

Polarized Raman Spectroscopy

Introduction

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Polarized Raman provides insightful information, such as molecular orientation and symmetries of molecular vibrations, to the Raman spectroscopy. These are additional information which is otherwise undetected by non-polarized Raman spectroscopy. Polarization of the molecule is brought about by the symmetrical vibrational modes, which can be determined by the vibrational selection rule using group theory [1-2]. Hence, polarized Raman spectroscopy has been extensively used to obtain valuable information relating to molecular shape in synthetic chemistry, orientation of molecules, and crystal lattice of liquid crystals and polymer samples. In this app note, we demonstrate the Raman polarization effect of cyclohexane, a well-known liquid sample with strong polarization effect. In addition, we use polarized Raman spectra to differentiate as-prepared and stretched states of semi-crystalline low density polyethylene (LDPE) plastic film.

Method and set up

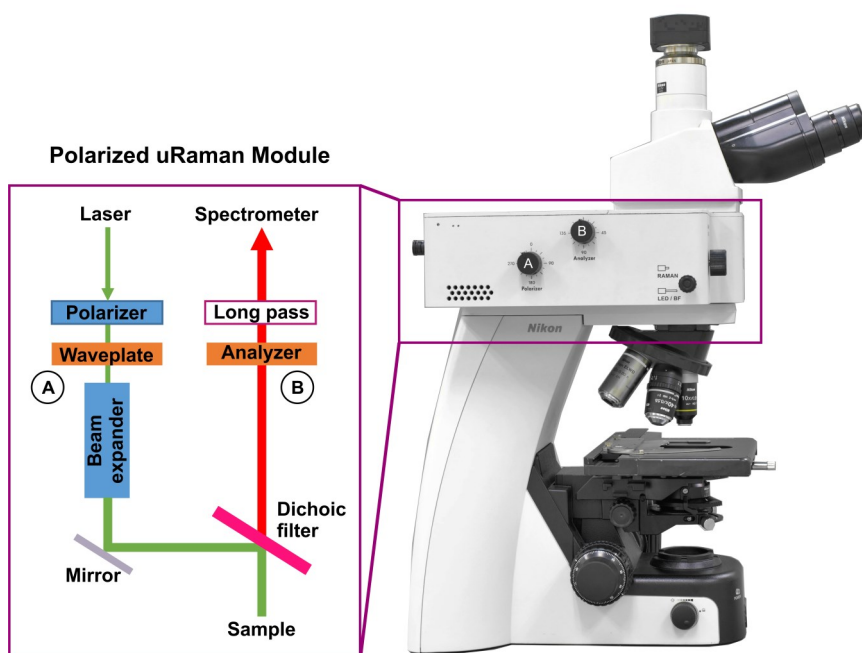


Figure 1. The optical layout of Technospex's polarized Raman microscope.

All the uRaman modules from Technospex can be easily upgraded to polarized Raman micro-spectroscopy (Figure 1) by adding a set of polarizer and wave-plate, and an analyzer at the excitation part and the spectrometer, respectively. Polarized laser is created by passing the laser beam through a polarizer and wave-plate as shown in Figure 1(A). The polarized Raman measurement can be performed either in solution (such as cyclohexane in Figure 2) with cuvette holder attached to the objective turret, or with objectives for the LDPE polymer sample (Figure 3). Cyclohexane was obtained from Sigma-Aldrich (CAS number 110-82-7) with purity of 99.5%. All measurements were performed with a fixed polarizer at the parallel direction to the xy plane ($I_{||}$). Polarized Raman scattering intensities perpendicular to the xy plane (I_{\perp}) and parallel components to the xy plane ($I_{||}$) were obtained by tuning the analyzer at cross (90°) and parallel (0°) angles, respectively.

Results and discussion

Cyclohexane is an ideal candidate for polarization study because it has a simple chemical structure and its totally symmetric vibrational modes that yield strongly polarized Raman signals. The depolarization ratio (r) of the cyclohexane refers to the ratio of Raman scattering intensity perpendicular to the xy plane (I_{\perp}) and parallel components to the xy plane (I_{\parallel}) [1].

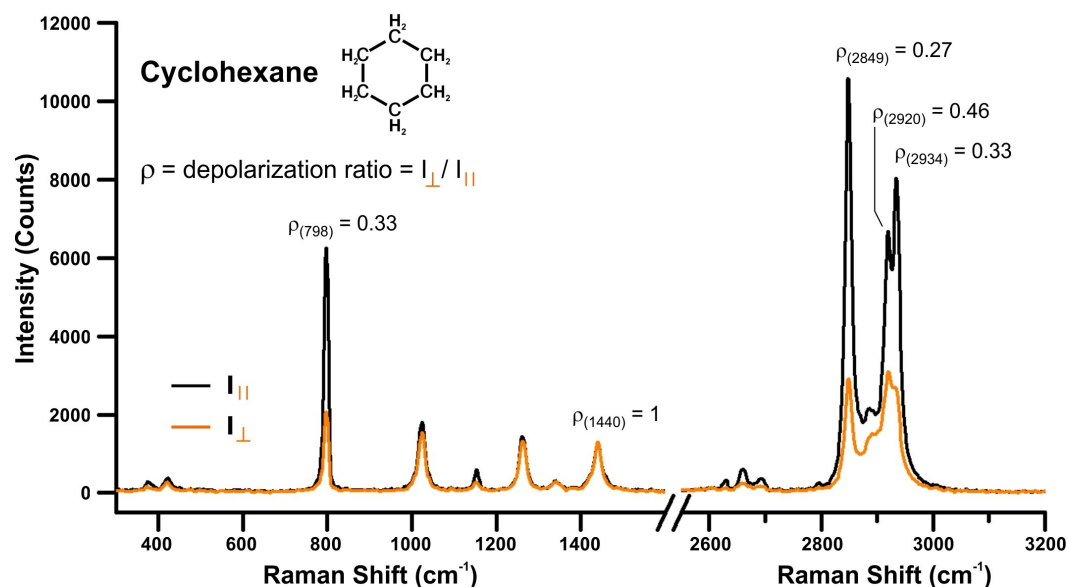


Figure 2. Typical polarized Raman spectra of cyclohexane

Generally, a specific vibrational mode is considered polarized when its depolarization ratio, $\rho < 0.75$. For instance, the parallel (black) and perpendicular (orange) spectra collected from the cyclohexane solution indicate a few bands with depolarization of cyclohexane $\rho < 0.75$ (Figure 2). The four bands with sharp reduction in intensities at perpendicular spectrum, therefore $\rho < 0.75$, are 798, 2849, 2920, and 2934 cm^{-1} . This corresponds to CH_2 -deformation and ring mode, two CH symmetric stretching modes, and CH asymmetry stretching mode, respectively. Table 1 details the band assignments to respective vibrational modes. These polarized bands demonstrate strongly polarized Raman effect in a specific direction, which is contributed by the molecule's symmetrical vibrational mode, even in solution. On the other hand, other bands, such as 1023, 1154, 1260, 1440 cm^{-1} are not polarization sensitive (depolarized). Hence their intensities remain relatively constant with respect to the analyzer position.

Table 1. Raman band assignment of cyclohexane.

Raman shift (cm^{-1})	Mode
798	CH₂ deformation + ring mode
1023	CH ₂ deformation + ring mode
1154	Ring mode + CH ₂ deformation
1260	CH ₂ deformation
1440	CH ₂ deformation
2849	CH symmetric stretch
2919	CH asymmetric stretch
2934	CH asymmetric stretch

Structural information on LDPE

LDPE is one of the most widely used polymer packaging films in the market due to their low cost and high ductility (stretching ability). Its stretching ability is due to its highly branched macromolecular structure with random distribution of short and long side chains. This hinders the chain alignment of LDPE in bulk state, which increases its ductility and reduces its crystallinity. The ductile LDPE undergoes permanent deformation during the wrapping process, where macromolecules are stretched and aligned with the stretching direction.

Here, we introduce polarized Raman spectroscopy as an effective tool to compare the differences between an as-received LDPEs and highly stretched (hence slightly aligned) LDPEs. All spectra are normalized against the C-C stretching at 1064 cm^{-1} . This band has been routinely used as an internal standard for Raman spectrum because it is attributed to the amorphous structure in LDPE, which show independent polarization effect [2].

The as-received sample demonstrate slight intensity changes for Raman bands located at 1129, 1440, 1460 cm^{-1} (Figure 3: As-received, $\theta = 0^\circ$ and 90°). The observation hints that the Raman spectrum of LDPE is highly sensitive to polarization. The overall band assignments of LDPE are presented in Table 2.

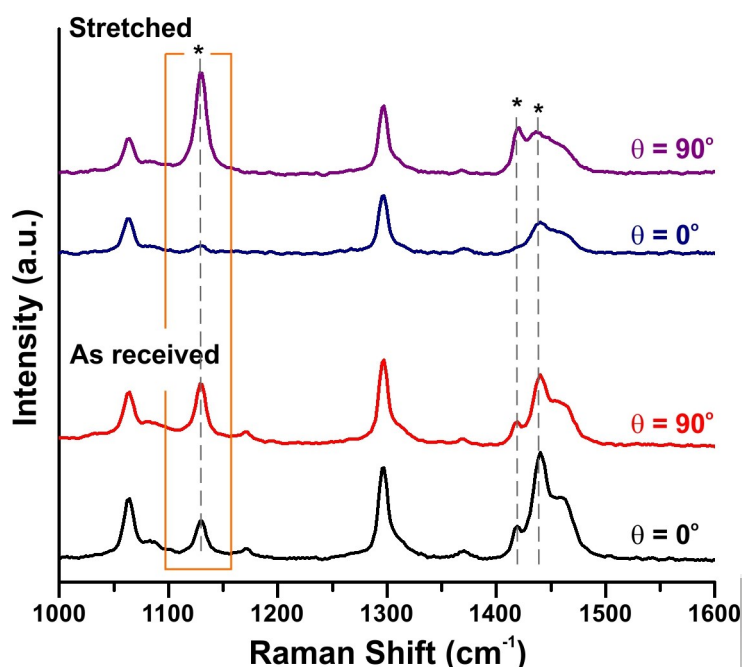


Figure 3. Polarized Raman of as received and stretch LDPE film

For the stretched LDPE film, strong polarization phenomenon is evident (Figure 3, Stretched), indicating molecular chain alignment during the stretching process. For instance, the 1129 cm^{-1} band (C-C stretching, asymmetric stretching) has the most significant change in depolarization ratio (r). Its peak intensity becomes weaker at $\theta = 0^\circ$ (Figure 3 stretched, $\theta = 0^\circ$), signifying the reduction of C-C asymmetric stretching along the parallel direction. But its intensity at $\theta = 90^\circ$ increases significantly. Similarly, peaks at 1440 and 1460 cm^{-1} also show polarization-dependent Raman effect, with r at 1.36 and 1.41 respectively.

Table 2. Raman band assignment of low density polyethylene (LDPE).

Raman Shift (cm^{-1})	Mode	As received	Stretched
		I_{90}/I_0	I_{90}/I_0
1064	C-C stretching, symmetric stretching	0.88	1.10
1129	C-C stretching, asymmetric stretching	1.54	9.10
1297	CH ₂ -Twisting	0.93	1.22
1440	CH ₂ -Bending (symmetric deformation)	0.67	1.36
1460	2X-CH ₂ rocking	0.70	1.41

Conclusion

Polarized Raman spectroscopy can be applied to determine the deformation of polymer in a more quantitative way. It can also be used as a complementary technique to other crystallinity techniques such as in-situ FTIR, DSC or X-ray scattering. Our polarized modules can be easily upgraded to the existing modules to accommodate your tight research budget.

Reference

[1] J. Org. Chem. 1973,38,134. [2] J. Polym. Sci. Polym. Phys. 1978, 16, 37.