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Imaging of Three-dimensional Orientation of Molecules in Polymers Using FT-IR, Raman, and O-PTIR Microspectroscopies

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Extended Abstract

Fourier transform infrared microspectroscopy (FT-IR) is a nondestructive, information-rich, and label-free technique successfully applied for years in material science. The introduction of linear polarization enriches the technique with the possibility of studying the orientation of macromolecules. Until now, experiments focused on using the absorbance of a single band to retrieve the in-plane orientation and the degree of order. The extended four-polarization (4P) method, which enables the visualization of the macromolecule orientation regardless of the choice of the direction of polarization, was proposed by Hikima et al. for polymers [1]. The application of IR imaging with 4P on heterogeneous structure, human tissue microarrays, was presented for the first time by our team in 2020 [2], [3].

A deeper characterization of the sample structure is the next step. Simultaneous analysis of two bands of roughly perpendicular transition moment orientations was proposed by Lee in 2018 as a method of determining the orientation of the molecule in three-dimensional space [4]. The first application of "concurrent analysis" (4P-3D) to infrared spectromicroscopic data and obtaining orientation angles of a model polycaprolactone spherulite sample was presented by our team in 2021 [5]. The applicability of this method ranges from high-resolution, diffraction-limited FT-IR and Raman imaging to super-resolution O-PTIR imaging. We proved that this method can be easily applied not only to FT-IR but also to O-PTIR and Raman imaging. Calculated orientation of asymmetrical stretching vibration C-O-C allowed concluding about fibrils orientation in spherulites formed with edge-on lamellae.

Spatial, non-destructive orientation studies are expected to have a profound impact on materials and life sciences as a method of extracting previously unattainable information from complex systems. The 4P-3D method will be available to users from all over the world on the SOLAIR Beamline in Solaris National Synchrotron Radiation Centre in the near future.

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