Standard Experimental Report

Proposal title: In situ/operando X-ray diffraction of a ferroelectric copolymer as a function of thermal annealing and electrical poling
Proposal number: 20201294
Beamline: IF
Shifts: 9
Date(s) of experiment: from: 7th to 10th April 2021
Date of report: 7th February 2022

- Objective & expected results (less than 10 lines):
The objective was to study the transition between the ferroelectric β phase and the paraelectric α phase for the copolymer polyvinylidene fluoride trifluoroethylene (PVDF-TrFE). The expected results were the structural evolution of the PVDF-TrFE phases a a function of thermal annealing and electrical poling. More precisely, as the direct α-β transformation requires high energy, the transition may proceed through an intermediate phase. One prototypical route from α to β consists in transforming the α phase to the polar δ one and then to the β one.

- Results and the conclusions of the study (main part):
The α-β transition of the PVDF-TrFE on a flexible substrate was studied during heating/cooling and after electrical poling by in situ synchrotron X-ray diffraction (XRD) on BM32 at ESRF. Without any electrical poling, the δ phase appears in PVDF-TrFE films at the transition from α to β during cooling after first and second heating. On the contrary, after short electrical pulses of $\sim$ 70 MV.m^{-1}, the δ phase can appear during heating at the transition from β to α (cf. Figure). Hence, the δ phase has been put in evidence starting from a ferroelectric β phase during heating after short pulses of relatively low electric field. In addition, we put in evidence that the coefficient of thermal expansion of PVDF-TrFE depends on the phase. After poling, a negative in-plane stress has been put in evidence for the δ phase. In general, heating could be used to significantly decrease poling field values. The advantages of δ over β are the higher Curie temperature and the larger crystallite height by a factor of three to four.
Moreover, permittivity and ferroelectric measurements are currently being done at the CEA/LITEN in order to correlate the structure with the properties as a function of electrical poling and temperature.

- Justification and comments about the use of beam time (5 lines max.):
The beam time of 9 shifts was used to study the PVDF-TrFE film as a function of temperature during annealing up to 160°C and cooling to room temperature. This experiment was repeated once. Indeed, PVDF-TrFE behaves differently during the first or second experiment. Then, a PVDF-TrFE-based capacitor was studied as a function of electrical poling and temperature.

- Publication(s):
C. Revenant *et al*., Ferroelectric δ phase of PVDF-TrFE copolymer on flexible substrate as a function of thermal annealing and electrical poling, in preparation

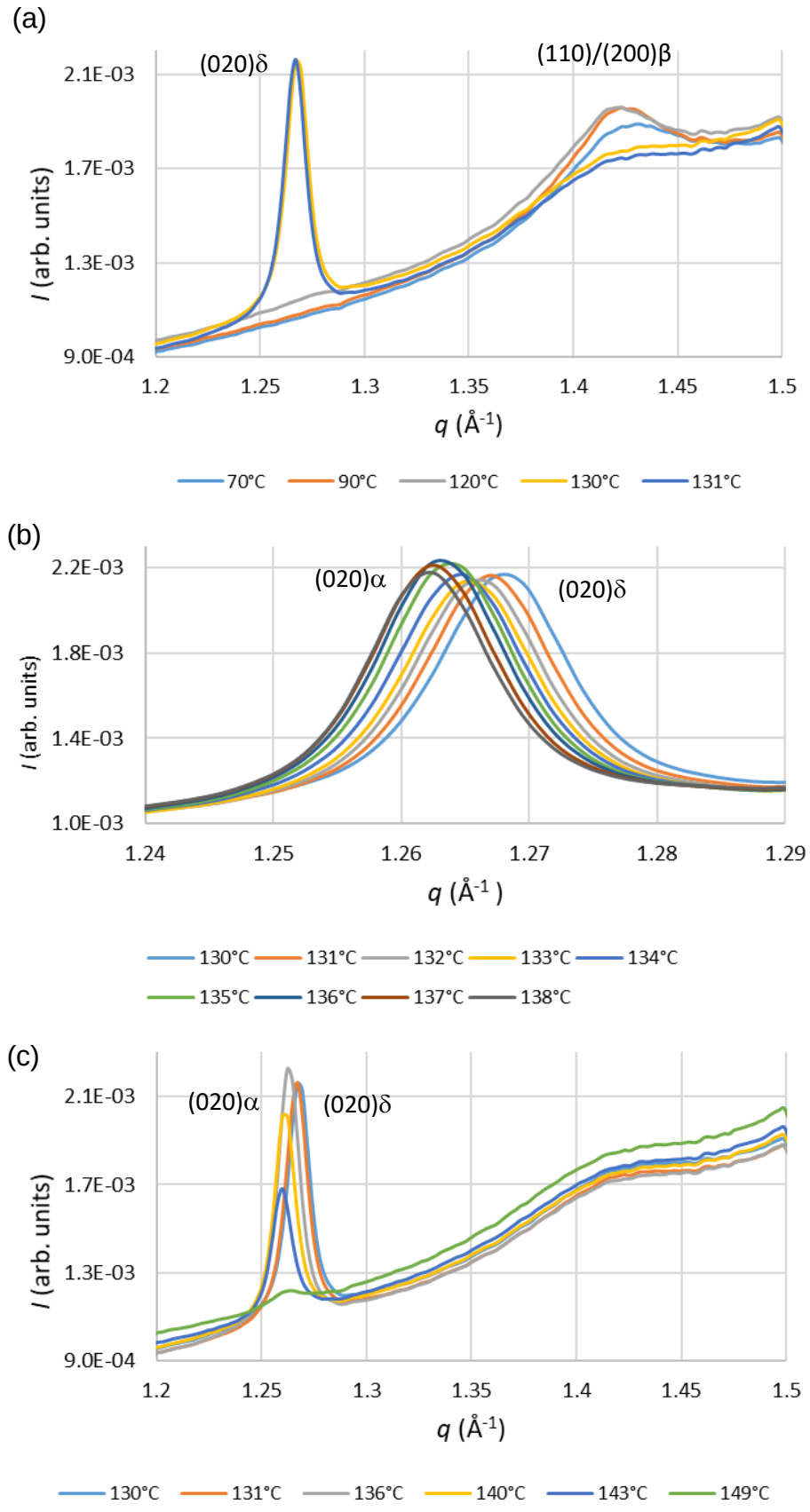

Figure. In situ XRD of the PVDF-TrFE capacitor during heating a) up to T_f =131°C (electrical poling is applied up to T_f =129°C), b) from T_f =130°C to 138°C (detailed view of the low-q peak) and c) from T_f =130°C to 149°C.