

P(VDF-TrFE) Copolymer Dynamics as a Function of Temperature and Pressure in the Vicinity of the Curie Transition

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We report on the phase behavior and the respective dynamics in random P(VDF-TrFE) copolymers using standard and temperature-modulated differential scanning calorimetry, X-ray diffraction, and a combination of temperature- and pressure-dependent dielectric spectroscopy measurements.¹ Depending on the copolymer composition, the coexistence of three/four weakly ordered phases was identified in the vicinity of the Curie temperature (T_c). With respect to the dynamics, we demonstrate that the segmental dynamics - reflecting the relaxation of constrained amorphous VDF segments at the crystal/amorphous "phase" - can be used as a marker of the Curie transition. The corresponding segmental relaxation freezes at about 50 K above the lower liquid-to-glass temperature associated with the freezing of amorphous segments away from the interface. Pressure-dependent dielectric measurements provided quantitative insight into (i) the molecular origin of the segmental processes (by employing the pressure sensitivity of relaxation times and the pressure coefficient of the respective T_g 's), (ii) the nature of the phase transition at T_c , as well as (iii) information about the stability of phases under the variation of temperature and pressure (through the T - P phase diagram). We show that T_c increases linearly with pressure and is accompanied by small volume changes, implying a *weakly first-order* thermodynamic transition. Furthermore, pressure stabilizes the ferroelectric phase over a broader temperature range. This could extend the operating temperature range of ferroelectric devices based on P(VDF-TrFE) copolymers.

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