ONDAX
Advanced Solutions for Optical Measurements

ANALYSIS OF CRYSTALLIZATION KINETICS OF POLYMERS

THE CHALLENGE

The development of new polymer materials requires an in depth understanding of the kinetics of crystallization. Raman spectroscopy is extremely well suited to the study of structure/process/property relationships in polymers, since it is sensitive to the base chemical structure, conformational states and to crystallinity. The crystal lattice modes found in the low-frequency regime from 10 to 200 cm-1 can greatly enhance structural analysis, but are outside the collection range of conventional Raman instruments. These modes are easily accessible using Ondax's low frequency/THz-Raman® spectroscopy solutions.

THE ONDAX THz-RAMAN® SOLUTION

In this example Ondax's THz-Raman® solution was used to study Nodax™ (introduced by MHG, Inc), a novel bio-based plastic, that is completely biodegradable. The sample was heated above the melt temperature, pressed, quenched and brought to the crystallization temperature of 25°C. **Figure 1** shows the time-dependent Raman spectra of this isothermal crystallization process in the first 10 min after reaching the crystallization temperature. As the crystallization of the polymer proceeds, gradual changes in the spectral features indicate a reduction in amorphous component and an increase in crystalline content. Visualization of the kinetics of crystallization are most effectively analyzed by using the generalized 2D correlation technique.*

Figure 2 shows the asynchronous 2D correlation spectra where a positive cross peak (unshaded) indicates the spectral intensity change at Raman shift Dn_1 occurs predominantly before that observed at Dn_2, while a negative peak (shaded blue) indicates the opposite. We observe that early crystallite nucleation (1734 cm^{-1}) occurs first, followed by the primary growth of well-ordered crystals (1725 cm^{-1}) of the polymer. Secondary crystal growth (1730 cm^{-1}) happens at a later stage accompanied by a reduction of the amorphous component (1735-1750 cm^{-1}), which occurs most dominantly during the primary crystal growth. The 2D correlation spectrum of the low frequency lattice modes, clearly identifies the known vibrational modes of 2_1 helical structure at 80 and 96 cm^{-1}, vibration between helices around 72 cm^{-1}, and the broad amorphous contributions stretching below 66 cm^{-1}.

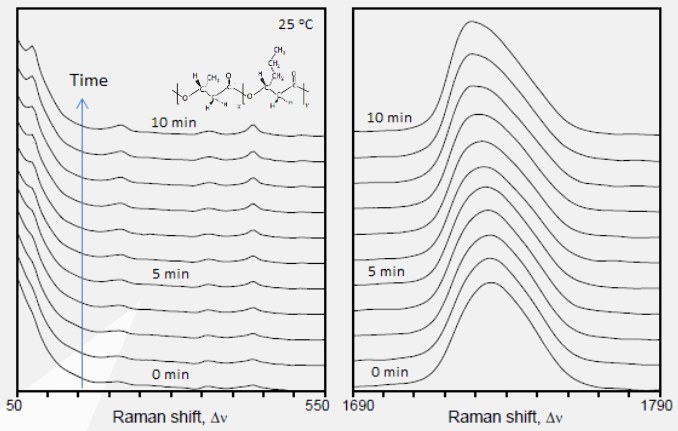
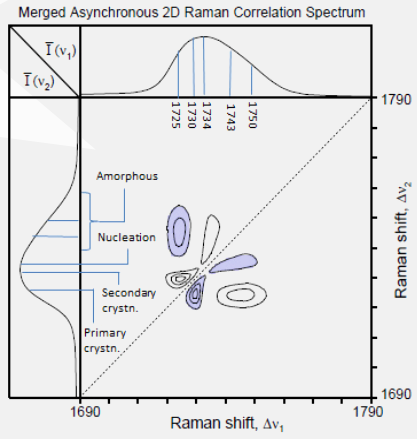


Fig 1. Time-dependent Raman spectra of Nodax™ PHBHx copolymer during the isothermal crystallization at 25°C comparing the low frequency THz region of Raman spectra (left) and C=O stretching region (right). Note the emergence of a low-frequency peak as time lapses and crystallinity increases.



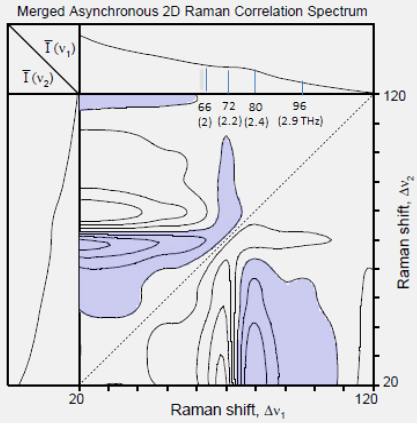


Fig 2. Merged asynchronous 2D correlation spectrum of the time-dependent THz-Raman® spectra showing the C=O stretching (top) and lattice modes (bottom).

*I. Noda, Appl. Spectroscopy 47 (1993) 1329-1336

THz-Raman®

CRUCIAL COMPLEMENTARY INFORMATION

The Ondax THz-Raman® system enables simultaneous collection of both the lattice modes and C=O stretch, enabling a comparison of crystallization kinetics with the corresponding lattice modes to learn what role lattice form plays in the crystallization process. The merged asynchronous 2D correlation spectrum of these two regions shown in Figure 3 reveals that the development of a fully formed lamellar structure comprising the 2_1 helices occurs after the primary growth of crystals. This suggests that internal restructuring within the lamellae is required for the coordinated vibration of fully formed helices to begin. The later stage secondary crystallization, which is believed to take place within the confined inter-lamellar space, occurs after the full formation of packed helices comprising the lamellae is complete. Using the complete Raman spectrum, a much deeper understanding of crystallization kinetics can be achieved.

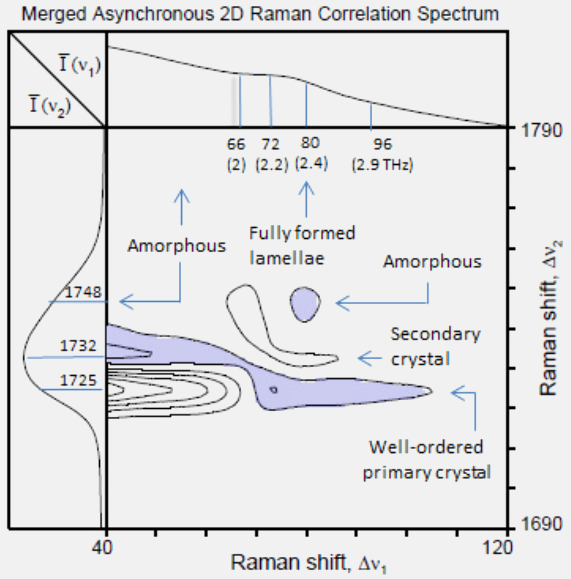
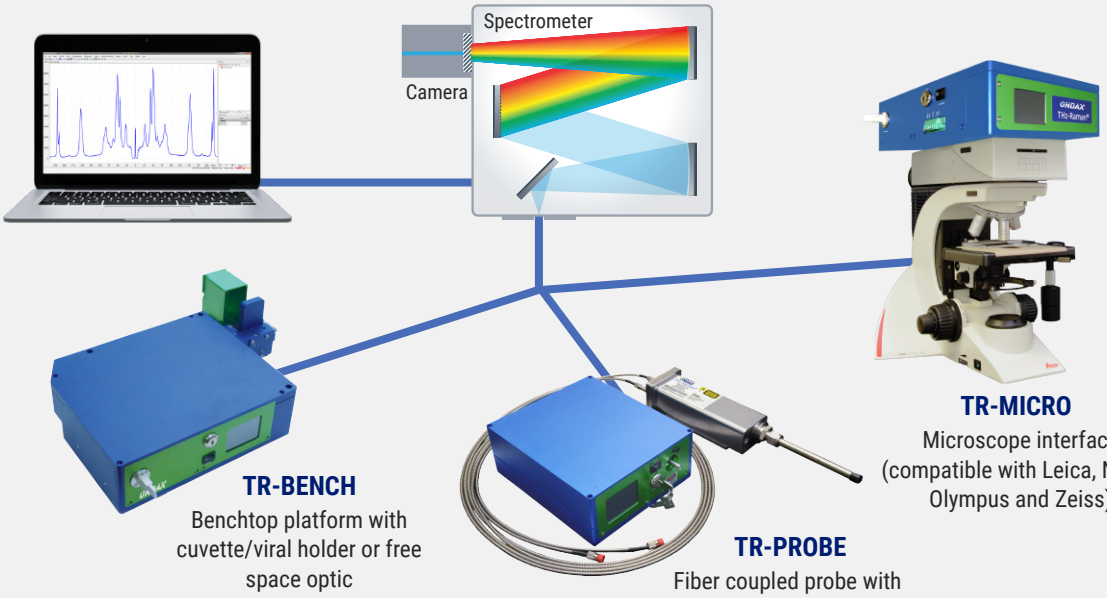


Fig 3. Hetero-mode 2D correlation between the C=O stretching region and the low frequency THz region of Raman spectra obtained simultaneously.

Ondax's patented THz-Raman® spectroscopy systems extend the range of traditional Raman spectroscopy into the THz/low-frequency regime, enabling simultaneous analysis of both molecular structure and chemical composition for advanced materials characterization. All THz-Raman® systems are compact, robust, plug-and-play platforms that deliver incredible speed, throughput and ease of use, all at an extremely affordable price. With a broad selection of excitation wavelengths from 488 nm to 1064 nm, optional polarization control and a wide variety of sample interfaces, there is a THz-Raman® solution for any application.



TR-BENCH
Benchtop platform with cuvette/viral holder or free space optic

TR-PROBE
Fiber coupled probe with interchangeable sample interface

TR-MICRO
Microscope interface (compatible with Leica, Nikon, Olympus and Zeiss)

[2] **8,184,285, 9,986,407, 9,599,565 and 9,587,983**

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