DUBBLE – EXPERIMENT REPORT

Beam time number: **26-02-906**		File number: 85593
Beamline: BM26-B	Date(s) of experiment: 16 June 2021 - 18 June 2021	Date of report: 13 Jan 2022
Shifts: 6	Local contact(s): Daniel Hermida Merino	

1. Who took part in the experiments?

Hamid Ahmadi[1], Ruth Cardinaels[1] , Stan F.S.P. Looijmans [1]
Affiliation:

1. Polymer Technology, Department of Mechanical Engineering, Eindhoven University of Technology, the Netherlands.

Were you able to execute the planned experiments?

YES. We were able to perform the planned experiments.

2. Did you encounter experimental problems?

NO. The setup and the beamline instrumentation had no problems. Regular loss of beam intensity caused loss of part of the beamtime.

3. Was the local support adequate?

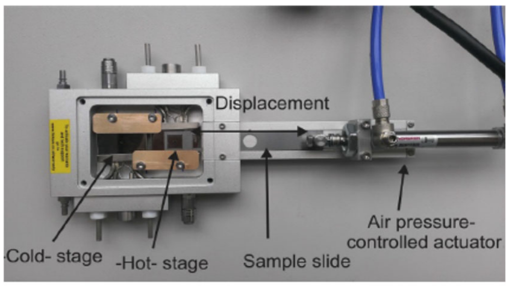
YES. The support of the local contact, D. Hermida Merino and of the technical staff, was adequate and allowed us to efficiently run the experiments. We had technical problems with one of the heaters in our jump stage (due to the transportation) and the local support staff helped very well to solve this defect so that we could still perform our measurements.

4. Are the obtained results at this stage in line with the expected results as mentioned in the project proposal?

YES. All the experimental data collected at BM26-B allowed us to study the effect of various initial combinations of mesophase precursors as well as α and α’ homocrystals on stereocomplex crystallization and to derive crystallisation kinetics models for the crystallization of PLA and its stereocomplex formation. The outcome of the experiments is briefly described below.

Experimental

We have used a custom-modified Linkam JHT350 temperature jump-stage to apply fast temperature jumps. This device contains two thermally separated heating blocks whereby the sample can be rapidly transferred from one stage (e.g. preconditioning temperature) to the second stage, at the temperature desired for the investigation (e.g. crystallization temperature). The commercial device was modified with a remotely controlled pressure valve to complete the 'jump' of the sample from the first to the second heating block reproducibly within tenths of a second. A sample consists of a simple compression moulded ~50 µm thick plate (Fig. 1).



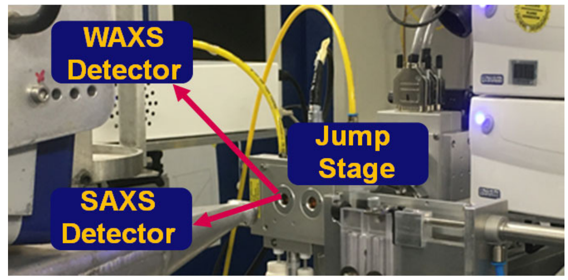


Figure 1 : Left) Custom-modified Linkam jump stage, Right) Linkam jump stage combined with SAXS and WAXS at ESRF

Experiments were conducted on PLLA/PDLA 50/50 Vol.% blends. The sample was placed on the preconditioning block for a specified amount of time at three different temperatures (80 ºC, 100 ºC, and 120 ºC) to form α', α'+α and α homocrystals and mesophases. Subsequently, the sample was quickly transferred to the crystallization block to follow SC crystal formation in time at 190 ºC and 215 ºC by collecting WAXS and SAXS data.

Results

The crystal types of PLLA/PDLA blends which are generated upon melt crystallization are dependent on the crystallization time and temperature. α' and α type homocrystals are formed at 80 ºC and 120 ºC respectively. In addition, melt crystallization at 100 ºC leads to the formation of a mixture of α' and α type. Also, stereocomplex mesophases can be generated by annealing the sample at 120 ºC for a short time (less than 1 minute). Fig. 2a presents WAXS profiles obtained simultaneously with SAXS measurements (Fig. 2b) of the α', α'+α, α, and SC mesophases, which are the starting point for SC crystallization in the PLLA/PDLA blends.

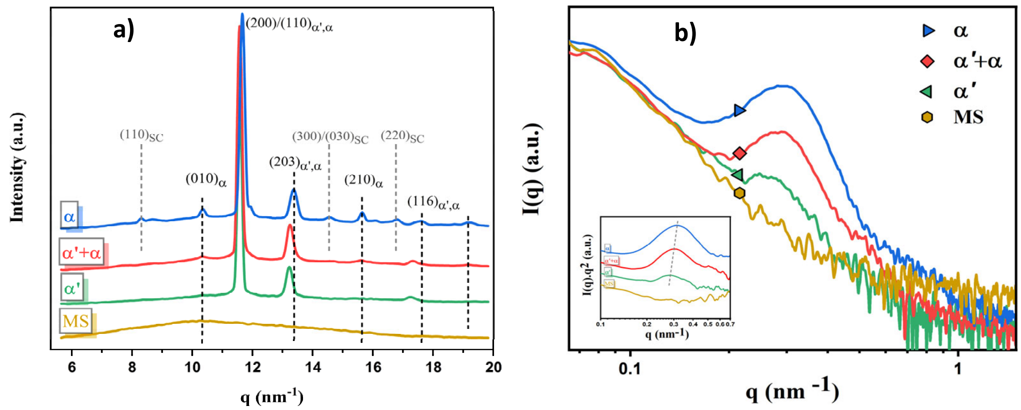
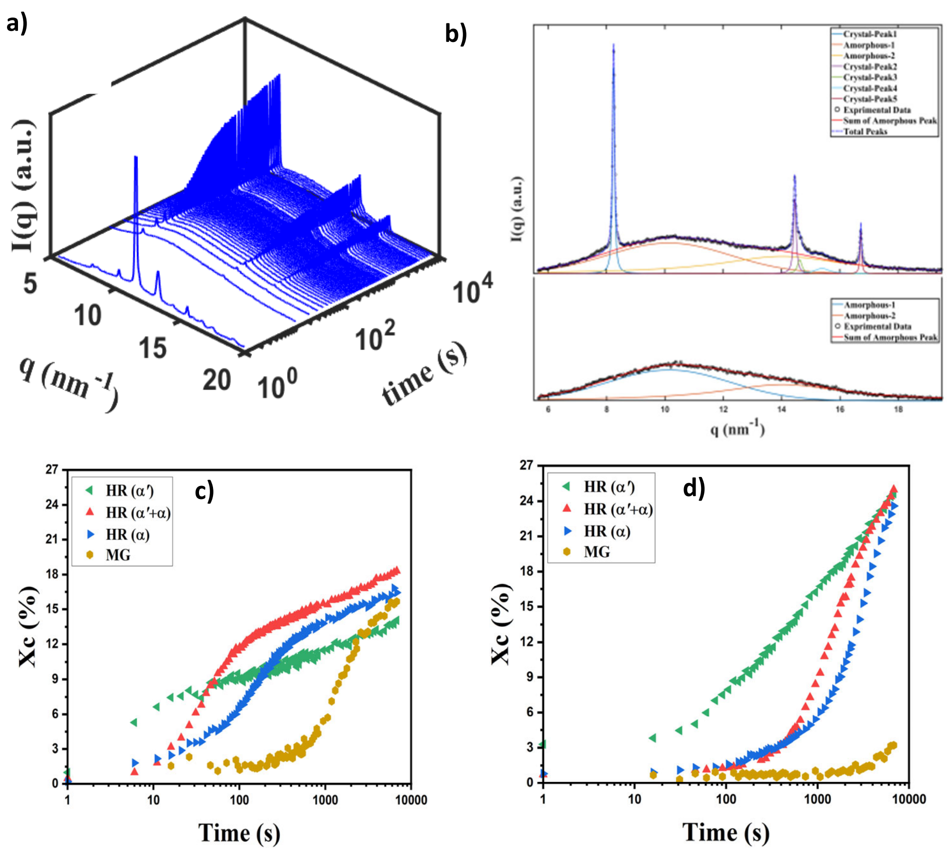


Figure 2: a) WAXS and b) SAXS profiles of stereocomplex crystal precursors.

The homocrystals or mesophase precursors convert to SC crystals at elevated temperature. As can be seen in Fig. 3a, the preformed homocrystals (in this case α-form) melt and recrystallize to SC crystals immediately after changing the place of the sample from the cold-stage to the hot-stage. To determine the degree of crystallinity at each timepoint, the total intensity was deconvoluted into the amorphous and crystalline contributions as shown in Fig. 3b. It is interesting to investigate the effect of crystallization temperature on the kinetics of stereocomplex crystallization from different sources. In Fig. 3c and Fig. 3d, the degrees of stereocomplexation obtained at 190 ºC and 215 ºC are shown. It can be seen that melting and recrystallization of homocrystals can facilitate stereocomplex formation at both the low and high crystallization temperature. In addition, stereocomplexation from the α'-type of homocrystals is ultrafast whereas homo recrystallization of the α' and α mixture leads to a higher amount of stereocomplex crystals.

Figure 3: In situ WAXS results of PLLA/PDLA racemic blend obtained during isothermal crystallization a) Time-resolved WAXS pattern collected at 190°C, b) Deconvolution of WAXS profile into the amorphous and crystalline contributions. Time evolution of SC crystallinity from in-situ WAXS c) at 190 °C and d) at 215 °C.



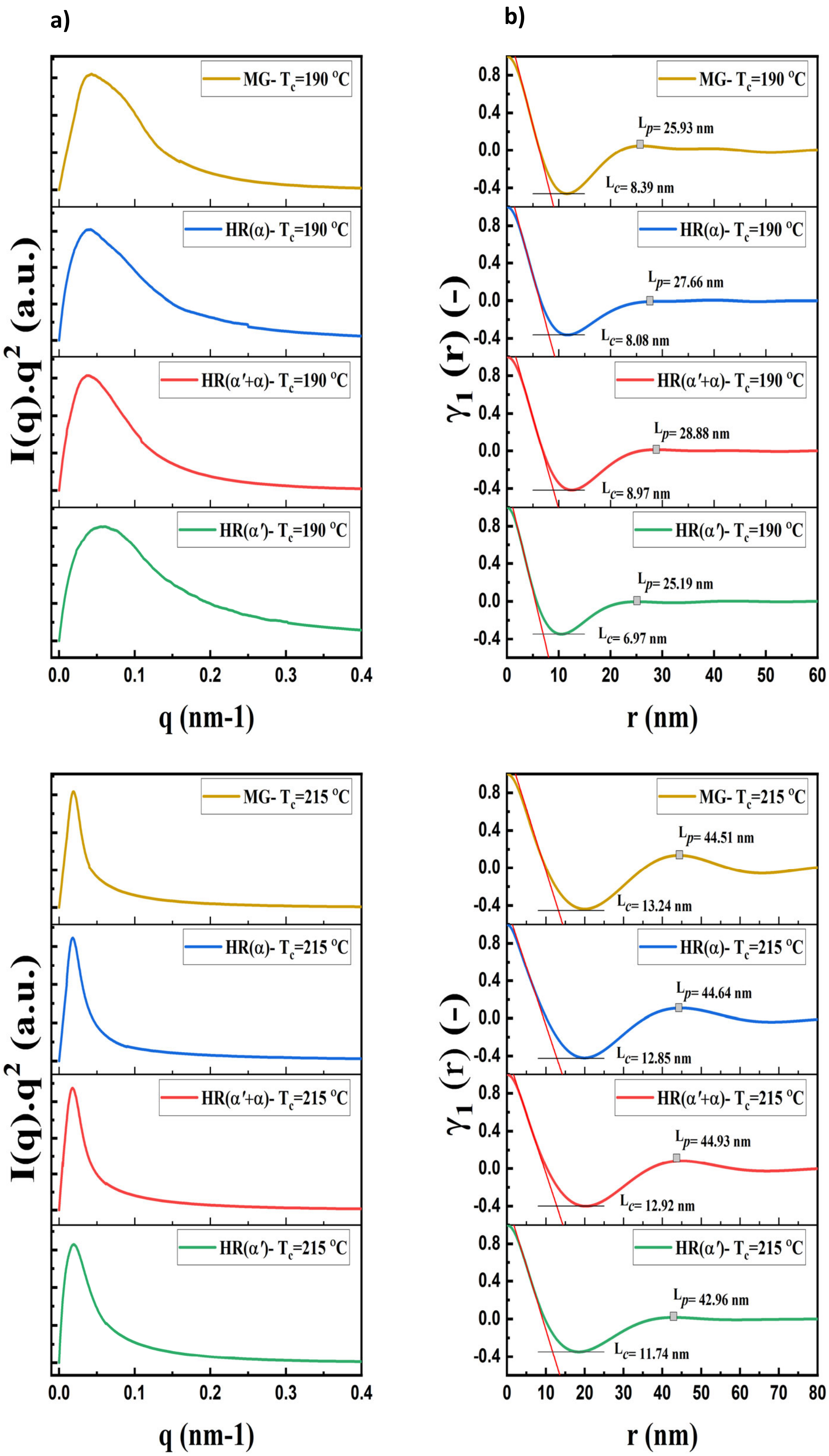


Figure 4: a) Lorentz-corrected SAXS patterns for samples crystalized for 120 min at 190°C and 215°C, b) Normalized correlation function.

SC crystalline lamellar structures crystallized at different temperatures were investigated via SAXS. Fig. 4a shows the Lorentz-corrected SAXS profiles of the different samples after 120 minutes of crystallization at 190 ºC and 215 ºC respectively. To determine the morphological parameters, the Lorentz-corrected SAXS profile was inverse-cosine Fourier transformed to a one dimensional correlation function. The determination of the long period (Lp) and lamellar layer thickness (Lc) from the 1D- correlation function is illustrated in Fig. 4b. In all cases, both Lp and Lc considerably increase by increasing the crystallization temperature. Comparing the lamellar layer thickness, it can be concluded that the smallest stereocomplex crystals are formed from homo recrystallization of the α'–type, both at low and high stereocomplexation temperature. Currently, atomic force microscopy measurements are on-going to get more information about the crystalline microstructure.

In conclusion, we successfully performed a systematic study of the crystal growth and transformation in PLLA/PDLA stereocomplex forming mixtures by coupling a custom-modified Linkam JHT350 temperature jump-stage with SAXS/WAXS techniques. Our custom-designed setup allowed quick temperature jumps with the possibility for high-frequency structure characterization. The results indicate that using melt-recrystallization of homocrystals to form stereocomplex crystals is a quite promising method to achieve improved stereocomplex crystallization rates and to expand the application areas of PLA. Future efforts will focus on using additional characterization techniques such as rheometry and calorimetric measurements for further understanding the intricate crystallization behaviour of the PLLA/PDLA blend system.

5. Are you planning follow-up experiments at DUBBLE for this project?

No. We plan experiments at DUBBLE for another project.

6. Are you planning experiments at other synchrotrons in the near future?

Yes, but for another project.

7. Do you expect any scientific output from this experimental session (publication, patent …)

YES. The experimental data collected at BM26-B will result in scientific publications. At present we are preparing a manuscript to submit to an international peer-reviewed journal.

8. Additional remarks

DUBBLE

NWO
Netherlands Organisation for Scientific Research

DUBBLE - CLAIM FORM FOR COSTS OF TRAVEL/SUBSISTENCE

Dutch users of beam time at DUBBLE can use this form to claim full/partial reimbursement of the associated costs of travel and subsistence. The form must be returned to NWO **within 2 months of the completion of the experiment** to dubble@nwo.nl

Reimbursement rules (costs are reimbursed to the Main Proposer)

Travel costs

€ 400 p.p. for max. 3 persons.

Subsistence costs

Subsistence costs are reimbursed for max. 3 persons @ € 60 p.p. per day (incl. 1 day before the experiment).

Applicant (Main Proposer) : Ruth Cardinaels

Beam time number : **26-02-906**

Experiment dates : 16 June 2021 - 18 June 2021

Participants (max 3 persons):

Name : Hamid Ahmadi
Name : Ruth Cardinaels
Name : Stan F.S.P. Looijmans

Payment details

Pay to account no.: NL42RABO0158249658 (Kostenplaats Nr. 353000 Polymer Technology)

Name: TECHNISCHE UNIVERSITEIT EINDHOVEN

City: Eindhoven

Costs:

Travel costs 3 persons x 400 euro = 1200 euro

Subsistence costs 3 persons x 3 days x 60 = 540 euro

Total = 1740 euro