

Polymer Polymorph

The Challenge

The commercial appeal of High-Density Polyethylene (HDPE) lies not only in its cost competitiveness but also its wide-ranging versatility. For example, HDPE's structural properties can be modified via annealing to affect the long-range order over a certain critical distance, known as the lamellar thickness. Varying the annealing method leads to variations in the lamellar thickness and the degree of crystallinity, which can directly affect the mechanical performance of the plastic. This variability makes it useful in applications from milk jugs and bottle caps to plastic bags and plastic lumber.

Traditional Solutions

Raman spectroscopy has potential for this measurement, as it requires no sample preparation and can provide real-time, non-contact, non-destructive measurements, making it an ideal tool for online or at-line monitoring of changes in polymers structure. However, as can be seen below, there is insufficient differentiation to distinguish HDPE samples with different lamellar thicknesses using the conventional region of the Raman spectra ($200\text{-}2000\text{ cm}^{-1}$). Alternative techniques, including X-ray diffraction (XRD), are incapable of providing real-time or actionable information.

The Coherent Solution

The figure below shows the complete THz-RamanTM spectra of HDPE samples that have different lamellar thicknesses. These spectra were measured using a Coherent TR-Micro-785 THz-Raman system, with an acquisition time of one minute. The Raman "chemical fingerprint" spectra (from $200\text{ to }2000\text{ cm}^{-1}$) for these four samples are remarkably similar. However, there is a clear difference in the peak positions and band shape for the low frequency region (from $-200\text{ to }+200\text{ cm}^{-1}$, also known as the "structural fingerprint" region), as highlighted in the figure on the right. While the chemical structure remains unaltered, the difference in lamellar thickness affects the position of the longitudinal acoustic modes (LAM) in the region below 150 cm^{-1} , which can be clearly seen.

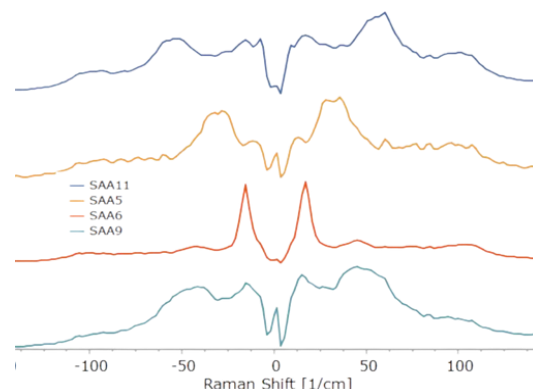


Figure 1. Low-Frequency/THz-RamanTM of HDPE

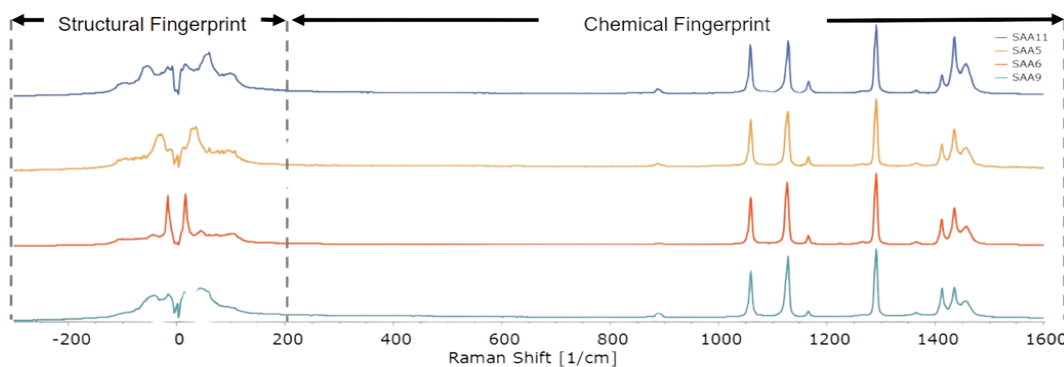


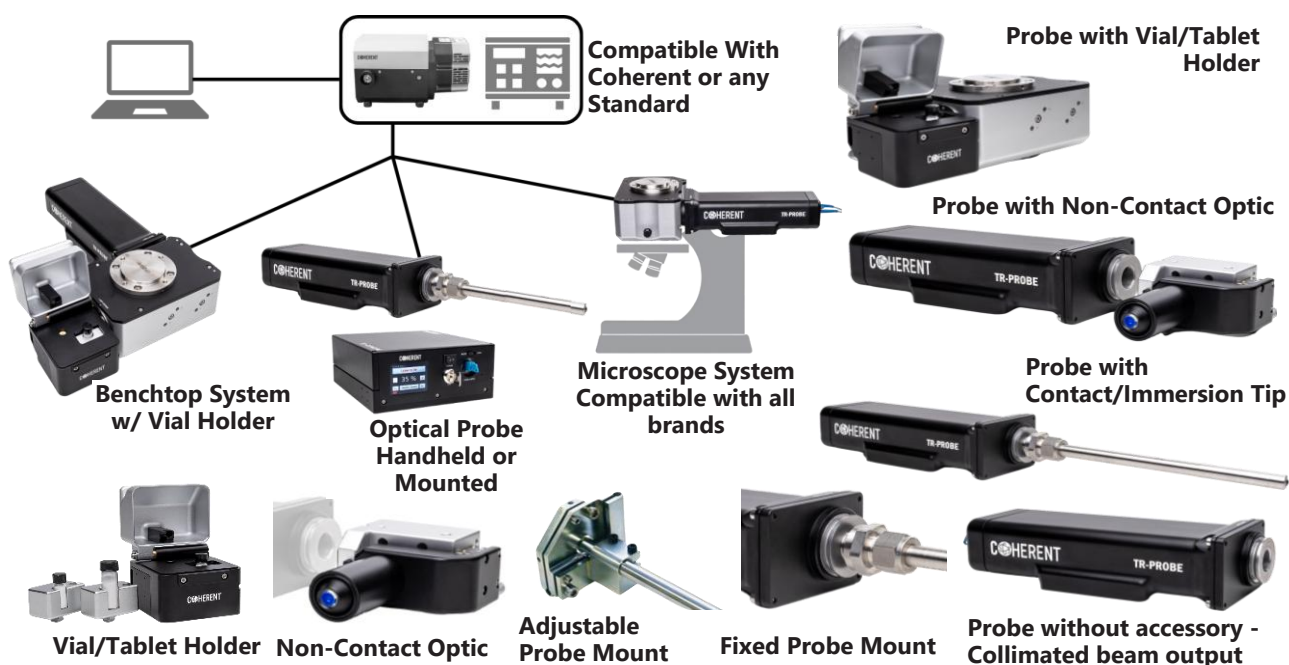
Figure 2. The complete THz-RamanTM spectrum of HDPE

THz-Raman PLUS fingerprint region measurement with the same system

All TR-Series THz-Raman™ modules are ultra-compact and simple to connect via fiber to almost any spectrometer or Raman system. A high-power, wavelength-stabilized, single-frequency laser source is precisely matched to the ultra-narrow-band ASE, beamsplitter and notch filters to assure maximum throughput and exceptional attenuation (>OD 9) of the excitation source. Systems are available in 532 nm, 633 nm, 785 nm, 850 nm, 976 nm and 1064 nm excitation wavelengths.

The new TR-PROBE is a compact, robust THz-Raman™ probe that enables in-situ reaction or process monitoring. The TR-PROBE can be configured with a variety of sample interface accessories, including immersion or contact probe tips, a convenient vial/tablet, or a steerable non-contact optic (see options below). A separate Cleanline™ laser provides ASE-free excitation via a multi-mode fiber, enabling the probe to operate in harsher environments where electrical connections are not permitted.

Coherent THz-Raman™ modules are compatible with virtually any commercial Raman system or spectrometer, and Coherent can recommend or integrate an appropriate spectrometer and deliver as a complete turnkey system.



A variety of sample interface accessories enable the TR-PROBE and TR-BENCH to be easily configured for a broad range of applications. Immersion or contact probe tips can be mounted with either a fixed SwageLok mount or, for longer probes requiring alignment, an adjustable tip/tilt probe mount. The Vial/Tablet Sample Holder includes an adjustable steering mirror, interchangeable focusing lens, and safety shutter. Additionally, the Steerable Non-contact Optic Mount allows for precise alignment of the output beam projection and steering, with interchangeable focusing optics for applications requiring long-range collection paths. The accessories can also be rotated around the dovetail mount to achieve any angle of incidence.