

Advanced Vibrational Microspectroscopic Study of Conformational Changes within a Craze in Poly(ethylene terephthalate)

Supporting information

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1. Correlation between the FWHM of IR and Raman bands and degree of crystallinity

In order to quantify the variation in crystallinity within the micron-sized crazes we first correlated the degree of crystallinity with the FWHM of the bands used to analyze crystallinity changes, i.e., the C=O stretching overtone (3434 cm^{-1}) in the case of IR spectroscopy and the C=O stretching mode (1726 cm^{-1}) in the case of Raman spectroscopy. For that purpose we prepared PET thin films under the same experimental conditions mentioned in the “Experimental Section” of the main text but with different degree of crystallinity. This was achieved by adding a small amount of carbon nanotubes (CNTs) to the PET films following the procedure described in¹. Due to the high nucleating ability of CNTs even at the fast cooling rates employed in this work, PET films with different crystallinity degree were obtained. On the other hand, only three different PET thin films (CNTs concentration of 0 wt.-%, 0.1 wt.-% and 1 wt.-%) were prepared because of the well-known linear relationship between the FWHM of these bands and the degree of crystallinity^{2,3}.

The degree of crystallinity of the PET thin films was calculated from X-ray diffraction measurements (Fig S1(a)) performed at the X-ray diffraction Laboratory of the Characterization Service in the Institute of Polymer Science and Technology, CSIC, using a *Bruker D8 Advance* diffractometer and employing the Cu K α line as illumination ($\lambda = 0.154\text{ nm}$). The diffraction patterns were acquired in an angular region from 5° to 35° at a scanning speed of $1^\circ/\text{min}$. The crystallinity degree was calculated by the deconvolution of the diffraction patterns.

In order to achieve a reasonable statistical relevance of the spectroscopic data, IR microspectroscopy (Global source; microscope *i-Series IMAGE* (Perkin Elemer) coupled to a *Spectrum GX 2000 FTIR* (Perkin Elemer) spectrometer; 15 \times Cassegrain objective with NA = 0.6; liquid-nitrogen cooled MCT detector; 64 accumulations; Aperture size: $25 \times 25\text{ }\mu\text{m}^2$) and Raman microspectroscopy (*Renishaw InVia Reflex Raman System* (Renishaw plc., Wotton-under-Edge, UK); $\lambda_{\text{LASER}} = 785\text{ nm}$; 50 \times objective with NA = 0.75; acquisition time: 1s; 15 accumulations; Approximate power density at the sample $0.5\text{ mW}/\mu\text{m}^2$), were performed at 30 different spatial points on each thin film. Fig S1(b) and (c) show a comparison of three representative IR and Raman spectra in the spectral region corresponding to the C=O stretching overtone (3434 cm^{-1}) and C=O stretching mode (1726 cm^{-1}), respectively.

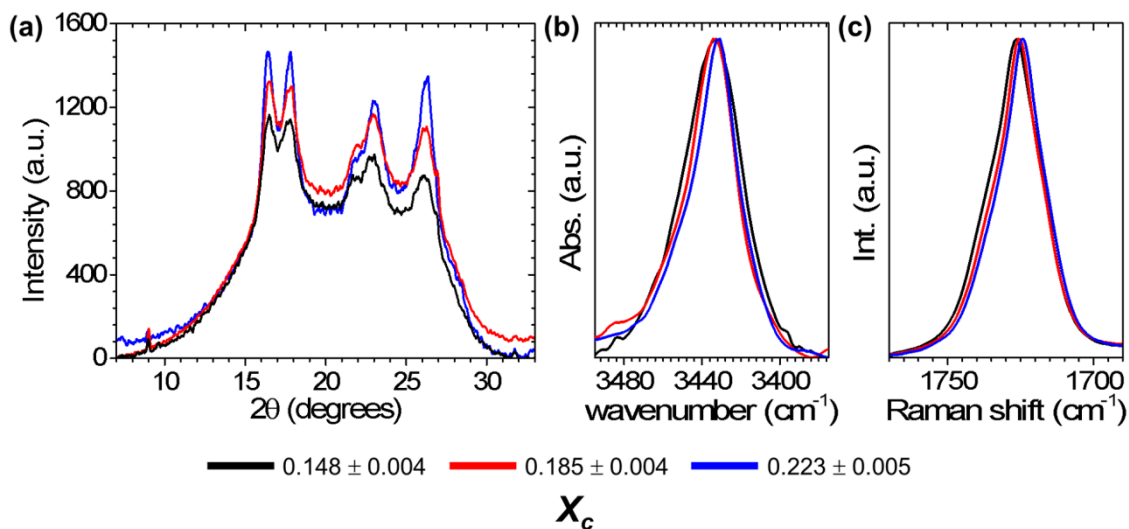


Figure S1. (a) Diffraction patterns corresponding to the prepared PET thin films with different degree of crystallinity. (b) IR C=O stretching overtone band of the prepared PET films. (c) Raman C=O stretching band of the prepared PET films. In (b) and (c) the bands have been normalized for a better comparison. The legend is the same for the three plots (bottom) in which the degree of crystallinity extracted from X-ray diffraction is indicated.

From the linear fittings of FWHM vs. X_c of the aforementioned bands (Fig. S2), the following relationships were found

$$FWHM_{3434}^{IR}(cm^{-1}) = (39.69 \pm 0.06) - (64.0 \pm 0.3) X_c \quad (S1a)$$

$$FWHM_{1726}^{Raman}(cm^{-1}) = (30.4 \pm 0.5) - (61 \pm 2) X_c \quad (S1b)$$

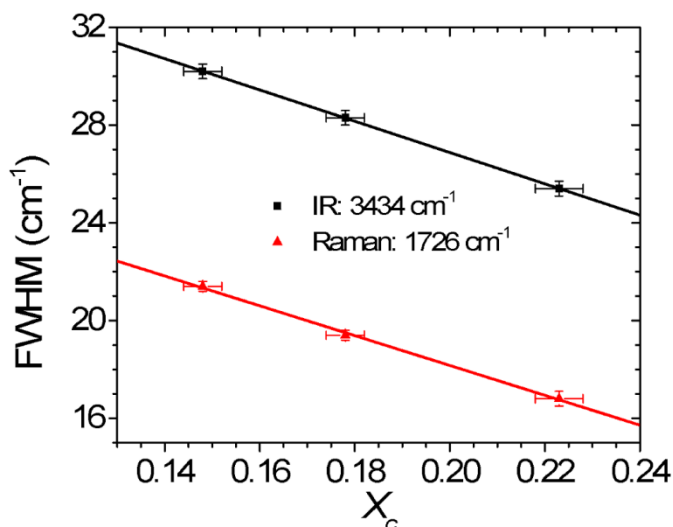


Figure S2. FWHM vs. X_c . The solid lines are linear fittings to the data.

2. FWHM spatial distribution of the bands associated with crystallinity

The spatial distribution of the C=O stretching overtone (3434 cm^{-1}) FWHM extracted from the SIRMS measurements as well as the spatial distribution of the C=O stretching mode (1726 cm^{-1}) FWHM extracted from the Raman microspectroscopy measurements are presented in Fig. S3.

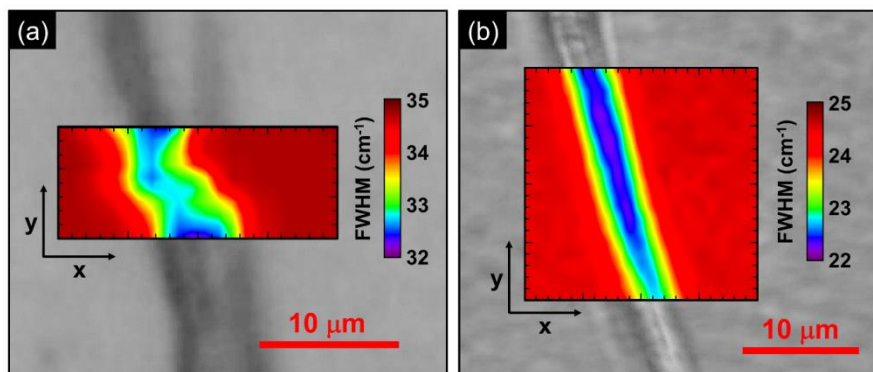


Figure S3. FWHM spatial distribution of (a) C=O stretching overtone (3434 cm^{-1} ; SIRMS data) and (b) C=O stretching mode (1726 cm^{-1} ; Raman data).

3. Orientation and conformational changes in PET across the deformation neck

Apart from the SIRMS measurements within the micron-sized crazes, we also studied the orientation and conformational changes taking place across the deformation neck. In this case IR microspectroscopy was performed using a global source and not a synchrotron (Microscope *i-Series IMAGE* (Perkin Elmer) coupled to a *Spectrum GX 2000 FTIR* (Perkin Elmer) spectrometer; 15× Cassegrain objective with $\text{NA} = 0.6$; liquid-nitrogen cooled MCT detector). The aperture size was $50 \times 50\text{ }\mu\text{m}^2$ and the spectra were acquired using $50\text{ }\mu\text{m}$ steps (no oversampling) with 64 accumulations at each spatial point. Due to the unpolarized nature of the global, an external IR polarizer (Perkin Elmer) was used to acquire spectra at two orthogonal polarization configurations. Afterwards, the structural factor spectra were calculated at each spatial point. The analysis of the orientation, conformation and crystallinity was identical to the one described in the main text. The results are shown in Fig. S4. It is important to point out the constant value of the TC conformational structure percentage and the lack of crystallinity development across the necking region.

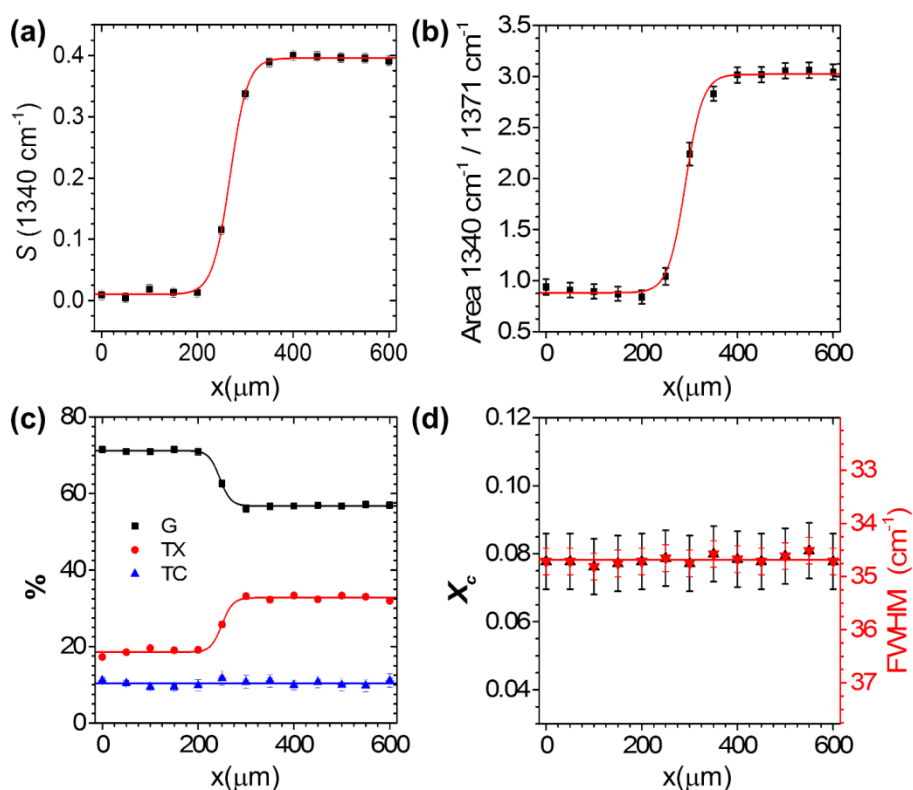


Figure S4. (a) Orientation parameter, (b) 1340 cm^{-1} to 1371 cm^{-1} band ratio, (c) conformational distribution and (d) degree of crystallinity and FWHM of the C=O stretching overtone (3434 cm^{-1}) across the deformation neck. The deformation neck was at around $x = 250 \mu\text{m}$. The solid lines are sigmoidal and constant fittings to the data.

4. SIRMS results from a different craze

Figure S5 presents point-by-point SIRMS line mapping results of a craze from a different sample prepared under the same experimental conditions as that presented in the main text. In this case, for the orientation and conformation analysis an aperture of $8 \times 8 \mu\text{m}^2$ was used with a step size of $4 \mu\text{m}$ (oversampling; 64 scans; spectral resolution 4 cm^{-1} ; 32 \times Schwartzchild objective with $\text{NA} = 0.6$) whereas for the crystallinity analysis we used a $4 \times 4 \mu\text{m}^2$ aperture size with a step size of $1 \mu\text{m}$ (oversampling; 128 scans; spectral resolution 4 cm^{-1} ; 32 \times Schwartzchild objective with $\text{NA} = 0.6$).

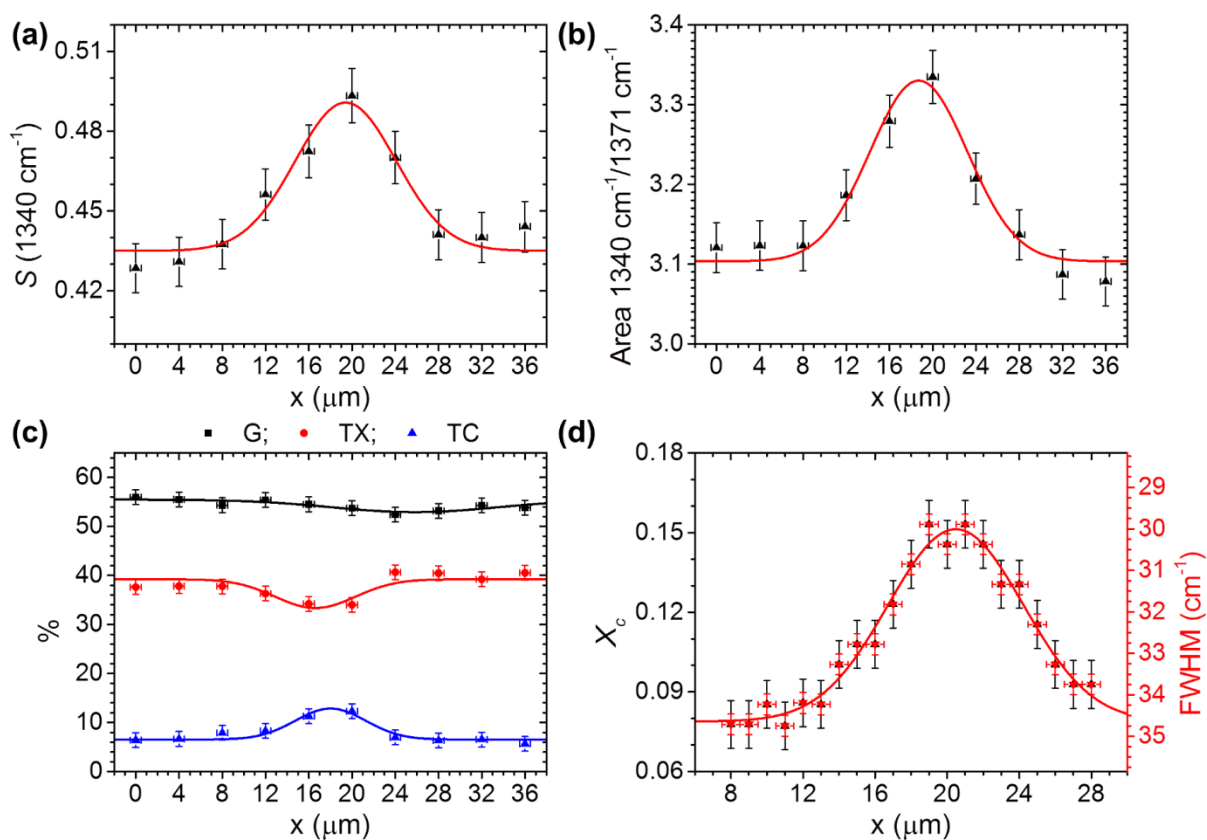


Figure S5. (a) Orientation parameter, (b) 1340 cm^{-1} to 1371 cm^{-1} band ratio, (c) G, TX and TC conformational and (d) degree of crystallinity and FWHM of the C=O stretching overtone (3434 cm^{-1}) across the craze. The solid lines are Gaussian fittings to the experimental data.

References

- (1) Santoro, G.; Gomez, M. A.; Marco, C.; Ellis, G. *Macromol. Mater. Eng.* **2010**, *295*, 652-659.
- (2) Melveger, A. J. *J. Polym. Sci. Part B Polym. Phys.* **1972**, *10*, 317-322.
- (3) Richard-Lacroix, M.; Pellerin, C. *Macromolecules* **2013**, *46*, 5561-5569.