

## Confined dynamics in poly(ethylene terephthalate): a coherent and incoherent neutron scattering study

Alejandro Sanz<sup>1</sup>, Aurora Nogales<sup>1</sup>, Inés Puente-Orench<sup>2,3</sup>, Mari-Cruz García-Gutiérrez<sup>1</sup>, Javier Campo<sup>2</sup>, Wolfgang Haussler<sup>4</sup>, Michelina Soccio<sup>5</sup>, Nadia Lotti<sup>5</sup>, Andrea Munari<sup>5</sup> and Tiberio A. Ezquerro<sup>1</sup>

<sup>1</sup>Instituto de Estructura de la Materia, IEM-CSIC, Serrano 121, 28006 Madrid, Spain

<sup>2</sup>Institut Laue-Langevin, BP 156-38042 Grenoble Cedex 9, France

<sup>3</sup>Instituto de Ciencia de Materiales de Aragón, ICMA-CSIC, Pedro Cerbuna 12, 50009 Zaragoza, Spain

<sup>4</sup>Forschungs-Neutronenquelle Heinz Maier-Leibnitz (FRM II), Garching, Germany

<sup>5</sup>Dipartimento di Ingegneria Civile, Ambientale e dei Materiali-Universit  di Bologna, Via Terracini 28, 40131 Bologna, Italy

E-mail: [alejandro.sanz@csic.es](mailto:alejandro.sanz@csic.es)

**Abstract.** We show that the combination of dielectric relaxation with neutron spin echo and incoherent neutron backscattering measurements performed in deuterated and protonated poly(ethylene terephthalate) suggests that the intrinsic dynamics of semicrystalline polymers occurs in an homogeneous scenario, similar to that valid to describe the dynamics of totally amorphous polymers. The quasielastic neutron scattering data are satisfactorily described by a theoretical model that considers that the proton mobility follows a random jump-diffusion in a restricted environment.

### 1. Introduction

The physics of soft matter in confining media has attracted plenty of attention during the last decades for its implications on nanoscience, nanotechnology and fundamental knowledge of condensed matters [1]. The  $\alpha$  relaxation mode is directly linked to the glass formation and becomes critically slow as temperature approaches the glass transition [2,3]. Polymers show the ability of self-assembling mainly through ordering processes like crystallization of homopolymers or phase separation of di-block copolymers. In both cases, hierarchical structures are generated at different length scales and normally one of the phases is confined by the surrounding media. The  $\alpha$  relaxation in semicrystalline polymers has been widely investigated as a paradigmatic case study of how the geometrical confinement at the nanoscale influences the primary relaxation [4]. Poly(ethylene terephthalate) (PET) is a commodity polymer that, depending of several experimental factors, may present a variable degree of crystallinity, from the fully amorphous state to a 40 % approximately. Here, we have investigated the amorphous chains dynamics in a semicrystalline sample of PET by quasielastic neutron scattering (QENS), elucidating in this way how the confining crystals that surround the amorphous domains affect their mobility. To tackle this problem, quasielastic coherent Neutron Spin Echo (NSE) and incoherent neutron backscattering (BS) have been used on deuterated and protonated PET respectively.



## 2. Experimental section

Deuterated and semicrystalline poly(ethylene terephthalate) d-PET (degree of crystallinity  $X = 32\%$ ) was specifically utilized for the NSE measurements. For the BS measurements, films of protonated poly(ethylene terephthalate) ( $X = 33\%$ ) were used. Differential scanning calorimetry was utilized to estimate the glass transition temperature  $T_g$  of semicrystalline PET, located at 348 K.

### 2.1. Coherent scattering: Neutron spin echo

By using neutron spin echo spectroscopy (NSE), we report on a direct observation of the intermediate scattering function, or the dynamic structure factor, on a fully deuterated sample of poly(ethylene terephthalate) [5]. The dynamics of the density fluctuations in the proximity of the structure factor maximum is governed by the  $\alpha$ -relaxation. Considering that the functional form for this process is a KWW (Kohkrausch-Williams-Watts) function [6], then for the NSE intermediate scattering function the following time dependence can be written:

$$\frac{S_{pair}(Q, t)}{S_{pair}(Q, 0)} = f_Q(T) \exp\left[-\left(\frac{t}{\tau_s(T)}\right)^\beta\right], \quad (1)$$

where  $f_Q(T)$  is related to the Debye-Waller factor,  $\tau_s(T)$  is the structural or  $\alpha$  relaxation time and  $\beta$  is the stretching parameter [14]. Neutron spin echo (NSE) experiments were performed at the RESEDA instrument at the FRM II Munich, Germany, at a  $Q$  value for the scattering vector of  $1.38 \text{ \AA}^{-1}$ .

### 2.2. Incoherent scattering: Neutron backscattering

The scattering law for quasielastic processes is generally expressed by a lorentzian function with a half width at half maximum that provides the time scale of the microscopic dynamics. The lorentzian function is modulated by the term (1-EISF), where EISF is the elastic incoherent structure factor, in such a way that the model used to fit the experimental data is the following:

$$S_{inc}(Q, \omega) = EISF(Q)\delta(\omega) + \left[ (1 - EISF(Q)) \frac{1}{\pi} \frac{\Gamma(\omega)}{\Gamma^2(\omega) + \omega^2} \right]. \quad (2)$$

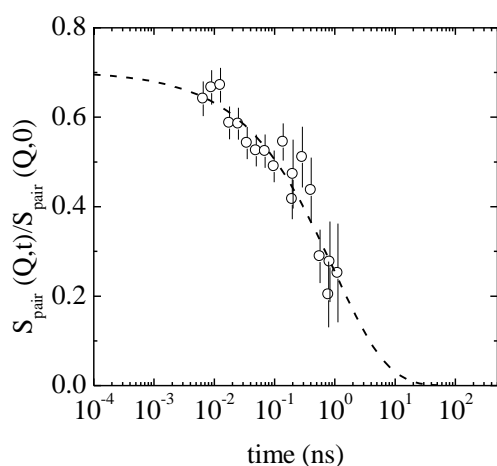
The convolution of this model function to the experimental resolution data for each value of  $Q$  is what we actually fit to the experimental data in order to extract the half width at half maximum  $\Gamma$  (time scale of the motion) of the quasielastic component and the elastic incoherent structure factor EISF. BS experiments were performed at the backscattering spectrometer IN10, at the ILL (Grenoble, France). The incident neutron wavelength was set at  $6.28 \text{ \AA}$  and the  $Q$  range was extended from  $0.5$  to  $2 \text{ \AA}^{-1}$ , with an energy resolution at half maximum of  $0.45 \text{ \mu eV}$ .

## 3. Results and discussion

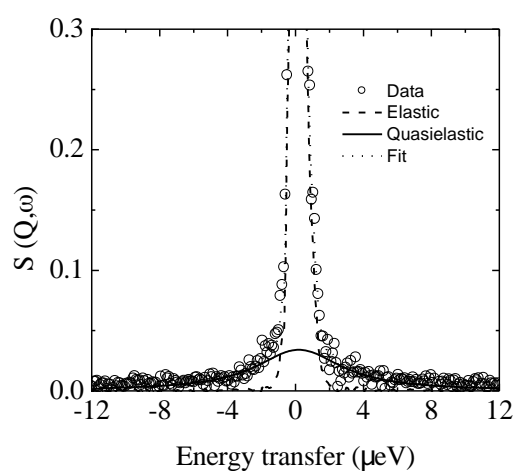
The dynamic behavior of semicrystalline PET has been investigated above its  $T_g$  by carrying out in parallel NSE and BS measurements. To illustrate the response of semicrystalline PET in time and frequency domain, figures 1 and 2 shows NSE and BS data respectively at 500 K.

Figures 1 and 2 nicely describe how the decay of the density correlations in the time domain, characterized by an exponential decay function, is on the contrary represented by a lorentzian function in the frequency domain [6]. The NSE data have been described by using the equation (1) where  $f(Q)$ ,  $\tau$  and  $\beta$  where adjustable parameters. The values of  $\tau$  are included in the relaxation map represented in figure 4, supporting our initial assumption that the dynamics observed in NSE is truly the  $\alpha$  relaxation [5]. While the stretching parameter  $\beta$  for the  $\alpha$  relaxation in semicrystalline PET, for instance obtained by dielectric spectroscopy, show values around 0.2, here NSE data present decay functions with values of  $\beta$  equal to 0.5. Values of the parameter  $\beta$  close to 0.5 are typical for fully amorphous polymers. Consequently, we can propose that the dynamic scenario for the  $\alpha$ -relaxation, studied by NSE, of a semicrystalline polymer is that of the homogeneous case. In order to extract additional information,

BS data were analyzed by using the formalisms described in equation 2, where the spectrum contains an elastic peak and the corresponding quasielastic broadening. As an example, figure 2 shows the best fit of the experimental BS data to equation 2 at 500 K and  $1.45 \text{ \AA}^{-1}$ . Following this approach, a good description of the data was obtained also at 400 and 450 K in a Q range between 0.5 and  $2 \text{ \AA}^{-1}$ . Unique information on the geometry of the motion is obtained through the Q evolution of the so called elastic incoherent structure factor EISF (ratio of the elastic intensity to the total scattered intensity). Two different approaches have been followed to interpret our EISF data, one in which the mobile species diffuse in a restricted environment defined by impermeable walls (DRE model) [7], and another where the confining elements behave like soft and permeable walls (Gaussian Model, GM) [8]. Fits of the GM and DRE models to our EISF experimental data are included in figure 3 as dashed and continuous lines respectively.

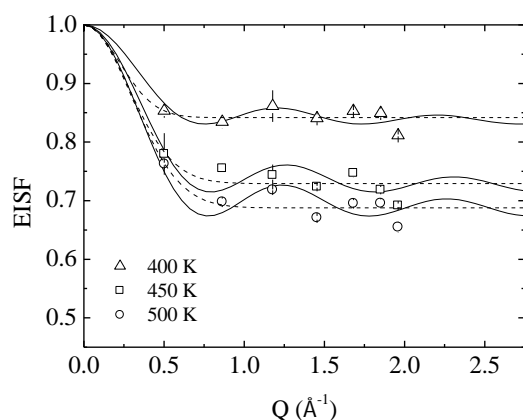


**Figure 1.** Dynamics of semicrystalline PET at 500 K. NSE relaxation decay at  $1.38 \text{ \AA}^{-1}$ . Dashed line corresponds to the best fit of the experimental data to a KWW function.

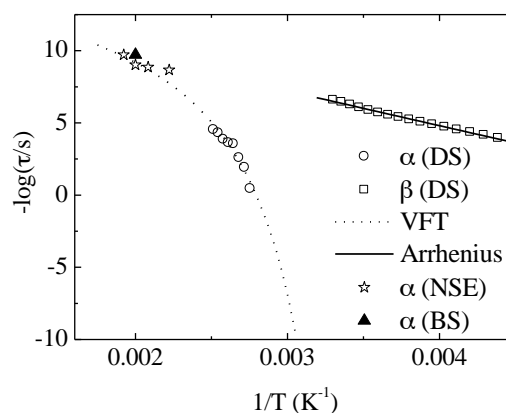


**Figure 2.** Dynamics of semicrystalline PET at 500 K. BS spectrum at  $1.45 \text{ \AA}^{-1}$ .

If one checks carefully the fits in figure 3, it seems that a better description of the experimental data is received when the DRE model is considered. Under the framework of this model, the confining size remains unchanged for the whole temperature at a constant value of  $6 \text{ \AA}$ , while the fraction of mobile protons increases with temperature. From the half width at half maximum  $\Gamma$  of the quasielastic component is possible to extract the time scale of the underlying motions. A detailed description of the data analysis procedure to estimate the relaxation time of particles diffusing in a restricted environment can be found elsewhere [9]. The relaxation times derived from both NSE and BS data are collected in figure 4, together to dielectric spectroscopy (DS) data. In figure 4, we have only included the 500 K data from the BS measurements considering that at lower temperatures the  $\alpha$  relaxation time scale should fall far away from the IN10 time window. The dotted line in Fig. 4 corresponds to the empirical Vogel-Fulcher-Tamman VFT equation that nicely reproduces the cooperative nature of the  $\alpha$  relaxation of glass forming systems. We see that the NSE data ( $\ominus$ ) fall into the VFT line, indicating that the collective dynamics observed through the coherent dynamic structure factor is actually the  $\alpha$  relaxation. Interestingly, the data at 500 K obtained from the backscattering data almost coincide with NSE values.



**Figure 3.** EISF data for semicrystalline PET. Solid lines represent the DRE model. Dotted lines correspond to the GM model. Read text for details.



**Figure 4.** Relaxation times as a function of reciprocal temperature for semicrystalline PET. The graph collects data from different techniques.

### Conclusions

The dynamics of semicrystalline PET at the mesoscopic level has been studied by quasielastic neutron scattering (QENS) using Neutron Spin Echo (NSE) and Neutron Backscattering (BS) techniques. Our EISF data have been modelled assuming that the scattering particles diffuse within a restricted environment (confining distance 6 Å). In addition to that, we observe an increase of the fraction of the mobile protons when temperature rises up. By doing NSE measurements above the  $T_g$  of deuterated semicrystalline poly(ethylene terephthalate), we were able to have access to the dynamics governed by the  $\alpha$  relaxation, revealing that the intermolecular cooperativity is expected to be rather similar in both amorphous and semicrystalline polymers, suggesting that the dynamics of semicrystalline polymers occurs in an homogeneous scenario, similar to that valid to describe the dynamics of totally amorphous polymers [5].

To conclude, the inclusion of the BS data at 500 K into the relaxation map of semicrystalline PET indicates that the dynamics observed in this spectrometer is connected to the genuine  $\alpha$  relaxation of semicrystalline PET. We demonstrate that the combination of coherent (NSE) with incoherent (BS) neutron scattering allows a complete description of the confined dynamics on a paradigmatic semicrystalline polymer like poly(ethylene terephthalate).

### Acknowledgments

This work has been funded by the Spanish MINECO (MAT2009-07789, MAT2011-23455 and MAT2008-03232). A. S. also acknowledges the Spanish MINECO for financial support. The authors thank the Institut Laue-Langevin for beam time, M. A. González for technical assistance during experiments and Irene Calvo for helpful discussions.

### References

- [1] Frick B, Koza M and Zorn R 2003 European Physical Journal E **12** 3
- [2] Angell C A 1995 Science **267** 1924
- [3] Schönhals A and Kremer F 2002 Broad Band Dielectric Spectroscopy (Berlin: Springer)
- [4] Ezquerro T A, Balta-Calleja F J, and Zachmann H G 1994 Polymer **35** 2600
- [5] Sanz A et al. 2011 Macromolecules **44** 8124
- [6] Bée M 1988 Quasielastic neutron scattering: principles and applications in solid state chemistry, biology, and materials science (Bristol and Philadelphia: Adam Hilger)

- [7] Hall PL and Ross D K 1981 *Molecular Physics* **42** 673
- [8] Volino F, Perrin J C and Lyonnard S 2006 *Journal of Physical Chemistry B* **110** 11217
- [9] Nogales A et al. 1999 *Macromolecules* **32** 2301.