Laser measurements of the refractive index of polymer solutions, thin films and bulk materials

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Abstract. We present two laser-based measurement techniques for investigating the refraction of polymer solutions, thin polymer films and bulk samples. Our results confirm the fact that the refractive indices of polymer films differ from those of bulk polymer samples and polymer solutions. However, the analysis of the dispersion yields similar results for all states of the polymer.

1. Introduction
Polymer materials are presently used in the design and fabrication of both consumer products and precise optical instruments. They offer advantages over optical glasses, including low cost and weight, high impact resistance, and ability to integrate proper mechanical and optical characteristics [1]. Optical polymers (OPs) are manufactured in view of a wide spectrum of photonic applications in which bulk polymer bodies with various dimensions as well as thin polymer films (TPFs) are used [2].

The possible usages of OPs are defined mainly by their refraction index (RI) value, which should be determined with a sufficiently high accuracy. The proper choice of a measuring technique depends on the material and the sample’s size and thickness. Our earlier results showed that TPFs refraction differs from that of bulk specimens and should be studied separately [3]. We propose here a set-up of a laser microrefractometer (LMR), based on the critical angle determination [4], to obtain refractive data of polymer solutions and films. The results are compared with measured indices of bulk samples obtained by a He-Ne laser and a goniometric set-up. One can thus analyze the refractive and dispersive properties of different states of polymers.

2. Experimental

2.1. Measuring the refractive indices of bulk polymer samples
We have studied the optical properties of various types of plastics, including principal and some newly developed polymers [5, 6]. The principal OPs are polymethyl methacrylate (PMMA), polystyrene (PS), polycarbonate (PC), methyl methacrylate styrene copolymer (NAS), and styrene acrylonitrile (SAN). Different trade-marks of OPs as NAS-21 Novacor, CTE-Richardson, Zeonex, Optorez, Bayer,

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etc. and polymers produced by the Eastman Chemical Company, USA (ECC) were also examined.

To obtain more extensive refractometric data, we have used different measuring techniques to determine RIs of OPs in the entire visible (VIS) and near-infrared (NIR) spectrum. The classical Zeiss Pulfrich refractometer with its V-type SF3 glass prism (VoF3) was used to measure the RIs of bulk OPs at five emission wavelengths \( \lambda \) of the spectral lamps of the device in the VIS region. An additional goniometric set-up with the VoF3 prism and a white-light module (a 250-W halogen lamp and a condenser system) with interference filters with spectral bandwidths of about 7 nm – 9 nm was assembled for measurements in the entire VIS and NIR regions up to 1060 nm. In both cases, the deviation angle method was used. Our metrological tests revealed that the goniometric measurements agree with the refractometric results with an accuracy of \( \pm 0.001 \) in the VIS spectrum [7].

The measurements of the RIs were carried out by a conventional 1-mW He-Ne laser and a goniometric set-up (figure 1). A G5-LOMO goniometer with an accuracy of one arc second was used to measure the angle \( \alpha \). The angle of deviation \( \gamma \) is formed by the sample located into the V-shaped prism. Polymer specimens were produced as injection moulded plates or cubes having two well-polished, mutually perpendicular surfaces. An immersion emulsion with a proper RI is required to ensure the optical contact during the measurements [7]. The thermostatic housing of the VoF3 prism allowed us to maintain a temperature of 20 °C with a stability of 0.2 °C. A photo detector was assembled with the aid of a plane silicon diode, an operational amplifier and an indicator for registering the output beam. The RI \( n_\lambda \) of the polymer examined is calculated as follows:

\[
\frac{\gamma}{\alpha} = \cos \gamma \left( \frac{N_\lambda^2 - \cos^2 \gamma}{N_\lambda^2} \right)^{1/2}, \quad \gamma = 90^\circ - \alpha,
\]

where \( N_\lambda = 1.7347 \) is the RI of the VoF3 prism at \( \lambda = 632.8 \) nm. This value is determined by means of a modified Caushy's dispersion formula (4) and the data published in [8]. A metrological analysis was carried out in [9] and a maximal combined uncertainty of \( u_c = 3.65 \times 10^{-4} \) was obtained for the case of laser goniometric measurements of polymer bulk samples.

![Figure 1](image.png)

**Figure 1.** Experimental set-up for refractive index measurements of bulk optical plastics.

### 2.2. Refractive index measurement of polymer solutions and thin films

Among the OPs studied, solutions and TPFs could only be obtained for the ECC materials, which were delivered in the form of pellets. Polyester, polyarylate, polyacrylate, and cellulose polymers were dissolved in chloroform and the two types of copolymers A and B, in 1,1,2,2-tetrachloroethane. Solutions of the first four materials were prepared with concentration of 10 wt% while the concentration of the copolymers’ solutions was 1 wt%. TPFs were obtained by dropping a certain amount of the polymer solutions on glass substrates. A TK21 glass plate was used for the low refractive cellulose material and heavy flint TF4 glass, for the other OPs. The samples were dried at a temperature of 20 °C for 48 hours and then heated up to 60 °C during 6 hours to evaporate the remaining solvent. The TPFs were preserved in a desiccator. The film thickness \( d \) was measured by a
digital micrometer (Mitutoyo Corporation) with an accuracy of ± 1 µm.

A three-wavelength LMR was assembled to obtain the RIs of polymer solutions and films. The experimental scheme is presented in figure 2. A 0.5-mW He-Ne laser 1 and two diode lasers 2 (7 mW and 25 mW) with emission wavelengths 632.8, 532 and 790 nm are used. The three beams are directed by splitters 3 to illuminate the internal surface of the prism 5 which is positioned on the goniometric table 4. The sample measured 6 is placed between the prism and a chromium diffraction grating 7 with a 40-µm period and 0.8-µm depth of the grooves. Unit 5 is made of TF4 optical glass with a vertex angle $A = 64.76^\circ$. In case of solutions, a drop of the examined liquid is poured on the grating and then pressed tightly to the prism. For TPFs, the polymer layer with the glass substrate is fixed between the prism and the grating. The optical contact is realized using methylene iodide. At small angles of incidence, the diffraction orders are observed in reflection on the screen 8. At the critical angle of the material, total internal reflection occurs and the diffraction pattern disappears. The incident angle $\phi_c$ is then measured on the goniometric scale. The RI of the examined material is calculated by:

$$n_s = N_s \sin \left[ 4 \pm \arcsin \left( \frac{\sin \phi_c}{N_s} \right) \right],$$

where $N_s$ is the RI of the prism at the illumination wavelength. The corresponding values are found by fitting with the data published in [10]. The signs “+” and “–” in equation (2) correspond to counterclockwise or clockwise rotation of the incident beam with respect to the normal to the entrance surface of the prism.

A metrological analysis of the results for the polymer solutions is given in [9]. The standard uncertainty, connected with the determination of $N_s$, $A$ and $\phi_c$ in equation (2) and the temperature effects, was found to be ±2×10^{-4} for standard liquids, as distilled water, ethanol and methanol.

In the case of microrefractometric measurements of TPFs, the accuracy is less because of the extra noise introduced by the multiple surface reflections in the film and the glass substrate. Some light scattering in the polymer medium also occurs. Several measurements of each polymer film were completed and the maximal value of the standard deviation was estimated to be ±2×10^{-3}.

3. Results and discussion

The RIs measured are presented in table 1 and illustrated in figure 3. The refractometric data of solutions, TPFs and bulk specimens differ substantially. A correlation between the RIs of polymer solutions and of volume samples is possible to be established based on the Lorentz–Lorenz formula, since the specific refraction of solutions $r_s$ is an additive quantity:

$$r_s = \frac{n_s^2 - 1}{n_s^2 + 2 \rho_s} = \left( \frac{n^2 - 1}{n^2 + 2 \rho} \right) w + \left( \frac{n_0^2 - 1}{n_0^2 + 2 \rho_0} \right) w_0,$$

where $n_s$, $n$, $n_0$ are RIs of solution, material and solvent, respectively; $\rho_s$, $\rho$, $\rho_0$ represent their density; $w$ and $w_0$ are the mass fractions of the polymer and solvent. For example, in the case of the PC material, the calculated value of $n$ is 1.5690 ($\rho = 1.195$ g/cm$^3$, $\rho_s = 1.452$ g/cm$^3$, $\rho_0 = 1.492$ g/cm$^3$).
measured RIs at 632.8 nm – table 1; \( n_0 = 1.4417 \). Thus, the result obtained is very close to the value of 1.5684 for the bulk sample measured by means of the goniometric set-up. In the case of the polyarylate material, the RIs of the bulk specimen and of the thickest film are very close. The results for the cellulose and polyester are similar. Some differences are observed for the other polymers. It should be underlined that the deviation angle method gives the average RI value for the volume of the specimen while the critical angle determination is a way of obtaining the local RI near the surface of the TPFs. The depth of light penetration during total internal reflection was evaluated in [4] to be about several microns.

The transmittance of TPFs measured in [11], as well as the RIs obtained, reveal normal dispersion

### Table 1. Measured refractive indices of polymer solutions, TPFs and bulk samples.

| Optical polymer | Solutions | TPFs | Bulk |
|-----------------|-----------|------|------|
|                 | \( \lambda \) (nm) | \( d \) (µm) | \( \lambda \) (nm) | \( \lambda \) (nm) |
| Polyarylate     | 532       | 632.8| 790  |
|                 | 1.4761    | 1.4675| 1.4592| 15 | 1.656| 1.644| 1.639| 1.6041|
|                 | 80        | 1.638| 1.626| 1.619|
|                 | 140       | 1.616| 1.603| 1.595|
| Polyester       | 1.4741    | 1.4694| 1.4652| 40 | 1.506| 1.500| 1.496| 1.5064|
|                 | 44        | 1.514| 1.509| 1.505|
| Polycarbonate   | 1.4621    | 1.4552| 1.4489| 35 | 1.599| 1.595| – | 1.5684|
| Copolyester A   | 1.5016    | 1.4882| 1.4786| 3  | 1.538| 1.525| 1.510| 1.5521|
|                 | 6         | 1.541| 1.526| 1.515|
| Copolyester B   | 1.5006    | 1.4882| 1.4793| 33 | 1.649| 1.635| 1.621| 1.5675|
|                 | 42        | 1.595| 1.562| 1.550|

### Figure 3. Dispersion curves of: a) PC bulk and solution with chloroform; b) cellulose TPFs, c) polyarylate films and solution; d) polyester films and solution.
of OPs in the spectral range considered. We applied a modified Caushy's formula involving six dispersion coefficients, which ensures a calculation accuracy better than ± 0.0001 [6]:

$$n_0^2 = A_1 + A_2 \lambda^2 + A_3 / \lambda^2 + A_4 / \lambda^4 + A_5 / \lambda^6 + A_6 / \lambda^8.$$ (4)

In the case of bulk polymer samples, the dispersion coefficients $A_1, \ldots, A_6$ are determined with the aid of a system consisting of six linear equations [7]. The dispersion of polymer solutions and films is fitted by the first three terms in the series (4), the calculation accuracy then being ± 0.001.

The dispersion curves of the OPs studied are presented in figure 3. A comparison between the results for the PC bulk sample and solution (figure 3a), cellulose TPFs (figure 3b), polyarylate (figure 3c) and polyester (figure 3d) TPFs, as well as their solutions, yield an equal slope of the dispersion curves of the materials, although the RIs differ depending on the polymer state and the TPFs thickness. The Abbe numbers, fitted to the measuring spectral range of the LMR, are calculated by the expression:

$$\nu_{633} = (n_{633} - 1)/(n_{532} - n_{790}).$$ (5)

The results are included in figure 3. Their values are very close for one and the same material. The only substantial difference is seen for the dispersion of the solvent (figure 3a) and its Abbe number.

The results presented in table 1 and figure 3b, c, d show a dependence of the TPFs refraction on the film thickness $d$. In the case of polyarylate, copolyester B, and cellulose films, the RIs values decrease as the film thickness is increased. A similar dependence for TPFs was established by other authors [4, 12]. The tendency for the RI to increase as the film $d$ diminishes could be explained by an increase in the polymer packing and a reduction in the free fractional volume near the layer surface, due to the surface tension forces. This dependence was not established for the styrenic films in [12]. We also observed some differences in the fluctuations of the RI values with the thickness for the copolyester A and polyester TPFs. As was explained in [13], the film thickness determines the over-molecular structure of TPFs and their structural non-uniformity at the surface, while inside the layer the structure is isotropic.

4. Conclusions

The experimental refractometric data of the OPs examined confirm the existence a dependence on the state of the polymer. The RIs of bulk samples, polymer solutions and TPSs differ substantially. A correlation is only found for the polymer solutions and the bulk samples by means of the Lorentz–Lorenz formula. A variation of the refraction of the polymer layers with their thickness is established. For some of the materials (cellulose and polyarylate), the RIs increase as the film thickness is decreased. This could be explained by the higher packing density of the macromolecules on the TPFs surface and alteration of the over-molecular structure of the material in the layer. The differences between the results for bulk and film RIs depend on the measuring method as well. The deviation angle method of the goniometric set-up measures an average volumetric RI, while in the case of LMR, the RI values near the surface are obtained.

Our study on dispersion of polymers in the measuring spectral range 500 nm ÷ 800 nm confirms a dependence only on the type of the material. Regardless of the state of the polymer, the dispersion curves and Abbe numbers of bulk samples, solutions and films are very close for one and the same material.

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