Experimental report

15/10/2019

Proposal: **9-11-1900** **Council:** 10/2018

Title: Probing the dynamics in the stereocomplex of poly(L-lactic acid) and poly(D-lactic acid)

Research area: Soft condensed matter

This proposal is a resubmission of 9-11-1863

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Samples: PPO-d3-PDLA-d3-PLLA
PPO-d3-PDLA
PPO-PDLA-PLLA (1:25:25, mol:mol:mol)
poly(propylene-oxide)-poly(D-lactide)

Instrument	Requested days	Allocated days	From	To
IN16B	5	5	02/10/2019	07/10/2019

Abstract:

The performance of the polymers is often modified by modulating inter-molecular interaction, such as inducing chiral-stereo interaction. The proposed project focuses on the impact of the chiral-specific interaction on polymer dynamics, using polylactide (PLA) as model system. Its racemic mixture of PLLA and PDLA forms stereocomplex in the crystallized state, and sometimes even in the melted state up to 500K. In this project, we focus on the reorientational motion of methyl group and the local motion of segments with ~100ps time scale, which are most probably affected by the formation of chiral-stereocomplex. Experiments will be conducted at IN16B with the standard energy resolution of 0.75micro-eV. Both the elastic scattering intensity and as well the inelastic scattering intensity at 2micro-eV will be measured with a temperature scan from 5K up to 530K, covering the methyl-reorientation (~120K), the glass transition (320K), the cold-crystallization temperature (360K), up to the melting temperatures (443~480K), and the temperature (~500K) where the local stereocomplex in the melted PLA is broken.

report on the experiment at IN16b, ILL Grenoble, 02.10.2019 – 07.10.2019
proposal 9-11-1900

1 brief description of experiment

The experiment aims at probing the dynamics in the stereocomplex poly lactic acid using high resolution neutron backscattering spectroscopy. The target dynamics are the onset of the methyl group rotation at low temperature [1], and the segment local diffusion above the cold crystallization temperature.
Two protonated samples - the chiral version PPO-PLLA (PL, 1:25, M_w~15×10^4) as the reference, and the racemic version PPO-PLLA-PDLA (PLD, 1:25:25, M_w~24×10^4) - were synthesized at Fan's group at Fudan University, Shanghai. All samples were initialized into the amorphous state by melting the film for 1.5min, followed by quenching in liquid nitrogen. The samples were then dried and packed into the QENS chambers. They were measured no more than 5 hours after the preparation. The semi-crystalline samples were obtained by heating the samples in the QENS chambers using the ILL cryofurnace to T_m+20K, followed by cooling to 5K, with both 5K/min ramping rate (fast mode cooling).
The incoherent neutron spectroscopy experiment was performed at the instrument IN16b, ILL, Grenoble, with an energy resolution of 0.75μeV (FWHM) at the analyzed energy of 2.08meV (λ~6.27Å). The samples were mounted 135° with respect to the beam. Fixed-window-scan (FWS) were performed at 0μeV and 2μeV during heating from 5K to T_m+20K using the high-flux (HF) mode. The ramping rate was 1K/min between 5K and 80K, 0.66K/min for the rest for the initially amorphous sample, and 5K/min in between 250K and 400K for the initially semicrystalline sample. The QENS spectra with the energy transfer between ±30μeV were measured for 1.5~2h at 5K and 180K using the high-signal-noise-ratio (HSNR) mode. The diffractograms were measured simultaneously despite of the beam divergence of ~7°. Vanadium (2 plates, 25mm*45mm*0.25mm) in the QENS chamber and as well the empty QENS chamber were measured for calibration.

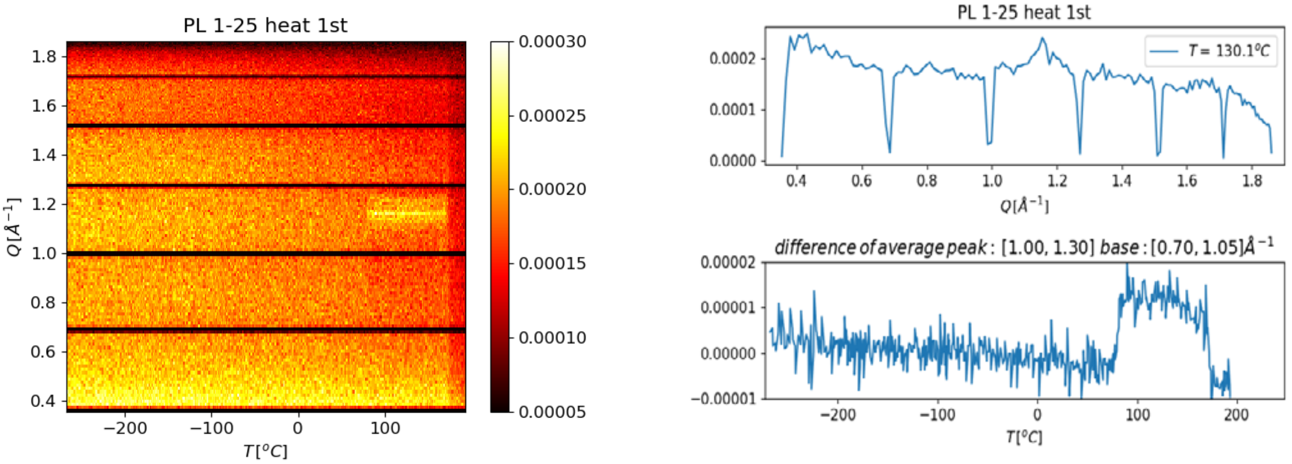
2 data reduction

The data were reduced only preliminarily using the "IndirectILLReduction" routine using Mantid 4.1 without the background (empty chamber) correction. The presented data in this report are all summed over the entire Q-range. The FWS data were normalized to the elastic scattering intensity (0μeV) at 5K for each heating scan. The same scaling factor was applied to the quasielastic data (2μeV).

3 preliminary results

3.1 structural transition of the sample

Fig. 3-1. diffractogram during heating of the amorphous PL

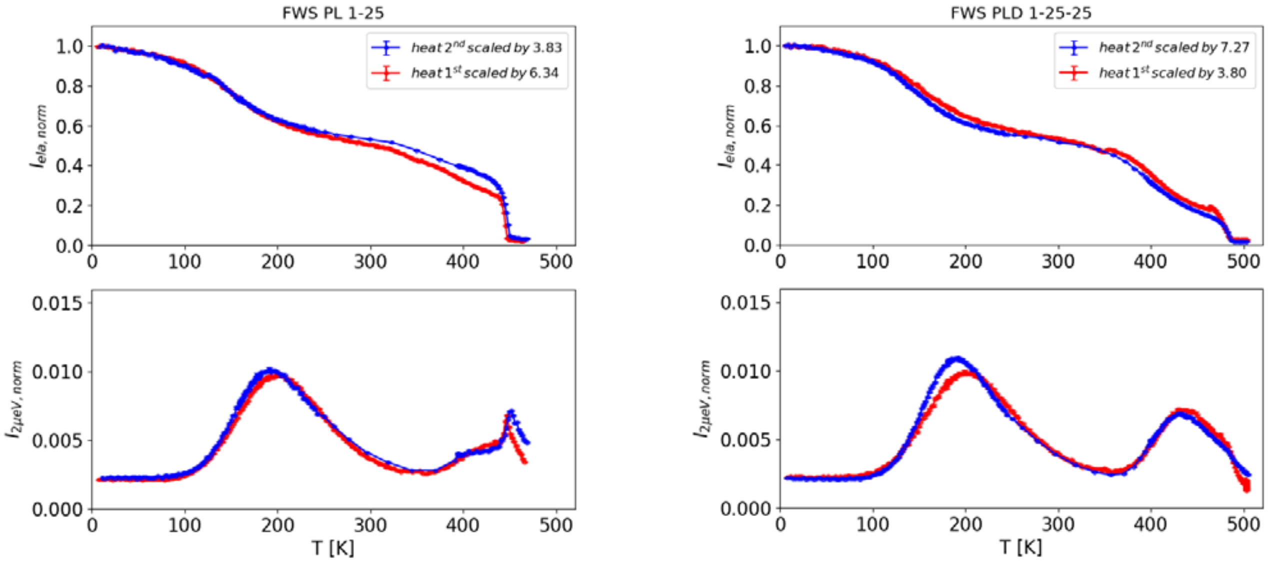


The newly installed diffraction detector at IN16b is very helpful to track the sample behaviour, and correlate the dynamics data with the X-ray structural data and the DSC data. As an example, Fig. 3-1 shows the diffractograms of PL during heating from the amorphous state. The line plots show the diffractogram at 130°C after the cold crystallization, and the difference of the average intensity over the diffraction peak and beside the diffraction peak. Heating the initially amorphous sample results in the appearance of the diffraction peak at ~100°C and its extinction at T_m. All samples behaved the same as in the previous DSC measurements.

3.2 FWS results

Fig. 3-2 depicts the drop of the elastic scattering intensity during heating and the corresponding variation of the quasielastic scattering intensity at 2µeV. The onset of the rotation of the methyl group, the glass transition and the melting transition can be seen from the steeper drop of the $I_{ela,norm}$ between 100K and 200K, the kink at ~320K and the last steeper drop at T_m (~445K for PL, and 485K for PLD), respectively, and as well from the peaks in the quasielastic scattering intensity. The data from heating the amorphous state samples (red curve) show an additional kink (PL case) or even a sudden increase (PLD case) of the elastic intensity at ~370K due to the cold crystallization of the sample. The FWS data and the diffraction data jointly demonstrate the correct phase transition behaviour of both the initially amorphous and the initially semicrystalline sample

Fig. 3-2. Elastic and quasielastic scattering intensity during heating from the amorphous state (red) and from the semicrystalline state (blue).



4 discussion and outlook

The detailed feature of the FWS data violates our expectation in both systems, though the general behaviour of the FWS data is reasonable.

Firstly, the courses of the elastic intensity shows unexpected deviation between the heating from the amorphous and from the semicrystalline state above the cold crystallization temperature (100°C). Starting from the amorphous state at 5K, both samples enter the semicrystalline / rubber state at ~100°C, and melt at higher temperature. Then the choice of the residing time above the melting point and the following cooling rate (<=5K/min) will allow the crystallization of the sample into the same crystallinity as the cold crystallization does, as shown by DSC and the X-ray diffraction data. Therefore the data above 100°C should be nearly identical between the red and the blue (fig. 3-2) since they are both in the semicrystalline / rubber state with the same crystallinity. However, in both the PL and PLD case they are different, and with opposite deviation. In the PL case, the elastic intensity from heating the initial amorphous sample is higher than the other curve, while in the PLD case it is lower. We don’t yet understand this deviation. To exclude the hysteresis effects, a ramping cycle of 2~3 times is needed. Secondly, the PLD data shows opposite deviation between the two curves from our expectation. The drop of the elastic intensity between 100K and 250K is usually attributed to the onset of the methyl group rotation. The DFT calculation predicts that, in crystalline phase of the PLD, all the methyl groups are connected by an unconventional hydrogen bond with the carboxyl group of the neighbouring chain [2]. Therefore we expect a more restricted methyl rotational motion in the semicrystalline PLD (blue curve below 370K) than the totally amorphous PLD (red curve below 370K). Such features should be rather pronounced in the FWS curve below 200K since the methyl group motion shall dominate the data. However, the higher elastic intensity at $T<200K$ in the amorphous PLD indicates the opposite: the motion in the amorphous PLD seems to have a slower time scale, therefore being more restricted. After the cold crystallization, the elastic intensity of the initially amorphous sample seems to be again higher, though both states shall be the identical semicrystalline / rubber state. Again, we would need more beamtime to exclude the hysteresis effect with repetitive ramping cycles on the semicrystalline sample.

5 conclusion

The data from this beamtime shows the general dynamic behaviour in the semicrystalline poly(lactic acid) with only the L version and with the sterecomplex of the L- and D- type. Differences are seen between the amorphous state and the semicrystalline state, and as well between the two versions. The deviations are small, but significant. Still, many essential features contradict with our expectation, which based on the structural data by X-ray diffraction, thermodynamic data from DSC, and the theoretical prediction. Yet, we could not exclude the hysteresis effect of the dynamics, as only one ramping of each state of the sample has been done due to the time restriction. We will apply for more beamtime to clarify these remaining questions.

6 references

[1] B. Frick and L. J. Fetters, Methyl-group dynamics in glassy polyisoprene - a neutron backscattering investigation, Macromolecules **27** (4), 974 (1994), (doi:10.1021/ma00082a014).

[2] T. T. Lin, X. Y. Liu, and C. He, A DFT study on poly(lactic acid) polymorphs, Polymer **51** (12), 2779 (2010), (doi:10.1016/j.polymer.2010.03.062).