Crystal-Crystal transitions in poly(VDF-*ter*-TrFE-*ter*-CTFE): Influence of CTFE termonomers

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The increasing industrial interest for printed organic electronics these last years has led to the development of VDF-based electroactive polymers for numerous energy-related applications (sensors, actuators, capacitors) [1]. Depending on their CTFE content (from 0 to 10 mol %), poly (VDF-*ter*-TrFE-*ter*-CTFE), poly(vinylidene fluoride-*ter*-trifluoroethylene-*ter*-chlorotrifluoroethylene) copolymers exhibit ferroelectric (FE) or relaxor ferroelectric (RFE) properties at low temperature whereas they all present paraelectric (PE) behavior at high temperature. This thermal evolution of their electro-active properties is related to reversible crystal-crystal transitions.

Using simultaneous SAXS-WAXS experiments along thermal cycles, we studied these structural transitions for three different copolymers with various amount of CTFE (0, ~ 5 and ~ 10 mol %).

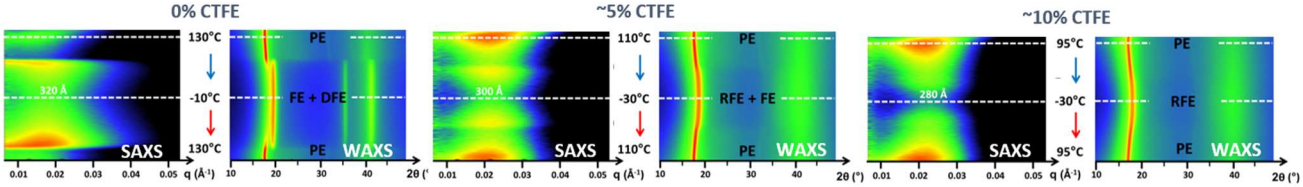

Fig. 1: *Results of simultaneous SAXS-WAXS experiments during cooling and heating for poly(VDF-ter-TrFE-ter-CTFE) with various amount of CTFE. The ordinate axis is the temperature and the abscissa axis is q (SAXS) or 2θ (WAXS). Each line represents the scattering intensity coded with color from black to red for lowest to highest intensity.*

We identified two types of crystalline phase at low temperature with their proper crystal-crystal transition: the first one containing all-*trans* conformations (orthorhombic FE phase) presents a discontinuous transition towards the hexagonal PE phase, the second one which incorporates *gauche* disordered conformations (orthorhombic DFE (Defective Ferroelectric) or RFE) transits continuously towards the same hexagonal PE phase. The discontinuous FE to PE transition is the predominant transition observed in the copolymer without CTFE, it is the well-known Curie transition. The unique transition observed in the terpolymer with 10 mol % of CTFE is the continuous RFE to PE transition. For the intermediate composition, we observe the coexistence of these two simultaneous phase transitions, FE to PE and RFE to PE.

These observations are well correlated with the ferroelectric and relaxor-ferroelectric behaviors of each terpolymer. All the conclusions and discussion of this study were recently published in Polymer [2]. At the epf2019 congress, we will focus on the SAXS-WAXS structural study.

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