

Differential Scanning Calorimetry –  
Raman Spectroscopy

## Polymer Crystallinity Studies by DSC- Raman Spectroscopy

Differential scanning calorimetry (DSC) and Raman spectroscopy are both used to investigate crystallinity but in rather different ways. DSC can determine the degree of crystallinity very precisely and can also follow the kinetics of crystallization by measuring the associated enthalpy changes. Because of its ability to rapidly stabilize at temperature and its heating and cooling rates of up to 750 °C/min in control, the PerkinElmer® DSC 8000 or 8500 is often used for crystallization studies. Since the double-furnace design allows precise control at true isothermal temperatures, isothermal studies are best carried out in this model.

Raman spectra of crystalline and non-crystalline forms generally differ with the bands of the former being much narrower. Additional possibilities provided by Raman are to monitor very slow changes and also to identify situations where crystallization leads to a mixture of forms. As the PerkinElmer RamanStation™ 400 and RamanFlex™ lines allow the timing of its laser pulses to be adjusted, the collection of the Raman spectra can be tuned to match the scanning rate. Simultaneous measurements remove the uncertainties that arise when the behavior of the material may depend on the thermal history of the sample.

Semi-crystalline polyethylene oxide illustrates the complementary nature of the two techniques. This material has a variety of clinical applications and is widely used in consumer products such as toothpaste. A sample was heated from 10 °C to 75 °C through melting, then cooled back to 10 °C and the cycle was repeated. The maximum of the melting peak is at 70.0 °C in the first cycle and at 66.7 °C in the second. The heat of fusion is also lower in the second heating (Figure 1 – Page 2). This implies that the initial melting and solidification increases the proportion of amorphous material.

Raman spectra were obtained at 5-second intervals during the DSC runs. In the spectrum after the first heat/cool cycle, there are broad features associated with the amorphous component (Figure 2). The difference between the spectra before and after the first cycle is obtained by subtraction. Although noisy, it is very similar to the spectra obtained from the melt, which is amorphous. So the Raman spectra confirm directly the inference from the DSC data that the first heat/cool cycle increases the amorphous content. Spectra of crystalline and amorphous components can be obtained from these data (Figure 3 – Page 3).

Polyethylene terephthalate (PET) has been much studied by both techniques. The sample examined here has significant amorphous content after rapid cooling from the melt. The heat-flow curve shows a glass transition ( $T_g$ ) at around 70 °C, crystallization, and then melting at 270 °C (Figure 4 – Page 3). Changes in the Raman spectra are small but can be followed by using principal components analysis (PCA). Analysis of the 1727  $\text{cm}^{-1}$  C=O Raman band gives two principal components: PC 1 has the shape of a first derivative, corresponding to a band shift and PC 2 is second-derivative shape representing a change in peak width. The temperature profile for the peak-width change clearly matches that for crystallization and melting. However, the temperature profile for the peak shift does not correspond to the events seen in the DSC heat-flow curve but reflects a continuous shift to lower frequency with increasing temperature.

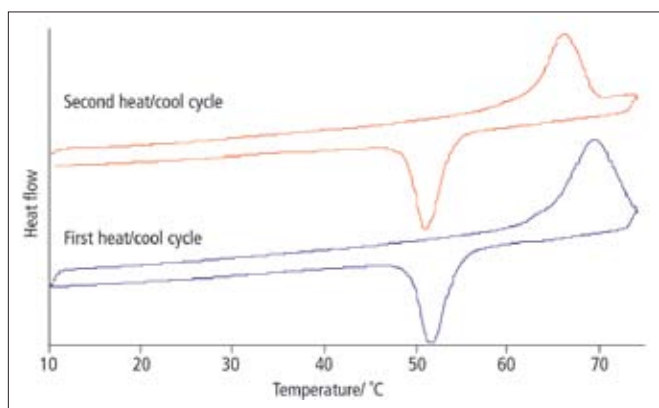


Figure 1. DSC run of polyethylene oxide (PEO). The first and second cycles have been offset for clarity.

Isothermal crystallization is readily monitored by DSC or Raman spectroscopy, with DSC being ideal for rapid processes while Raman is applicable even when crystallization is very slow. The comparability of the data from the two techniques is seen in a study of two blown polyethylene films, one of which was from a batch of bad material. Crystallization at 121 °C was measured after rapid cooling at 500 °C/min from the melt. This type of experiment requires a HyperDSC®-capable instrument like the DSC 8500 to cool rapidly and still precisely come to the isothermal holding temperature. After a stabilization transient, the DSC data (Figure 5a – Page 3) show that the bad material crystallizes more rapidly and with higher enthalpy than the good material. The Raman data (Figure 5b – Page 3) are shown for the initial heating and cooling of the samples as well as the isothermal period. In this case, a factor score from PCA is directly related to crystallinity. Here too the bad material is seen to crystallize more rapidly and also achieves a higher degree of crystallinity than the good material. From both sets of data, it appears that the final degree of crystallinity in the bad material is about 50% higher than the good. In both cases, the final degree of crystallinity is much lower than in the starting materials.

DSC-Raman spectroscopy allows us to precisely probe the crystallization behavior of polymers under various thermal conditions and correlate the energy changes from the DSC to changes in structure as seen in the Raman. This approach allows precise correlation of the two methods and promises a greater understanding of crystallization behavior.

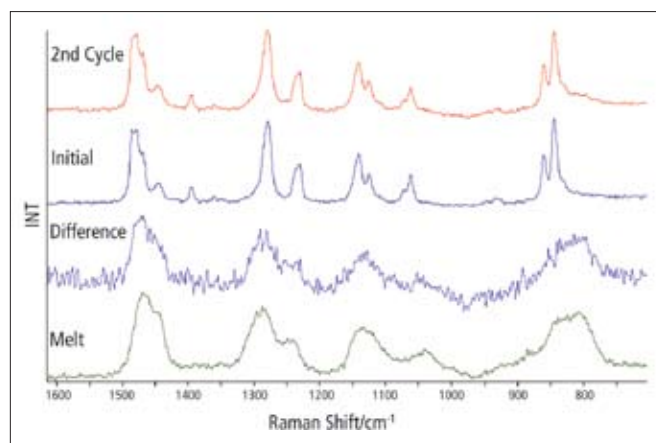


Figure 2. Spectra from DSC run of PEO.

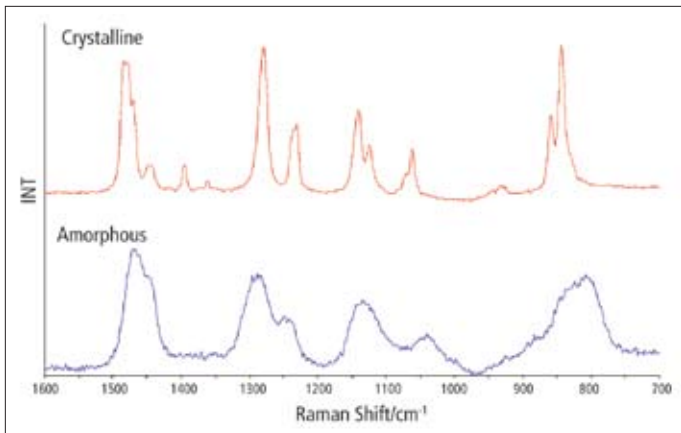


Figure 3. Raman spectra of crystalline and amorphous PEO.

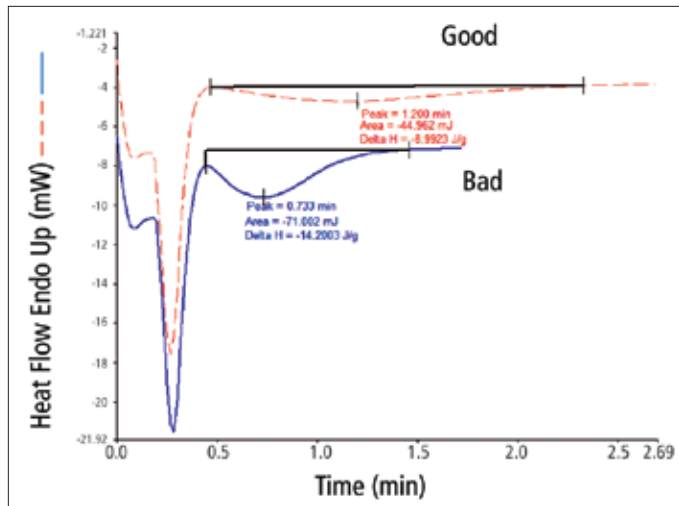


Figure 5a. DSC of HDPE isothermal crystallization.

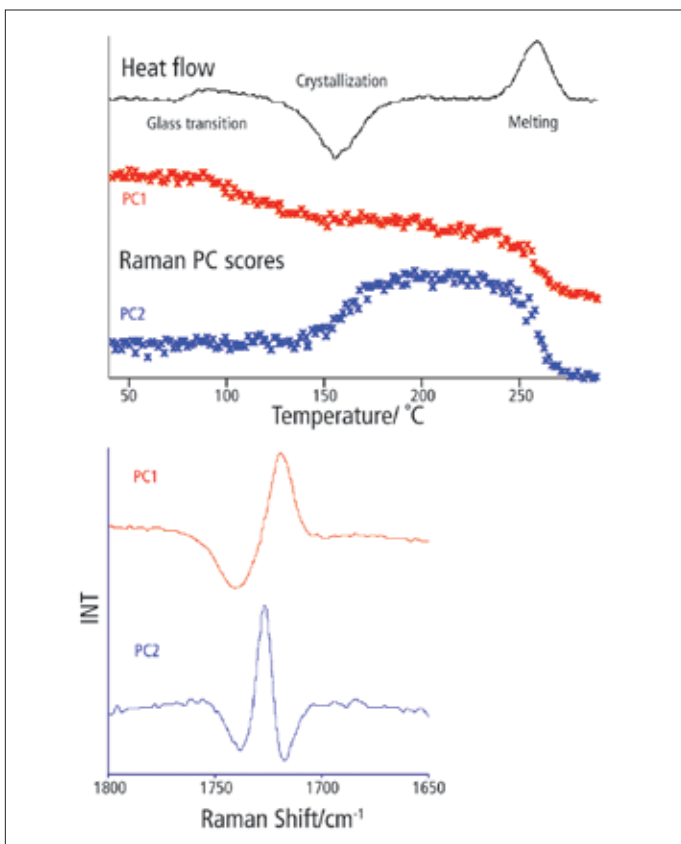


Figure 4. DSC and Raman data for PET.

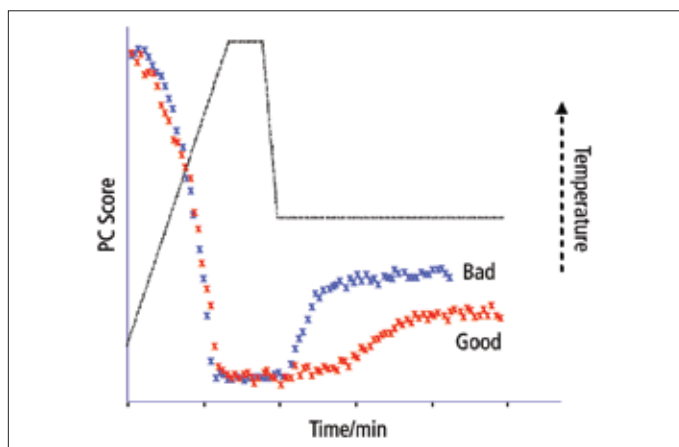


Figure 5b. Raman of HDPE melting and isothermal crystallization.