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Infrared synchrotron radiation from bending magnet and edge radiation sources for the study of orientation and conformation in anisotropic materials

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Over the last decade the use of synchrotron infrared microspectroscopy to spatially discriminate chemical and structural features in many different types of materials has grown considerably and has made significant impact in numerous research areas, in particular, in biological sciences and medicine. Although the brightness advantage of the synchrotron infrared (IR) source is well accepted as the key to high spatial discrimination, little attention has been given to measure the polarization properties of the synchrotron light at the sample stage in IR microscopy. In this work the intrinsic polarization of the IR source and its consequences for the study of anisotropic materials are discussed. The polarization characteristics of predominantly bending magnet radiation and predominantly edge radiation sources were measured at the microscope focus and compared. To illustrate the direct use of the intrinsic polarization of these sources in microscopy, the orientation and conformational details of a drawn polymer sample are considered. © 2011 American Institute of Physics. [doi:10.1063/1.3562900]

I. INTRODUCTION

Synchrotron infrared microspectroscopy, SIRMS takes advantage of the high brightness of synchrotron radiation, up to 10^3 times greater than conventional IR sources,^{1,2} providing spectroscopists with diffraction limited spatial resolution that approximates the wavelength of light,^{3,4} providing spatial discrimination between 3–15 μm in the mid-infrared spectral region, and up to $\lambda/2$ when a confocal optical arrangement is employed.⁵ It is known that relativistic sources generate well defined polarized light,⁶ which has to be added to the unique characteristics of the infrared synchrotron radiation. For IR microspectroscopy the possibility of exploiting the nature of this polarization is of great interest for the study of orientation and/or conformational behavior in anisotropic materials. Also, since no additional polarizing optical elements are needed when the light is well polarized, the analyst can take advantage of the whole flux available, a crucial point when high spatial discrimination with high signal-to-noise performance is required.

Synchrotron IR radiation at beamlines worldwide⁷ is extracted either at bending magnets, denominated bending magnet radiation (BM), and/or at the entrance of the bending magnet, denominated “edge” radiation (ER). While the polarization properties of these two sources has been well documented,⁸ from the users’ or analysts’ standpoint, the properties of the IR beam at the microscope focus on the sample stage are of fundamental interest.

In this work the polarization characteristics of BM and ER measured at the microscope focus point are described, and the validity of their use is discussed. Examples of the direct use of these polarized sources for the study of anisotropic polymeric materials are presented.

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II. EXPERIMENTAL

The work was performed at the SMIS beamline at the French Synchrotron SOLEIL.⁹ Both BM and ER are collected from a 2.75 GeV electron storage ring operating at a current of 400 mA in the top-up mode. In the optical design of the beamline, the BM and ER are spatially separated into two branches using a mirror.¹⁰ At the BM branch, a Continuum XL microscope coupled to a Nexus 5700 FTIR spectrometer (Thermo Scientific, CA) was used, and at the ER branch a Nic-Plan microscope coupled to a Nicolet Magna-FTIR 560 spectrometer (Thermo Scientific, CA) was used. In both microscopes, $32\times$ Schwartzchild objectives (N.A. 0.65) were employed and all measurements were made in the transmission mode.

The polymer sample used was a commercial resin of poly(ethylene terephthalate), PET (CAS Registry: 25038–59-9) kindly supplied as granules by Polyseda S.L. (Madrid, Spain). Thin films of around 20 μm thick were prepared in a Collin P200P Heated Press by melting for 5 min at 280 °C and 240 bar, and cooling rapidly to 15 °C between water-cooled plates to obtain a predominantly amorphous film (crystallinity <10%). Subsequently, rectangular samples with dimensions of 0.5 mm \times 40 mm were cut from the aforementioned film, and drawn in an Instron 3366 UTM dynamometer at a draw rate of 1 mm min⁻¹, to an extension ratio of 1.5 times the initial length. The samples were mounted on a rotatable sample holder for the SIRMS measurements.

III. RESULTS AND DISCUSSION

The calibration of the beam polarization on the sample stage of each microscope at both synchrotron branches was performed. In order to compare the results obtained with those from an almost perfectly linearly polarized IR source,

an independent experiment was initially performed using two separate wire-grid polarizers. First, IR light from a global source was polarized using a ZnSe wire-grid polarizer (Perkin Elmer), P1, a Harrick KRS-5 wire-grid polarizer, P2 was placed at the microscope focus point, and the detector intensity was measured through a $25 \times 25 \mu\text{m}^2$ aperture as a function of the angle of the electric vector of P2 with respect to that of P1. Figure 1(a) represents the peak-to-peak values of the voltage at the detector, V_{pp} as a function of the polarizer angle, normalized to the maximum V_{pp} value obtained when both polarizers were in the parallel arrangement. The expected graph for almost perfectly polarized light was obtained. The efficiency or the degree of extinction was calculated by taking the ratio of the minimum to maximum values of V_{pp} , i.e., when the electric vectors of P1 and P2 were perpendicular, it was found to be around 98%. This confirmed an almost perfect degree of linear polarization for both external polarizing elements, P1 and P2.

For the beamline branch measurements, the Harrick wire-grid polarizer, P2, was placed at the microscope's focus, was rotated, and the detector signal voltage was obtained in the same manner. However, in this case a projected aperture of $10 \times 10 \mu\text{m}^2$ could be employed due to the high brightness of the synchrotron IR source. Figures 1(b) and 1(c) show the results obtained for the BM branch and the ER branch, respectively. At the BM branch, it was observed that while the sig-

nal maxima and minima alternate every 90° with a substantial change in the signal values, complete extinction of the beam was not achieved. Quasilinear polarization of the source was observed, and a value of around 82% was estimated for the degree of linear polarization. At the ER branch a very similar behavior to that observed at the BM branch was found, and although pure ER is radially polarized, quasilinear polarization at the microscope focus was once again observed [Fig. 1(c)]. The degree of linear polarization in this case was estimated at around 78%. Further, at the ER branch the same behavior was observed when the polarizer was placed before the entrance to the microscope, implying that the various optical elements in the microscope do not appear to affect the overall polarization response. These experiments demonstrate that the BM portion of the extracted beam in the ER branch provides the dominant contribution to the polarization characteristics at the sample stage. The mixture of the two sources does not appear to significantly degrade the quasilinear polarization at the microscope focus point observed at the ER branch. Finally, while at the microscope focus the polarization axis of the synchrotron beam was found to be almost coincident with the x -axis of the microscope stage, the angular positions of the external polarizer for the maximum signal intensity, i.e., parallel polarization were found to be between 5° and 10° offset with respect to the experimental axis defined by the x -axis of the microscope stage. We expect that these values may vary slightly from beamline to beamline, given the many optical elements involved in the extraction of the source and its transfer to the experimental area, and careful calibration is important.

To demonstrate the validity of the direct use of the polarization properties of these sources, a series of spectra of a uniaxially oriented polymer film of PET were collected at polarization geometries parallel and perpendicular to the draw direction, using the polarization of the beam (by rotating the sample) and using a global source plus a polarizer (by rotating the polarizer). The spectra obtained are compared in Figs. 2(a) and 2(b) and show very good agreement between the data observed for both beamline branches. In Table I, the values of the absorbance ratios for some selected bands are presented for the case when the electric vector of the incoming light is parallel and perpendicular to the stretching direction. The 1370 cm^{-1} band is assigned to a CH_2 wagging mode, and 1505 and 1578 cm^{-1} are assigned to ring deformation modes. The broad band at 1456 cm^{-1} is associated with the CH_2 bending modes and is generally used as a reference band.¹¹ Slight differences can be observed in the values found, which can be expected taking into account the

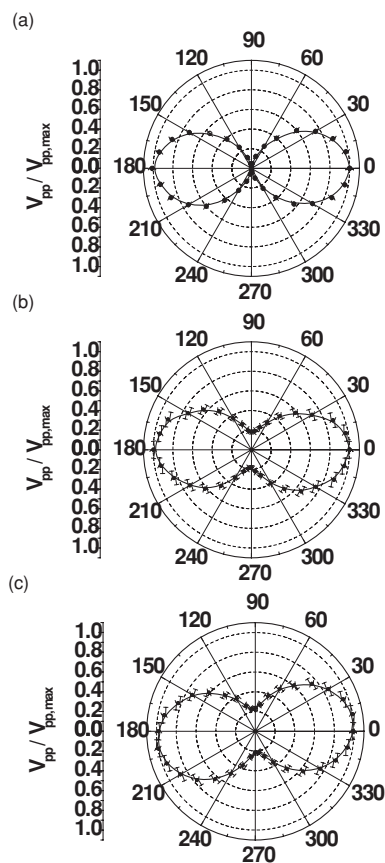


FIG. 1. Calibration of the polarization of the beam at the microscope's focus point: (a) Global plus external polarizer; (b) BM branch; and (c) ER branch. Horizontal axes correspond to the x -axis of the microscope stage and the electric vector of the synchrotron IR beam.

TABLE I. Absorbance values for some PET bands, ratioed to the 1456 cm^{-1} band.

Band (cm^{-1})	Parallel (\parallel)			Perpendicular (\perp)		
	Global + polarizer	BM branch	ER branch	Global + polarizer	BM branch	ER branch
1370	0.18	0.22	0.21	0.21	0.21	0.21
1505	0.47	0.43	0.44	0.16	0.22	0.22
1578	0.40	0.40	0.40	0.12	0.18	0.18

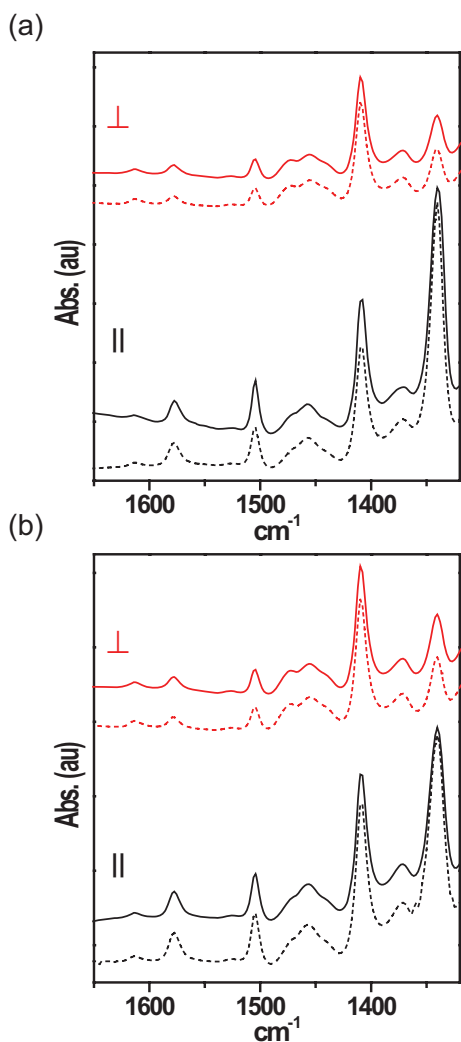


FIG. 2. (Color online) Comparison of the polarized spectra of oriented PET with and without external polarizer: (a) BM branch; (b) ER branch. Continuous line: beam; Dotted line: global plus polarizer; \parallel and \perp refer to orientation of the sample draw axis with respect to the x -axis of the microscope stage.

greater degree of linear polarization of global source plus external polarizers. This variation is more important for the 1505 and 1578 cm^{-1} bands. This is due to the fact that the 1370 cm^{-1} band shows little IR dichroism, whereas the ring deformation modes are highly parallel polarized, and thus a more significant deviation appears in the perpendicular arrangement. It is relevant to indicate that bands that show strong orientation behavior have very slightly larger absorbance difference values when the external polarizer is used, to be expected due to the higher degree of linear polarization obtained with the commercial polarizer.

While the excellent agreement validates the possible exploitation of the natural polarization of the synchrotron beam, it should be noted that very careful positioning of the sample is required. This is generally not a difficult issue at synchrotron facilities, as often samples must be moved between several techniques, and position referenced sample holders are habitual.

Thus, it is very important to carefully control both the sample characteristics and positioning. Slight variations in the

positioning of the sample at the micron scale may lead to important differences in the data that may be misinterpreted by the analyst. This is a fundamental point to consider when performing SIRMS with anisotropic materials, since the source is highly polarized and the spectra will respond to orientation effects.

The polarization properties of infrared BM sources have already been exploited to measure orientation and anisotropy in semicrystalline polymers.^{12,13} However, to illustrate the possibility of the direct use of the polarization properties at both BM and ER beam branches, spectral line maps have been acquired for uniaxially stretched PET (aperture size: $8 \times 8 \mu\text{m}^2$; $2 \mu\text{m}$ step; spectral resolution: 4 cm^{-1} ; 64 scans). This polymer deforms through the so-called bottle-neck formation when subjected to a cold-drawing process, i.e., at temperatures below its glass transition temperature. The necking region is the frontier between the randomly ordered polymer and the zone where the polymer chains are oriented along the direction of the applied external deformation.¹⁴ The high brightness of the synchrotron IR beam at both beamline branches allows the inspection of this micrometric sized area with an adequate spatial resolution, and exploitation of the polarization characteristics allows orientation information to be obtained across the necking region of the material by using the classic dichroic ratio, $D = A_{\parallel}/A_{\perp}$, where A_{\parallel} and A_{\perp} correspond to the absorbance values obtained when the electric vector of the beam is parallel or perpendicular, respectively, to the draw axis of the material. Clearly, other more complicated orientation functions can be applied. In addition, in order to study conformational changes in anisotropic samples we can calculate the so-called *structural factor* spectra¹⁵ that can be effectively employed to remove orientation related effects in the spectral data.¹⁶ In the present case, the cylindrical symmetry of the applied uniaxial deformation means that the *structural factor* absorbance, A_0 can be calculated by the simple relation $A_0 = (A_{\parallel} + 2A_{\perp})/3$. Spectral line scans were recorded for each polarization by precisely positioning the sample draw axis parallel and perpendicular to the beam polarization direction at the same measurement points within an experimental error estimated at $\pm 1 \mu\text{m}$. A schematic representation of the line along which the spectra were acquired is shown in Fig. 3. The orientation behavior of the polymer was examined by calculating D for several bands at each spatial position. The conformational changes were then considered by analyzing the calculated *structural factor* spectra.

Figure 4 shows, from the spectra recorded at both the BM and ER branches, the calculated dichroic ratios of key bands providing information from the two moieties present in the structural repeat unit that constitutes the polymer: the 1340 cm^{-1} band corresponds to CH_2 wagging and is related with the aliphatic portion, while the 1505 cm^{-1} band is assigned to a ring deformation mode giving information on the terephthaloyl moiety.¹⁷ At position A in Fig. 3, a value of $D = 1$ is observed that is expected for a randomly oriented polymer. Through the necking region a progressive increase in D is observed. Since both bands show parallel dichroism, i.e., $D \geq 1$, this rise in D is indicative of orientation of the polymer chain segments in the draw direction. Moreover, the high spatial contrast allows us to discriminate slightly higher

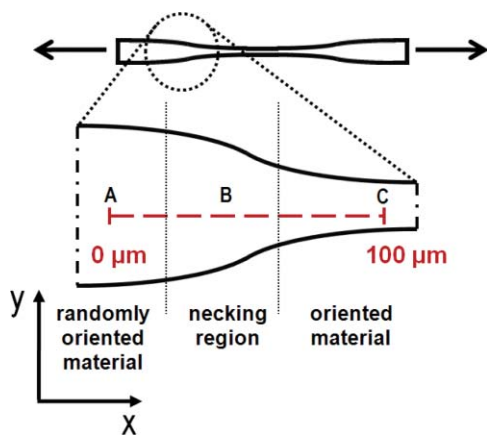


FIG. 3. (Color online) Schematic representation of the line along which the spectra were acquired.

orientation of the polymer chains at the necking point, B. This is coherent with a greater degree of tension in the chains at the necking point, which subsequently relax to some extent in the plastic deformation region, C with respect to the necking zone. By comparing Figs. 4(a) and 4(b), we can observe that the results are essentially similar at both branches.

Conformational changes can be revealed by obtaining the ratio of the $1340\text{--}1370\text{ cm}^{-1}$ bands from the structural factor spectra (Fig. 5). Both bands are attributed to a CH_2 wag-

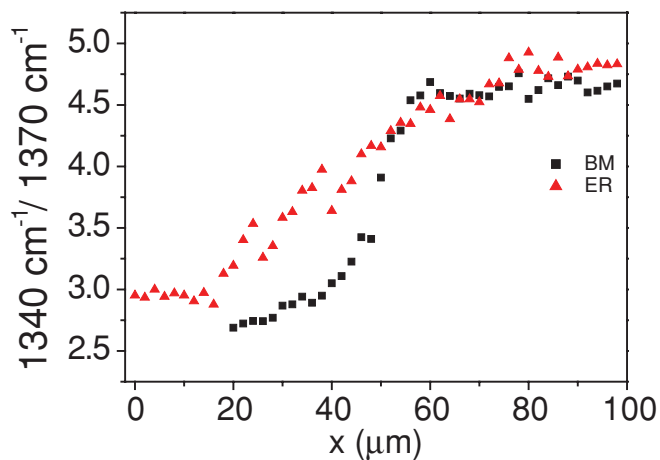


FIG. 5. (Color online) $1340/1370\text{ cm}^{-1}$ band ratio (*trans* to *gauche* conformers) from the calculated structural factor spectra along the line mapped.

ging mode, the former associated to a *trans* conformation of the $\text{CH}_2\text{--CH}_2$ bond, while the latter is related to *gauche* conformations.¹⁸ A rise of the *trans* to the detriment of the *gauche* conformers is found along the necking region, as expected, since *trans* is the extended chain conformation of the aliphatic moiety. Slight differences were observed between BM and ER measurements across the neck, however, these are most probably related to slight variations in the sampled region and focusing across the neck, and the orientation and conformational results obtained are essentially the same at both beam branches.

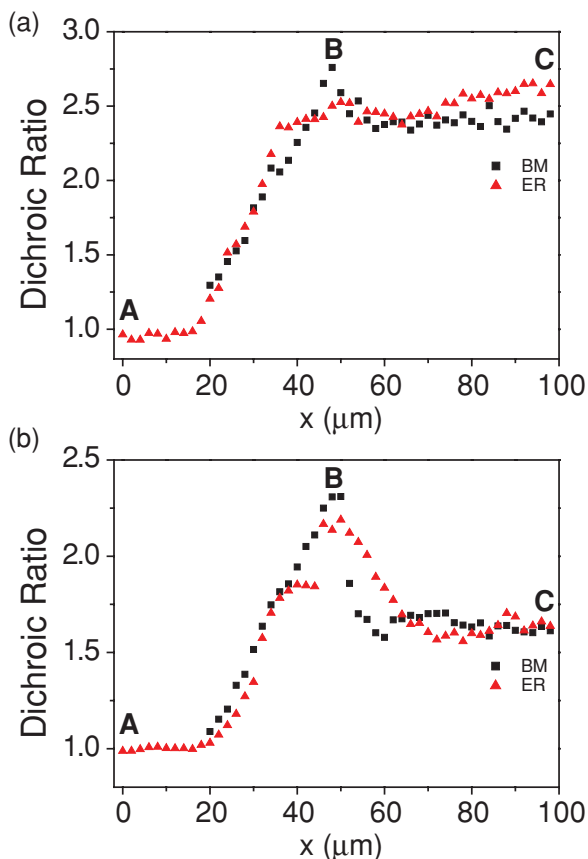


FIG. 4. (Color online) (a) Dichroic ratio for the 1340 cm^{-1} band (CH_2 wagging mode) at both beamline branches. (b) Dichroic ratio for the 1505 cm^{-1} band (ring deformation mode) at both beamline branches.

IV. CONCLUSION

The calibration of the polarization properties of the IR beam at the microscope focus point at BM and ER branches of the SMIS beamline at SOLEIL reveal that both sources present quasilinear polarization. In the case of the BM branch this behavior was expected, while for ER sources the impossibility to isolate pure ER from the continuous field contribution leads once more to a quasilinear polarization at the microscope sample stage. Examples of the feasibility of the direct use of the polarization properties of these sources to obtain information on orientation and conformation in a drawn polymer sample has also been presented, confirming that the natural polarization of the IR beam from both BM and ER sources can be effectively exploited with high spatial discrimination. Finally, it is very important to point out that the high degree of polarization of synchrotron IR sources will clearly affect the spectral data obtained from anisotropic materials, and compensation must be for this when a sample presents orientational heterogeneity.

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⁷A full list of synchrotron facilities including those with IR beamlines can be found at www.lightsources.org.

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