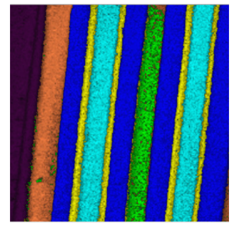
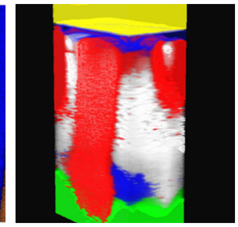
Raman Microscopy

# Raman Microscopy Applied to Polymer Characterization: An Overview





Application Note

Polymers RA76

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**Abstract:** Raman microscopy is an excellent tool to address the polymer research. Raman microscopy can be used to characterize raw materials, to inline or outline monitor polymerization process, to investigate orientation and crystallization changes, and also to control the quality and traceability of genuine products, by understanding defects and compounds distribution. In this article we present how HORIBA Raman microscopy solutions can support the polymer chemical and structural understanding.

**Keywords:** Raman microscopy, Polymer, Product control, Process monitoring, Crystallinity

## Introduction

In the polymer field, Raman microscopy has become one of the most important characterization tools due to the large number of chemical and structural information which could be extracted from a single result. Thus, Raman microscopy can help from raw material characterization to genuine product control, from synthesis process to defect investigation, covering the whole process of polymers manufacturing. These unique capabilities of Raman microscopy, are presented in this article, focusing on some academic and industrial applications for polymers field.

## Raw material characterization

Raman microscopy is an optical technique providing a spectra based on the polarization changes of molecular vibrations. Each band of a Raman spectrum is the fingerprint of a specific molecular vibration in its chemical environment. Thus, each molecule will have its specific Raman spectrum. Consequently, two molecules based on similar chemical bonds, but with a different chemical structure, will have two different Raman spectra. Raman spectra can be so used as identification tools by cataloging a collection of spectra. Nowadays, a huge number of spectra are already cataloged and converted to a robust spectra library, which can be installed on the instrument computer for a fast, automatic and precise identification by software. Figure 2 demonstrates how easy it can be to identify an unknown polymer from its Raman spectrum. For instance, polymers with a carbonyl group have a band between 1650 and 1750 $cm^{-1}$.

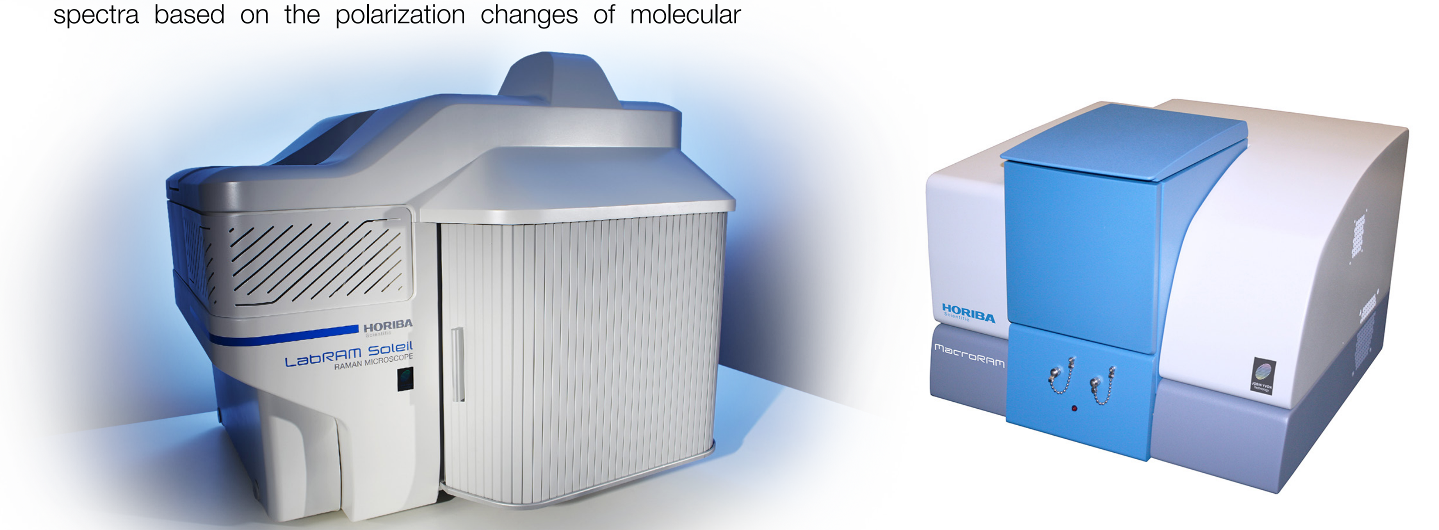


*Figure 1: Our Raman solutions for the polymer industry. Left:* ***LabRAM Soleil™****. Right:* ***MacroRAM***

Such spectral differentiation requires a Raman instrument with high sensitivity and a good spectral resolution. It becomes so easy to characterize the exact type of polymers using a state-of-the art Raman microscope as the HORIBA **LabRAM Soleil™**. Indeed, this system is the perfect combination between spatial resolution, spectral resolution and sensitivity, all integrated in an easy-to-use platform.

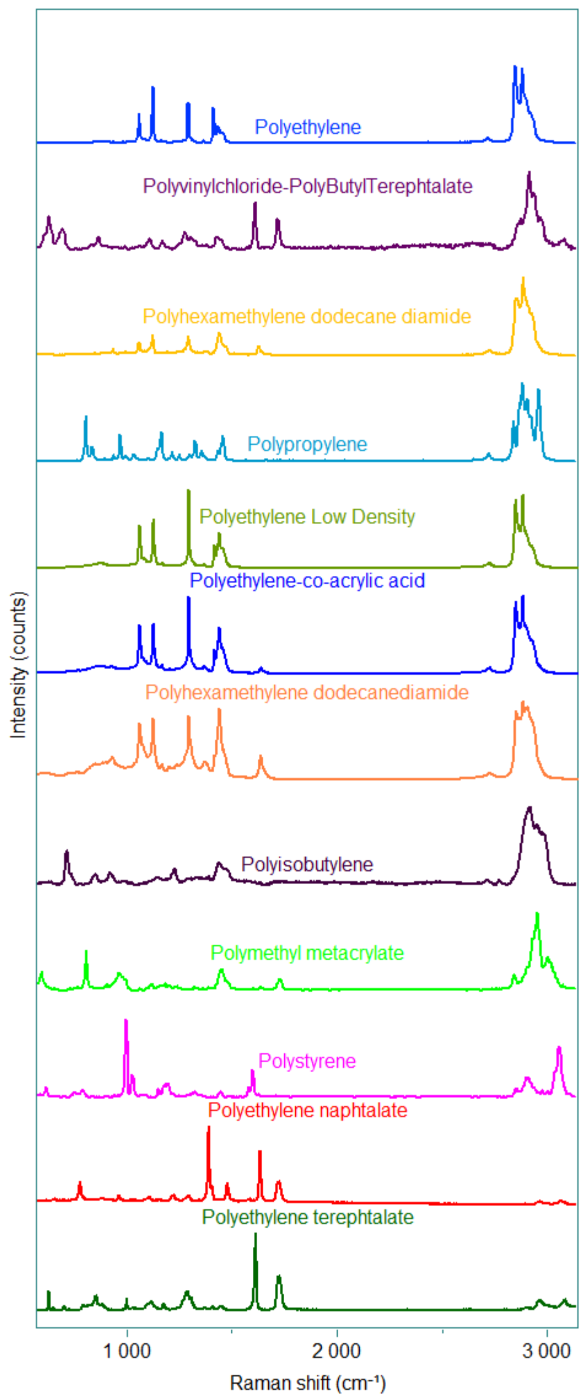


*Figure 2: Raman spectra of different polymers*

## Polymerization process monitoring

The characteristics of the Raman microscopy instrument (non-invasive, non-destructive, in-line measurements) make it an excellent tool for polymerization monitoring. As each process compound has its own fingerprint, monitoring the polymerization becomes easy using specific process probes, coupled with an integrated Raman instrument as **MacroRAM**. An example of process monitoring is shown on Figure 3. The concentrations of reagents ($VC_2$ in green and ACM in purple) decrease over time, where the polymer contribution increases during this polymerization process.

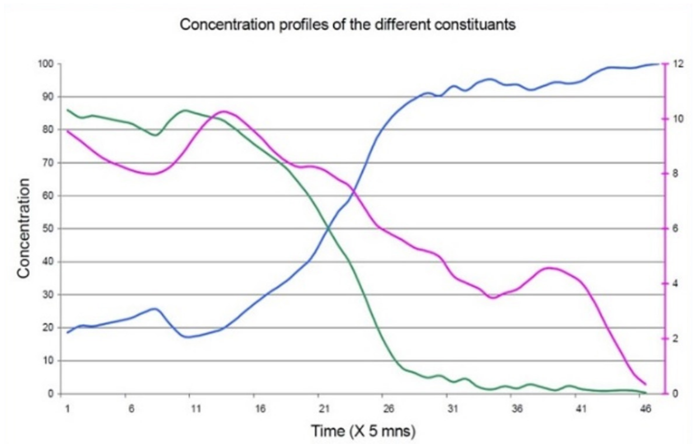


*Figure 3: Polymerization monitoring based on Raman microscopy. Reagents are in green ($VC_2$) and purple (ACM), polymer synthesized in blue.*

## Orientation and Crystallization

When extruded, polymers tend to "orient". That means that the molecular axis aligns along the extrusion direction. By orienting the sample in the instrument coordinate holder and analyzing the polarization of the Raman light, it is possible to infer information about the orientation of the polymer. This can have implications on the mechanical and other physical properties of the polymer. For example, Richard-Lacroix & Pellerin (*Macromolecules*, 2012, 45,1946-1953) demonstrate that confocal Raman microscopy is a powerful method to quantify molecular orientation and structure at the individual fiber level. They applied this technique on single electrospun nanofibers used for producing nanomaterials for catalysis, biosensors, drug delivery, and other applications. On such fibers, being able to characterize them one by one is a critical point. That is what can be easily done with the HORIBA **LabRAM HR Evolution**.

Like inorganic materials and molecular crystals, polymers can exist in a crystalline form. The degree of crystallinity which is usually not greater than 50%, is determined by the thermal and stress history of the sample. Thermal and stress modifications induce very small spectral changes observed as spectral shifts of the bands. In order to observe such shift, the highest spectral resolution becomes necessary. The HORIBA **LabRAM HR Evolution** is the perfect solution for thermal and stress investigations. Thus, one can monitor the crystalline form of polymers by following some details in the spectra: In polyethylene terephthalate, for example, the >C=O band tends to sharpen significantly in the crystalline form. The effects of both orientation and crystallinity in the Raman spectra of polyethylene terephthalate fibers have been documented by Adar and Noether, *Raman Microprobe Spectra of Spin-Oriented and Drawn Filaments of Polyethylene Terephthalate*, Polymer, 1985 26 1935-1943.

## Genuine product control

Most of the time, polymer films are combined to improve the physical and chemical properties of the desired product. For this reason, multilayer films are developed, where each layer brings its own chemical and physical characteristic to the final product. The order, the thickness of the different layers and the layer stitching, as well as the crystalline form and the polymer orientation, are critical parameters in polymers. The HORIBA **LabRAM Soleil™** Raman microscope is the perfect tool to characterize these products based on its selectivity and high spatial resolution, at micron size. An example of multilayer film characterization is shown on Figure 4. This sample is the combination of Low-density polyethylene **(orange)**, Blue low-density polyethylene **(blue)**, Ethylene vinyl alcohol **(cyan)** and Ethylene vinyl acetate **(green)**, interlayered with Polyamide **(yellow)**.

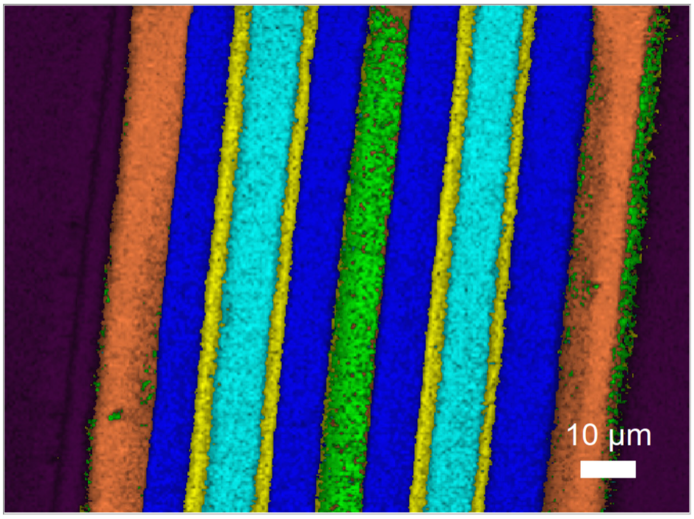


*Figure 4: Multilayer film characterization by Raman mapping. Each color represents a specific type of polymer. **Orange**: Low-density polyethylene. **Blue**: Blue low-density polyethylene, **Cyan**: Ethylene vinyl alcohol, **Green**: Ethylene vinyl acetate, **Yellow**: Polyamide.*

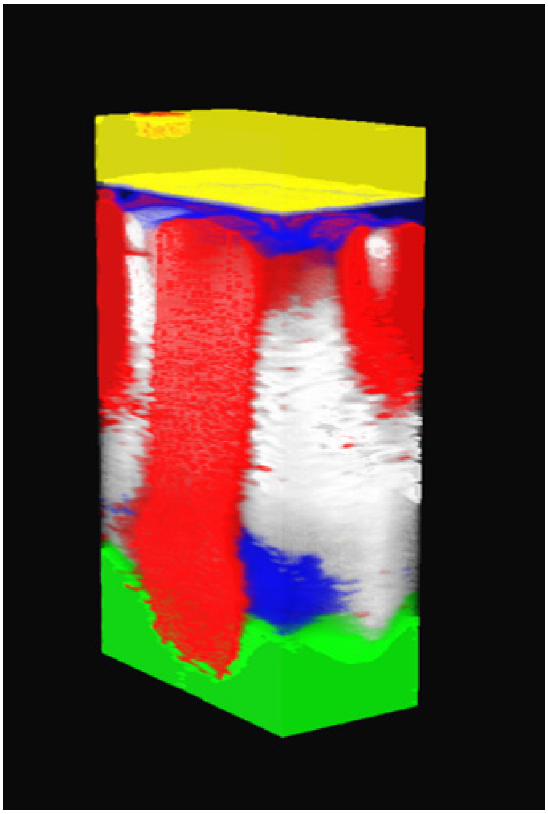

*Figure 5: 3D Raman map of a multilayer film polluted with an outlier (white). **Yellow**: Polypropylene, **Blue**: Polyethylene, **Red**: Polyethylene low-density, **Green**: Polyvinyl-chloride, **White**: Polyamide.*

## Defect investigation

Another major requirement for the polymer industry is the investigation of defect sources. Such defects can come from an outlier during the manufacturing process, from a polymorphism issue, or simply from a physical or temperature stress and/or strain on the film. Each of these sources can be identified based on the Raman spectrum of the defect. Confocal Raman microscopy allows a high spatially resolved characterization of multilayered film on the surface, but also along the depth axis of the film. The HORIBA **LabRAM Soleil™** microscope, with its the true confocal pinhole and its high sensitivity, is the perfect tool to characterize and investigate origin of defects. On Figure 5, such investigation is illustrated by using the capabilities of outstanding LabSpec 6 software, presenting a 3D Raman mapping of a multilayer film with visible defects. The Raman map shows the different layers (yellow: Polypropylene, blue: Polyethylene, red: Polyethylene low-density, green: Polyvinyl-chloride), but also the presence of an outlier (white: Polyamide). Based on the Raman map, it becomes easy to understand that the outlier occurred in the manufacturing process at the level of the red layer.

## References


- Raman Microprobe Spectra of Spin-Oriented and Drawn Filaments of polyethylene terephthalate", Adar & Noether, *Polymer*, 1985, 26, 1935-1943.
- "Orientation and Structure of Single Electrospun Nanofibers of Poly(ethylene terephthalate) by Confocal Raman Spectroscopy", Richard-Lacroix & Pellerin, *Macromolecules*, 2012, 45,1946-1953.
- "Polarized Raman analysis of polymer chain orientation in ultrafine individual nanofibers with variable low cristallinity.", Papkov and al., *Macromolecules*, 2018, 51(21), 8746-8751.
- "Cold gas spray titanium coatings onto a biocompatible polymer.", Gardon M. and al, *Materials Letters*, 2013, 106, 97-99.
- "Direct detection of analyte binding to single molecularly imprinted polymer particles by confocal Raman spectroscopy.", Bompart M. and al., *Biosensors and Bioelectronics*, 2009, 25(3), 568-571.



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