JANUSZ JAGLARZ[1),*)], JAN CISOWSKI[1),2)], HALINA CZTERNASTEK[3)], WOJCIECH ODSTERCZYL[1)], JAN JURUSIK[2)], MARIAN DOMAŃSKI[2)]

Diffuse scattering in polyazomethine thin films

Summary — The results of optical studies of the diffuse reflectance and transmittance of polyazomethine (PPI) thin films prepared by the chemical vapor deposition (CVD) technique are reported. The obtained experimental data prove the presence of centers causing the Rayleigh-type scattering of light. These centers, with a spherical structure (spherolites), are formed in the process of crystallization during the growth of PPI films and they are responsible for the volume scattering of light.
Key words: polymer layers, thin film optics, polyazomethine, diffuse reflectance and transmittance.

ROZPRASZANIE DYFUZYJNE W CIENKICH WARSTWACH POLIAZOMETYNY
Streszczenie — Przedstawiono wyniki badań odbicia i transmisji optycznej cienkich warstw poliazometyny (PPI) utworzonych metodą CVD (osadzania chemicznego z fazy gazowej, Chemical Vapor Deposition) z *p*-fenylenodiaminy i aldehydu tereftalowego. Wyniki te (rys. 1—4) dowodzą istnienia centrów odpowiedzialnych za rozpraszanie światła typu Rayleigh'a. Centra rozpraszania mają strukturę sferyczną (sferolity) i tworzą się w procesie krystalizacji w toku narastania warstw PPI; są one odpowiedzialne za rozpraszanie objętościowe światła. Określona metodą profilometrii optycznej grubość badanych warstw (rys. 5) mieściła się w przedziale 0,15—1,2 μm. Scharakteryzowano za pomocą mikroskopu sił atomowych (AFM) chropowatość PPI nie wywierała istotnego wpływu na badaną transmitancje i odbicie.
Słowa kluczowe: warstwy polimerowe, optyka cienkich warstw, poliazometyna, dyfuzyjne odbicie i transmitancja.

Thin polymer films are currently intensively investigated because of their promising optical and electrical properties which can be substantially changed by addition of various nanoparticles during the preparation process. In such conditions, additional optical phenomena, like the light scattering, can appear, if an admixture differs optically from the polymer matrix leading to complication in an analysis of the optical spectra of thin polymer films.

The light scattering originates from roughness of the film surface and from the volume scattering caused by nanoparticles embedded in the medium layer. Therefore, the diffuse reflectance is a sum of the surface scattering (a) and volume scattering (b) described below:

a) The surface scattering is connected with irregularities appearing on the polymer-substrate and polymer-air interfaces. The relation between the surface scattering reflection I_{ds} and root-mean square (*rms*) roughness σ_{rms} can be expressed in the first approximation as [1]:

$$I_{ds} = I_0 \frac{(4\pi\sigma)^2}{\lambda^2} \quad (1)$$

where: I_0 — *intensity of the specularly reflected light*, σ — *rms surface roughness*, λ — *wavelength of illuminating light.*

The validity of the above relation is fulfilled for $\sigma_{rms} >> \lambda$.

b) The attenuation of light described by the loss function is defined as the inverse distance, when the intensity of specular light decreases e-fold due to scattering by particles and the absorption process. Then the total loss coefficient is equal to

$$s_t = a + s_v \quad (2)$$

where: a — *absorption*, s_v — *volume scattering coefficient.*

In agreement with the Rayleigh classical theory, s_v at a given wavelength λ equals:

$$s_v = \frac{8\pi^3}{3N\lambda^4}\left(n^2 - 1\right)^2 \quad (3)$$

where: N — *concentration of scattering centers*, n — *the refractive index*.

For most polymer films, below the absorption edge, n decreases slowly with λ, in accordance with the Cauchy relation

$$n(\lambda) = n_0 + A/\lambda^2 \quad (4)$$

where: A — *constant coefficient.*

For longer wavelengths in the infrared range, the refractive index is practically constant.

The aim of this work is the presentation of simple interpretation of the optical reflectance and transmittance spectra of thin polymer films with nanoparticles.

*) Corresponding autor, e-mail: pujaglar@cyfronet.krakow.pl
1) Cracow University of Technology, Institute of Physics, ul. Podchorążych 1, 30-084 Kraków, Poland.
2) Polish Academy of Sciences, Centre of Polymer Chemistry, ul. M. Skłodowskiej-Curie 34, 41-819 Zabrze, Poland.
3) AGH University of Science and Technology, Dept. of Electronics, ul. Mickiewicza 30, 30-059 Kraków, Poland.

As an example, we chose one of polyazomethines, namely poly(1,4-phenylenemethilidynenitrilo-1,4-phenylenenitrilomethilidyne) (abbreviated as PPI) with nanoparticles in the form of natural crystallites formed during the deposition process.

EXPERIMENTAL

Preparation of PPI thin films

PPI thin films have been prepared by us using CVD technique (*Chemical Vapor Deposition*) *via* polycondensation process of *para*-phenylenediamine (PPDA) and terephthalic aldehyde (TPA), with Ar as a transport agent [2—4]. The Ar stream has been divided into two equal streams — one flowing over a boat containing PPDA and the other over a boat with TPA. The PPDA and TPA source temperatures have been fixed at 340 K (67 ^{o}C) and 326 K (53 ^{o}C), respectively, while the substrate temperature has been kept at 298 K (25 ^{o}C). Then, both streams have merged into one stream, molecules of both monomers have been mixed on their way to the substrate (glass or crystalline Si) forming finally a thin film of PPI on it.

Experimental equipment

The total and diffuse transmittance and reflectance spectra have been measured using a Perkin-Elmer Lambda spectrophotometer equipped with an integrating double-beam sphere (covered with spectralon) of 120 nm diameter (sphare 1) [5]. This instrument in which the xenon lamp is used as a light source, allows to measure the reflectivity spectra in 190—2500 nm wavelength range with a mean accuracy of 1 nm. Sample is illuminated with light beam of 10 mm diameter and the reflected light signal is collected under an angle of 8^{o} from the normal at the output port of 10 mm wide. A light trap switch made it possible to include the specular reflectance (switch on) or only the diffuse reflection (switch off). A simultaneous measurement of a white reference tile WS-2 placed on the second port, made from spectralon, has been also performed. The specular reflectance have been taken by subtraction of the diffuse reflectance from the total one.

Measurements of reflectance by means of a double-beam reflectometer or integrating sphere inform us about optical properties on the large area, *i.e.* 1—6 cm^{2}, of the samples. The results obtained on a much less reflecting area surface will be similar if the coverings and surfaces are homogeneous over the area and inside the layers. For the inhomogeneous surfaces, when topographic or material non-uniformities differ from tens micrometers to several mm, the measurements taken from the sphere and reflectometer give rather averaged reflectance over a larger scale of sample surfaces.

We have also measured the total and diffuse reflectances using a complementary reflection method applying a single-beam sphere technique with an OOI ISP--REF integrating sphere [5] of a diameter of 60 mm (sphere 2) with a build-in tungsten-halogen lamp as a light source. In this arrangement, a sample is illuminated with the diffuse light. The reflected light signal is then collected under an angle of 8^{o} from the normal (the so-called d/0^{o} geometry) and transmitted through an optical fiber to a PC-2000 spectrofotometer.

To get reflectance over smaller areas, the reflection probe R200-7 has been used. It consists of a bundle of 7 optical fibres, namely 6 illumination fibres around one "read fiber" (which read reflected light), each of diameter 100 μm. The probe is coupled by a read fiber to a A/D converter connected with a computer and by an illumination fibers to a laser diode 638 nm wavelength as a light source. The probe is mounted on a XY positioning stage A, commercial lead screw stepper motor actuating device is used in scanning XY (10 mm × 10 mm) with step of 0.1 mm. Optical profilometry (OP) measurements have been normalized with the calibration sphere method [6, 7]. It allows to obtain an optical map of topography with 0.1 mm lateral resolution.

Roughness of the PPI films studied have been determined by atomic force microscopy (AFM) yielding a typical value of roughness of the PPI films σ_{rms} = 12 nm.

RESULTS AND DISCUSSION

As it appeared from the roughness measurements, the contribution of the surface scattering to the total diffuse reflectance, calculated according to Eq. (1), is equal to 4 % and 1 % for 1000 and 2000 nm, respectively, and has been neglected in the further consideration.

An information related to the surface morphology can be also obtained from the optical measurements. Figure 1 shows the $R(\lambda)$-dependence (R — specular reflectance) determined by means of sphere 2, while Fig. 2

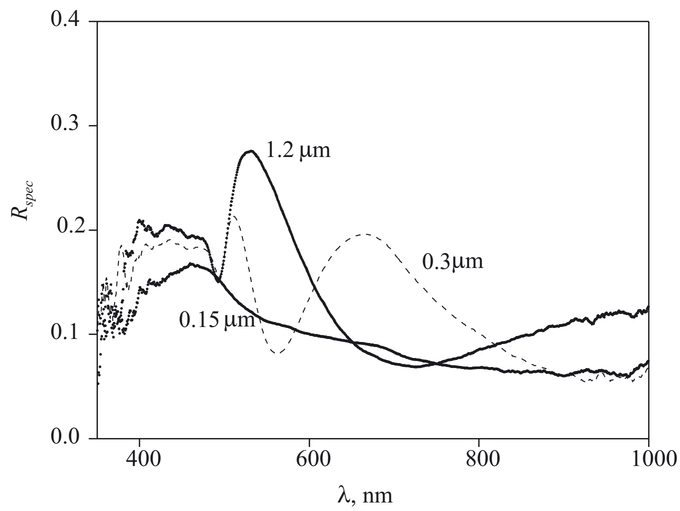

Fig. 1. Specular reflectance ($R_{spec.}$) spectra of PPI films with different thicknesses gathered with sphere 2

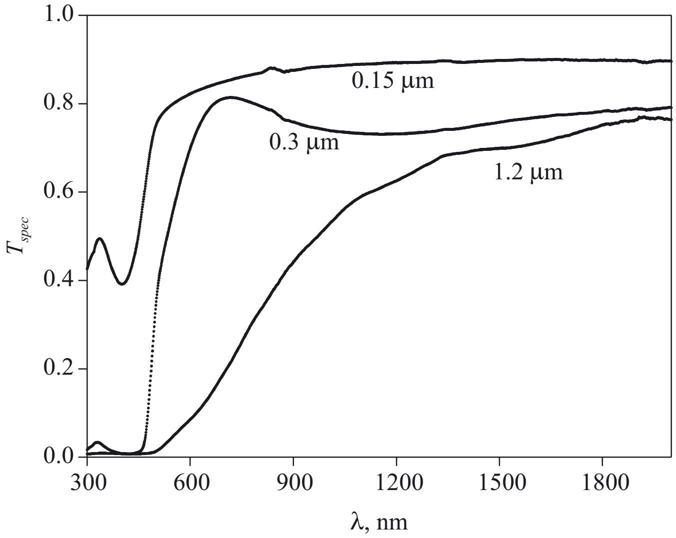

Fig. 2. Specular transmittance ($T_{spec.}$) spectra of PPI films from Fig. 1 gathered with sphere 1

presents the $T(\lambda)$-dependence (T — specular transmittance) for PPI thin films of various thicknesses.

In the investigated PPI films the spherolites crystallizing during the CVD process play the role of scattering centers. The type of scattering may be concluded from the wavelength dependence of the intensity of scattered light. If the average size of spherolites is less than 1/10λ, $I_{diff} \sim \lambda^4$ (Rayleigh scattering), for a greater size than 1/10λ, $I_{diff} \sim 1/\lambda$ (Mie scattering) and, finally, for a much greater size than λ, the diffraction scattering should be observed. In order to identify easily the type of light scattering, an integrating sphere can be used allowing measuring the diffuse reflectance R_{diff} and transmittance T_{diff}. If the spectra of R_{diff} and T_{diff} are close to each other, it results in a symmetrical distribution over the angles of scattering and the spatial distribution of intensity is independent on wavelength. These features are characteristic for the Rayleigh-type of scattering as can be seen from Fig. 3, which presents the diffuse transmittance of PPI samples with different thicknesses.

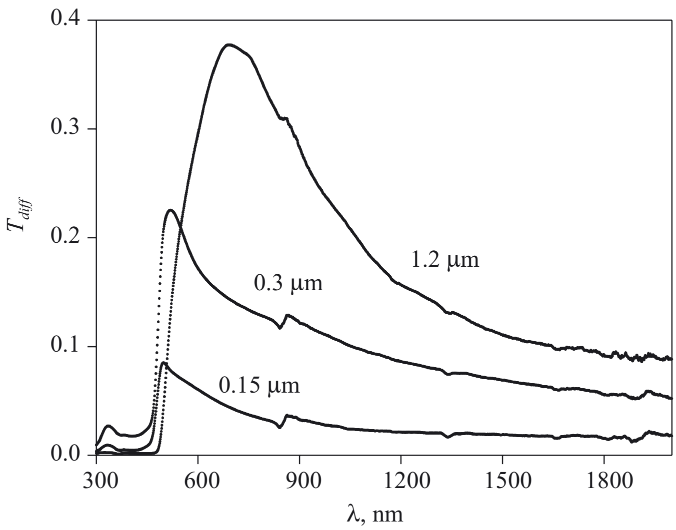

Fig. 3. Diffuse transmittance ($T_{diff.}$) spectrum of the PPI films, with different thicknesses (sphere 1)

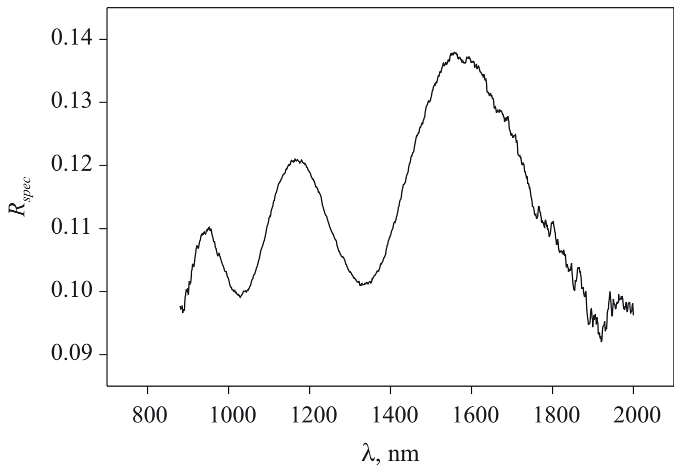

Fig. 4. Specular reflectance ($R_{spec.}$) of the 1.2 μm thick PPI film vs. wavelenght (sphere 1)

a)

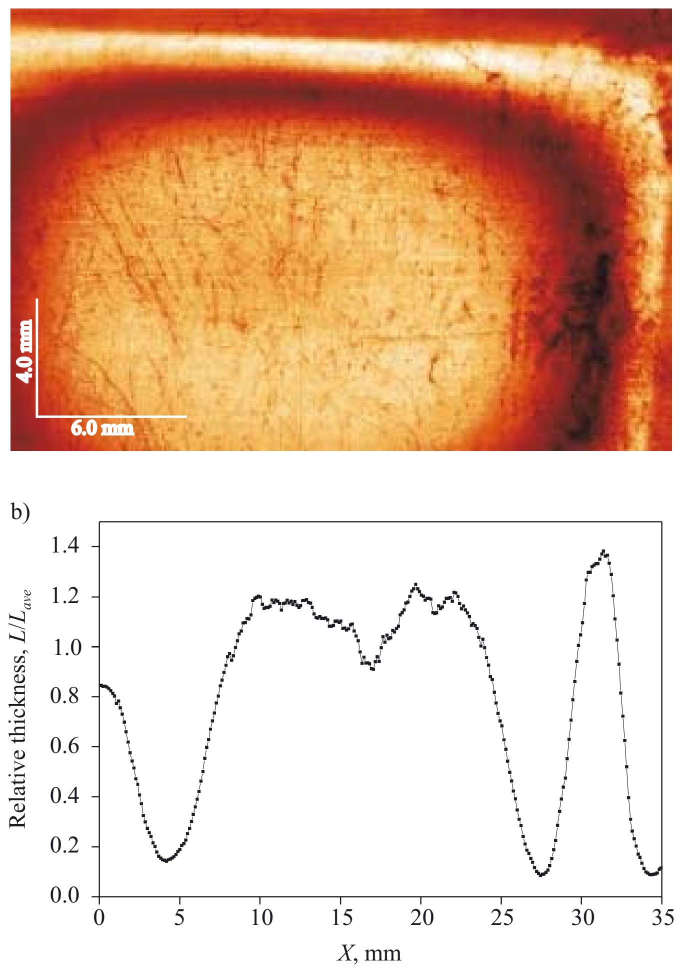

Fig. 5. Optical profile of the 1.2 μm PPI film (a) and X along cross — section (b)

The reflection from thin PPI film (thickness 1.2 μm) *vs.* wavelength (Fig. 4) shows interference maxima. If we neglects the Rayleigh scattering over the 1000 nm wavelength, the Fresnel reflection theory could be used. If also we assume the refractive index n is unchangeable in measured wavelength range (*e.g.* from 80 to 2000 nm), the thickness d can be determined from the phase difference $\phi = 4\pi n\ d/\lambda$. From these data, we have found thicker PPI sample: refractive index $n = 1.8 \pm 0.1$ and thickness $d = 1.2 \pm 0.1$ μm; other PPI films from Figs. 1 and 2 had thickness less than 300 nm.

For the thicker 1.2 μm sample, the optical map has been obtained using a XY profilometer as shown in Figs. 5a and b.

CONCLUSIONS

PPI films obtained by CVD technique exhibit strong optical scattering in the 500—2000 nm wavelength range. It is due to crystallites (spherolites) formed during the deposition process. The wavelength dependence of the diffuse reflectance shows the Rayleigh-type of scattering. For wavelengths longer than 1000 nm, the absorption and scattering are smaller, allowing to estimate the refractive index and thickness of PPI films from the specular reflectance data. Below 400 nm, the absorption process plays more significant role in the optical phenomena and therefore the diffuse scattering disappears, and the specular reflectance and transmittance are clearly observed. In spite of rather rough profiles of the investigated PPI films, their roughness does not give substantial contribution to the total transmittance and reflectance.

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