{d \cdot \lambda}{h \cdot t} \quad (5)$$

Deviation of fringes was determined using 0th-order fringe. Deviation of fringes was measured precisely using intensity profiles drawn outside and in the middle of the fiber. Registration and quantitative analysis of images was done using Q-Imaging Go-3 CMOS camera and Q-Capture Pro Software.

Application of optical microscope to nanofibers faced with a problem of resolution limited by light diffraction. In order to increase the resolution, immersion objective of magnification 100 $\times$ with numerical aperture NA = 1.25 was used, and the space between cover glass and the front lens was filled with cedar wood oil. The use of cedar wood oil with refractive index 1.515 being almost identical to that of the glass used for slides and cover slips allows capturing by the objective the light from larger cone with subsequently higher NA and therefore better final resolution.

Estimation of the molecular orientation was performed using Eq. (3), assuming the same orientation for both phases, $f_c = f_a = f$. Using this assumption, orientation factor, f , can be determined after rearrangement of Eq. (3):

$$f = \frac{\Delta n}{x_c \Delta n_c^0 + (1 - x_c) \Delta n_a^0} \quad (6)$$

Up to date there is no literature data of intrinsic birefringence of poly(caprolactone) (PCL) and it was necessary to calculate it for crystal region and estimate for amorphous

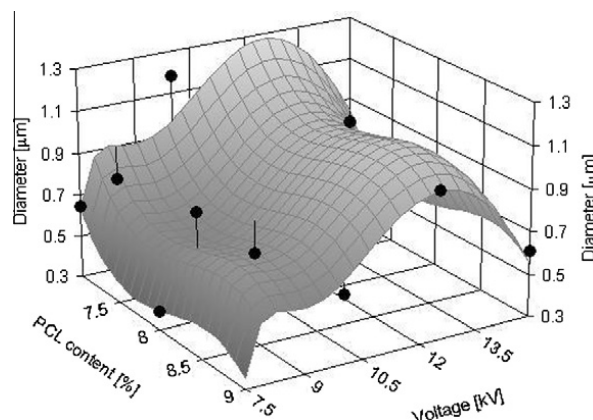


Fig. 2. Diameter of fibers spun from CHCl₃/CH₃OH 75:25 vs. PCL concentration and applied voltage.

one. The crystalline intrinsic birefringence was calculated by summation of polarizabilities of the individual bonds. The additivity rule has the merit of great simplicity; however it neglects the effect of internal fields on polarizability. The molecule is considered to consist of several bonds, each of which has a constant polarizability. Calculation of bond positions requires information on location of atoms in the unit cell. There have been a few studies on the crystal structure of PCL. PCL is an aliphatic, linear polyester with the repeating unit O-(CH₂)₅-CO-; it crystallizes in orthorhombic cell. There are in general two models of PCL chain conformation in a crystal structure. One of them, proposed by Bittiger et al. [7], is planar while the other one is nonplanar as suggested by Chatani et al. [8]. We used for our calculations crystal structure with planar chain conformation as

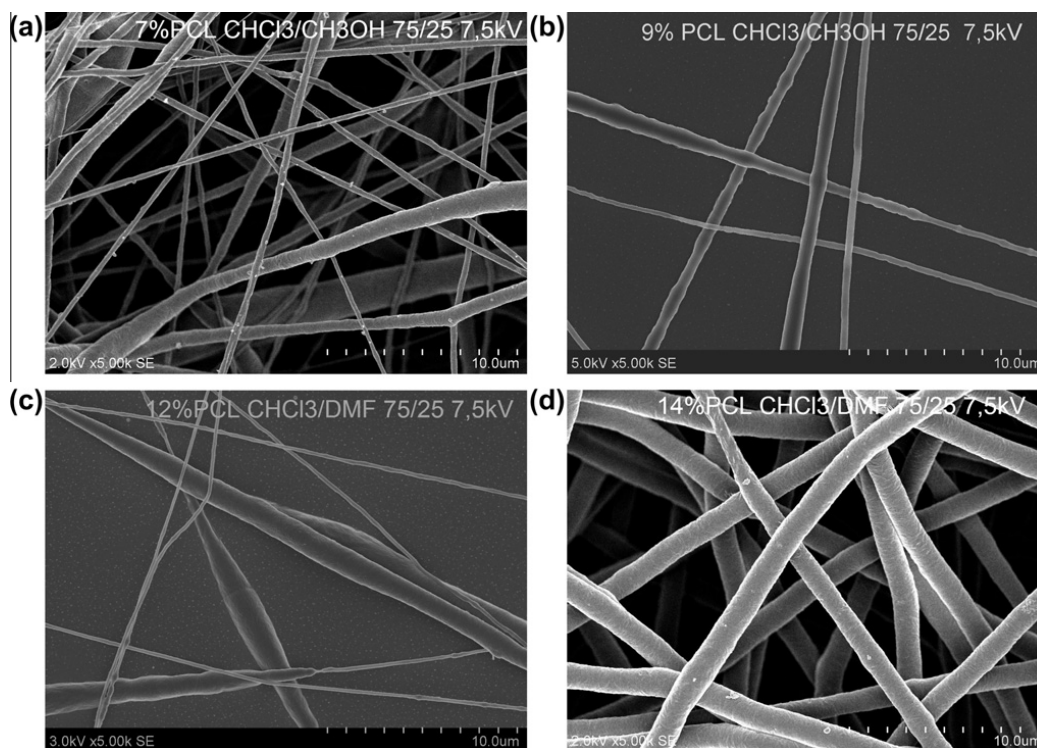


Fig. 1. SEM images of electrospun PCL fibers.

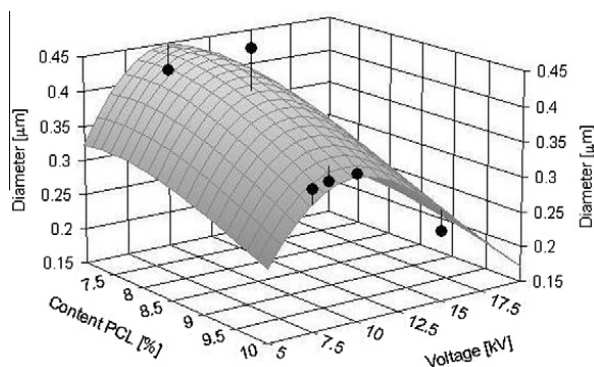


Fig. 3. Diameter of fibers spun from CHCl_3/DMF 50:50 vs. PCL concentration and applied voltage.

proposed by Bittiger et al. [7]. According to [7], the unit cell contains two chains with opposite orientation (“up” and “down”), with the planes of the chains rotated about their axis to an angle 28° with respect to the a axis. The cell unit parameters are: $a = 0.7496$ nm, $b = 0.4974$ nm and $c = 1.7297$ nm [7]. The unit cell dimensions determined by Chatani et al. [8] are slightly different, particularly in c -dimension ($a = 0.747$ nm, $b = 0.498$ nm and $c = 1.705$ nm).

The polarizability α_m , along the m crystallographic axis was obtained using the relationship:

$$\alpha_m = \sum b_{ii} \sin^2 \theta_{im} + \sum b_{ii} \cos^2 \theta_{im} \quad (7)$$

where b_{ii} and b_{ii} are the bond polarizabilities along and normal to the i 'th bond axis, and θ_{im} is the angle between the bond and m axis of unit cell.

The Lorentz–Lorenz equation relates molecular polarizability, with refractive indices, n_m , along the m 'th crystallographic axis:

$$\frac{n_m^2 - 1}{n_m^2 + 2} = \frac{4\pi N \rho_c}{3M} \alpha_m \quad (8)$$

where ρ_c is density of crystal, M – molecular weight per unit cell, and N – Avogadro's number.

Eq. (8) was used for calculation of refractive indices n_a , n_b , n_c along crystallographic axis, a , b , and c , respectively. The crystalline intrinsic birefringence, Δn_c^0 , was then calculated as:

$$\Delta n_c^0 = n_c - \frac{(n_a + n_b)}{2} \quad (9)$$

Bond polarizabilities, b_{ii} and b_{ii} , along and normal to the i 'th bond axis, the angle θ_{im} between the particular bond and m axis of unit cell used for our calculations are shown in Table 1. Density of PCL crystal, ρ_c was taken as 1.20 g/cm³ [9] and molecular weight per unit cell, $M = 128$.

The intrinsic birefringence of amorphous phase was estimated using the empirical relationship proposed by Cakmak [11]:

$$\frac{\Delta n_c^0}{\Delta n_a^0} = \frac{\rho_c}{\rho_a} \quad (10)$$

where ρ_c and ρ_a are crystal and amorphous densities, taken for PCL as 1.20 g/cm³, and 1.021 g/cm³, respectively [9]. The relationship given by (10), seems to be a fair approximation for several polymers, including polyethylene terephthalate (PET) and polyamide-6. For instance, in the case of PET, $\frac{\Delta n_c^0}{\Delta n_a^0} = \frac{0.22}{0.19} = 1.158$ [12], vs. $\frac{\rho_c}{\rho_a} = \frac{1.485}{1.335} = 1.112$ [13,14]. In the case of α modification of polyamide-6, $\frac{\Delta n_c^0}{\Delta n_a^0} = \frac{0.089}{0.078} = 1.141$ [15], vs. $\frac{\rho_c}{\rho_a} = \frac{1.232}{1.080} = 1.141$ [16].

2.1.3. Differential scanning calorimetry

Crystallinity, x_c , of nanofibers needed for determination of molecular orientation from birefringence was determined from DSC, using Pyris-1 apparatus. Measurements were performed during heating at 10 K/min. Before measurements, nanofibers were impregnated by special mass based on epoxy resin with addition of polymeric mercaptan. This procedure allows reducing of thermal shrinkage

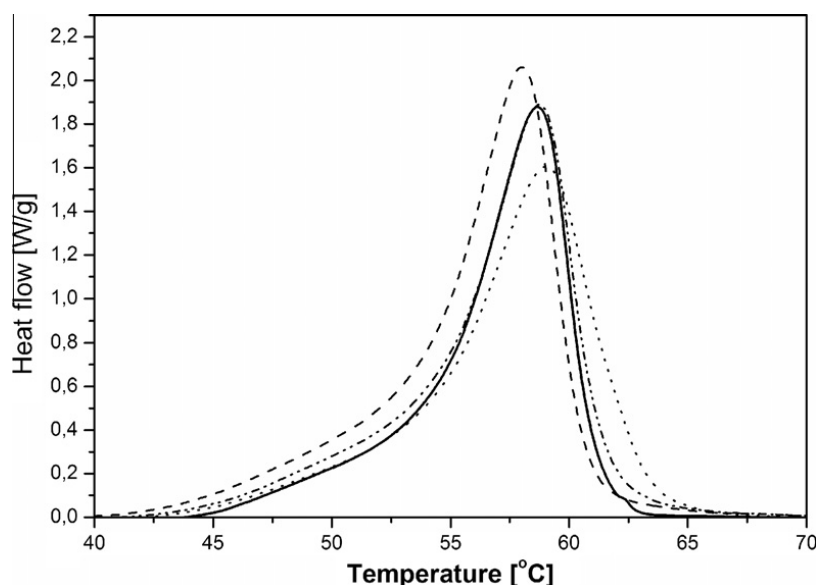


Fig. 4. DSC scans for 7% PCL fibers spun from $\text{CHCl}_3/\text{CH}_3\text{OH}$ (75/25) at 10 kV (various samples cut from the same mat).

of nanofibers before melting. The sample mass was around 1 mg. Standard temperature/heat calibration of DSC was performed using indium and zinc. Crystallinity was determined using equation:

$$x_c = \frac{\int_0^\infty \frac{dH}{dt} dt}{\Delta H^0} \quad (11)$$

where dH/dt is the rate of melting per unit mass, while ΔH^0 is the specific heat of fusion of 100% crystalline PCL taken as 142.9 J/g [17]. Melting temperature and crystallinity is an average value from four measurements.

2.1.4. Scanning electron microscopy

In addition to the measurements of the fiber thickness using optical microscope, we used scanning electron microscopy (Hitachi S-5500) as a classical method for measurements of nanofibers. Specimens were coated with gold in a sputtering device for 1.5 min at the voltage of 15 kV. The diameter of fiber was determined using average value for five point measurements along particular fiber averaged then from measurements of ten fibers.

3. Results and discussion

Fig. 1 illustrates SEM images of few electrospun fibers.

The diameter of fibers reflects all of the forces acting on the fiber during electrospinning. Figs. 2 and 3 show the effect of PCL concentration and applied voltage on the average diameter of PCL fibers spun from two solvent mixtures. It is seen that fiber diameter is smaller for chloroform/DMF than for chloroform/methanol. This is caused by relatively high electrical conductivity of DMF, resulting in high charge density and hence higher elongation of polymer jet by electric field. Analyzing the effect of applied voltage, it is seen in Figs. 2 and 3 that there is a maximum of fiber diameter at the voltage between 12 and 13 kV. This type of dependence can be explained by the fact that voltage can

have in general two opposite effects on fiber diameter [18]. When a voltage is increasing, a diameter can be reduced as an effect of increasing jet elongation by electrical force from one side and increased from the other one as a result of increasing mass of flowing polymer. As a result, the maximum of fiber diameter can be observed at particular voltage. Regarding the effect of polymer concentration, it is expected that the diameter should increase with polymer concentration as a result of larger polymer mass. Such dependence is not evident from our results.

Fig. 4 illustrates typical DSC scans registered during heating of constrained nanofibers at 10 deg/min. The broad melting peak is observed in temperature range between 40 and 65 °C. There is relatively large scattering of melting curves depending on the cutting place (curves 1–4 in Fig. 4), reflecting thus the structure inhomogeneity of mats formed by electrospinning.

DSC measurements show that the melting temperature of nanofibers does not significantly change with electrospinning conditions (Fig. 5). On the other hand, crystallinity of electrospun nanofibers is essentially lower than for raw pellets; the same trend was observed for comparison with PCL crystallized from quiescent solution. This is consistent with literature data for various polymers spun either from solution or melt [2,19–22]. Crystallinity depends on electrospinning conditions, changing between 36% and 58% (Fig. 6). It is seen in Fig. 6 that the lowest crystallinity was obtained for nanofibers spun from solution containing 9% of PCL.

Fig. 7 illustrates fringed interference white light field of one of the PCL fiber. The shape of fringes inside fibers is parabolic indicating cylindrical symmetry of investigated objects. It suggests that the evaporation of solvents occurs on the way between the needle and the collector, allowing to prevent a circular cross section of fiber when reaching the collector.

Optical birefringence was determined from deviation of fringes using Eq. (5). The measurements of birefringence

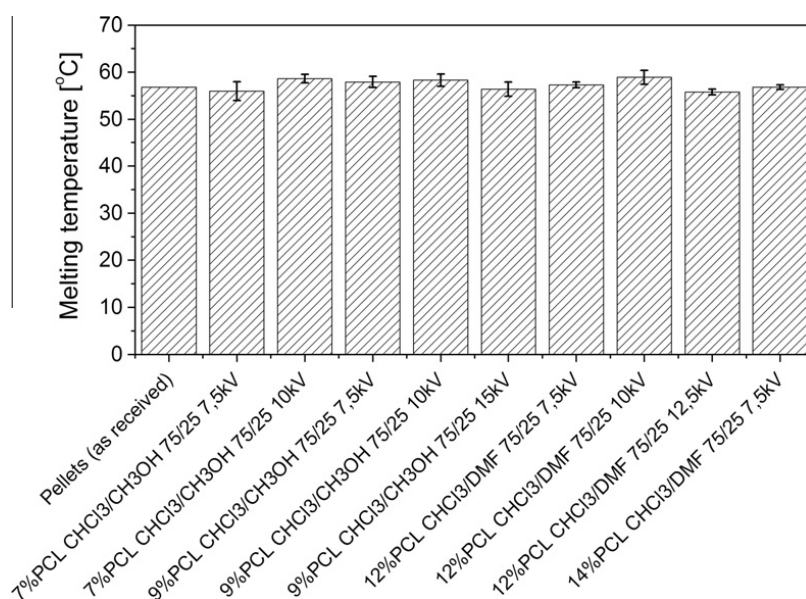


Fig. 5. DSC melting temperature (at maximum of the peak) for nanofibers spun at various conditions.

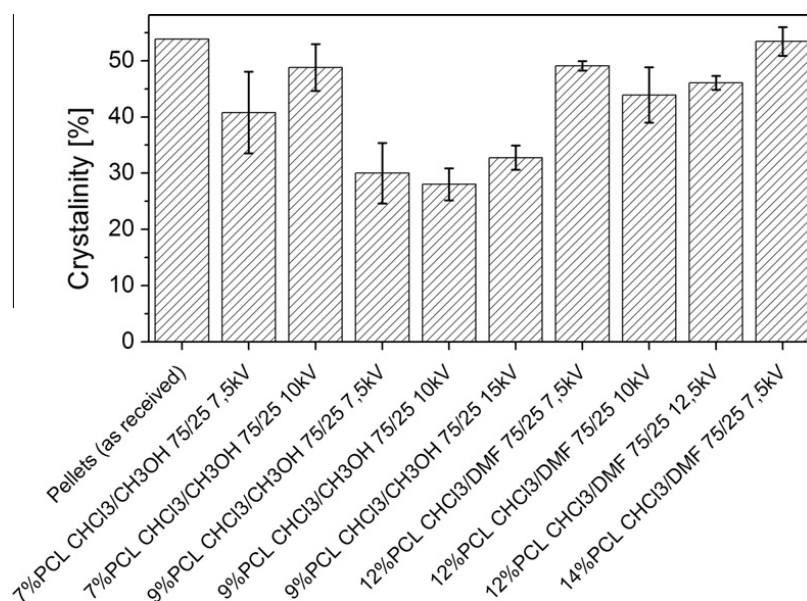


Fig. 6. DSC crystallinity for nanofibers spun at various conditions.

along single fibers indicate strong spatial inhomogeneity (Figs. 8 and 9). The birefringence changes from positive to negative values depending on the spatial position indicating changes in molecular orientation along the fibers. It is highly probable from our measurements that the

changes of birefringence along the fibers are periodical (Fig. 9).

Estimation of molecular orientation from the measured birefringence needs calculation of unknown values of intrinsic birefringence of crystal and amorphous phase. Table 2 shows refractive indices, n_a , n_b , n_c , along crystallographic axes, a , b , and c , respectively, as well as crystal and amorphous intrinsic birefringence, Δn_c^0 , and Δn_a^0 , respectively, calculated by us using Eqs. (7)–(10). To our knowledge, the intrinsic birefringence of PCL calculated by us is the first attempt as yet.

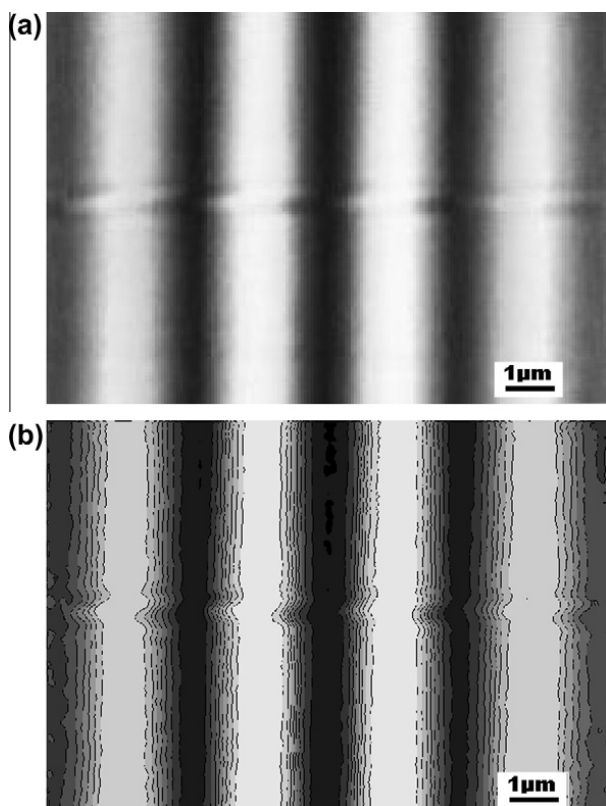


Fig. 7. Fringed interference image of PCL fiber spun from 7% solution of chloroform/DMF at 20 kV in magnification 100 $\times$, (a) microscopic image using white light, (b) contour-line image.

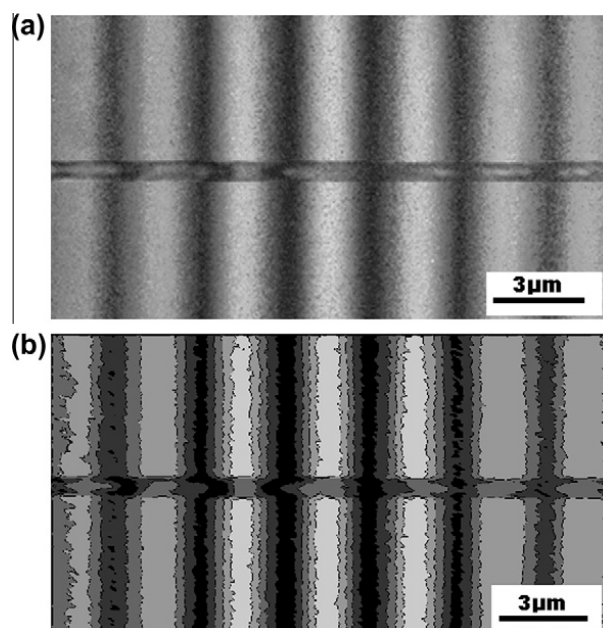


Fig. 8. Fringed interference image of PCL fiber spun from 12% solution of chloroform/DMF at 7.5 kV showing inhomogeneity of birefringence along a fiber, (a) microscopic image using white light, (b) contour-line image.

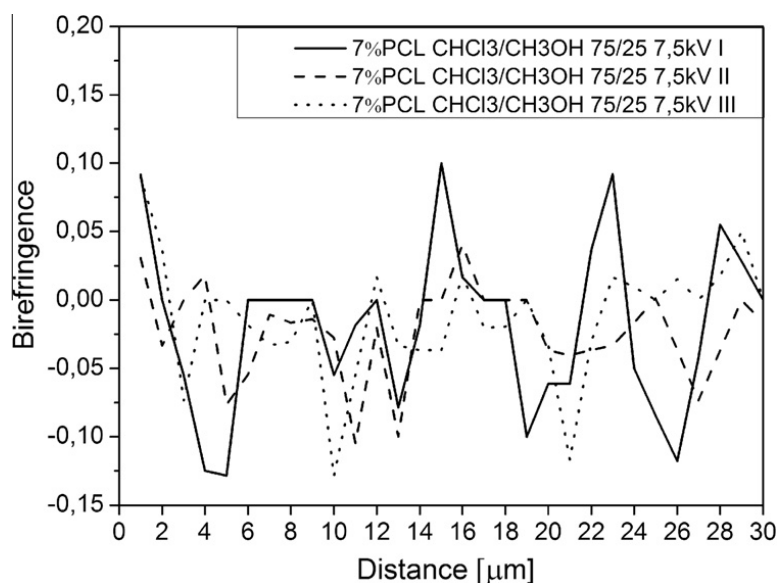


Fig. 9. Changes of birefringence along the length of nanofibers (three various fibers spun from 7% PCL solution in CHCl₃/CH₃OH 75/25 at 7.5 kV).

Table 2

Calculated optical properties of PCL.

Parameter	Value calculated
n_a	1.230
n_b	1.167
n_c	1.376
Δn_c^0	0.177
$\Delta n_{ca} = n_c - n_a$	0.146
$\Delta n_{cb} = n_c - n_b$	0.209
$\Delta n_{ba} = n_b - n_a$	−0.063
Δn_a^0	0.151

Table 3

The mean value of optical birefringence and molecular orientation of PCL fibers.

Sample	Voltage [kV]	Average optical birefringence	Standard error of optical birefringence	Average orientation factor
7% PCL CHCl ₃ /CH ₃ OH 75/25	7.5	−0.018	0.005	−0.110
7% PCL CHCl ₃ /CH ₃ OH 75/25	10	−0.022	0.007	−0.131
9% PCL CHCl ₃ /CH ₃ OH 75/25	7.5	−0.019	0.011	−0.119
9% PCL CHCl ₃ /CH ₃ OH 75/25	10	0.052	0.039	0.326
9% PCL CHCl ₃ /CH ₃ OH 75/25	15	−0.006	0.003	−0.040
12% PCL CHCl ₃ /DMF 75/25	7.5	−0.024	0.033	−0.144
12% PCL CHCl ₃ /DMF 75/25	10	−0.008	0.003	−0.032
12% PCL CHCl ₃ /DMF 75/25	12.5	0.021	0.046	0.085
14% PCL CHCl ₃ /DMF 75/25	7.5	−0.011	0.011	−0.069

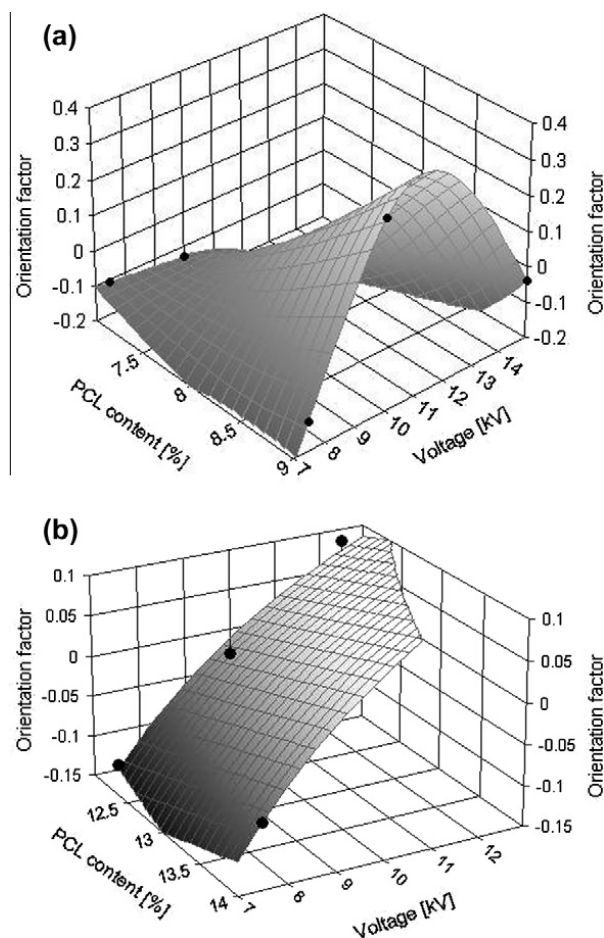


Fig. 10. Average orientation function of fibers spun from, (a)CHCl₃/CH₃OH 75:25, (b)CHCl₃/DMF 50:50, vs. PCL concentration and applied voltage.

The averaged birefringence of fibers spun at various conditions is given in Table 3. The averaging was done for measurements for various fibers. The orientation factor calculated from the average birefringence assuming the same orientation for crystalline and amorphous phase (Eq. (6)) is in general very weak, being dependent on the electrospinning parameters (Table 3). There are both fibers with small positive and negative orientation factor, indicating weak orientation either along the fibers or in transverse direction. However it should be noticed that the standard error of measurements is often comparable with absolute value of average birefringence. It suggests that there is large scattering of orientation between single fibers spun at particular conditions.

At this stage of work, we do not have sufficient amount of data to analyze in details the effect of spinning conditions on the molecular orientation. However our recent data indicate that in the range of applied polymer concentration there is an increase of molecular orientation with increasing polymer concentration (Fig. 10). Regarding the effect of voltage on molecular orientation it is highly probable that there is a local maximum of orientation as a function of applied voltage like it was observed for the analysis of fiber diameter (Figs. 2 and 3). The position of this maximum is similar to the position observed for the analysis of fiber diameter.

4. Discussion and conclusions

We show the potential of the polarizing-interference Pluta microscope for determination of optical birefringence and hence molecular orientation of individual nanofibers formed by electrospinning. In the case of nanofibers this technique needs special treatments like application of immersion technique in order to increase resolution. We estimate that polarizing-interference microscopy can be used for birefringence measurements of fibers with diameters above 300 nm. Supplementary results on crystallinity as well as molecular orientation of one of the phases, crystal or amorphous, allow estimating the molecular orientation of the second one in individual fibers from birefringence measurements. At this stage of investigations we have shown the possibility of determination of molecular orientation of individual PCL nanofibers assuming the same orientation of both phases, crystal and amorphous. In the case of PCL, calculation of unknown value of intrinsic birefringence was needed. To our best knowledge, our calculation of crystal intrinsic birefringence and estimation of amorphous intrinsic birefringence are the first data in the literature. Our results indicate that the birefringence and thus molecular orientation are strongly inhomogeneous along the nanofibers, reflecting a complex nature of forces acting during electrospinning process. The average molecular orientation is weak if any, being dependent together with fiber thickness and crystallinity on electrospinning parameters, like applied voltage, concentration and type of solvent. General trend of very weak orientation of electrospun nanofibers is consistent with observations found in literature [2]. Much higher orientation is reported for electrospun nanofibers collected on rotating wheel as a

result of mechanical stretching of fibers [23]. Our results obtained at this stage of work indicate that the fiber diameter depends on applied voltage in a similar mode as molecular orientation.

Relatively low melting temperature of electrospun nanofibers suggests low crystal size and/or high concentration of defects in crystals. This observation corresponds with low crystallinity and molecular orientation, indicating together relatively low degree of crystal ordering due to high rate of cooling and solvent evaporation during electrospinning, limiting thus crystallization process. Some theoretical descriptions [24] indicate that electrospinning process is not controllable well and some instabilities in fact are responsible for fluctuation of diameter and molecular orientation. Systematic analysis of the effect of electrospinning parameters on internal structure of polycaprolactone nanofibers is planned to be performed in future work.

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