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Effect of Vitrimers on the Structure and Dynamics of High-Density Polyethylene

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To address the growing demand for recyclable and high-performance plastics, this study investigates the incorporation of vitrimer networks into a semicrystalline polymer—high-density polyethylene (HDPE). While vitrimers have been widely explored in amorphous systems, their influence on semicrystalline materials is especially compelling in terms of crystallization behavior, structural organization, and molecular dynamics.
In this work, HDPE samples were modified with progressively increasing concentrations (from 0 to 1 mol%) of a dynamic crosslinker, azidotriazine. Thermal properties were characterized using Differential Scanning Calorimetry (DSC). To assess the impact of vitrimer incorporation on structure and dynamics, we employed a complementary set of techniques. Specifically, structure was probed using Small- and Wide-Angle X-ray Scattering (SAXS/WAXS) and Polarized Optical Microscopy (POM), while DSC and Dielectric Spectroscopy (DS) were used to investigate dynamic behavior. This combined approach enables analysis across the three principal length scales of polyethylene morphology: the unit cell, lamellar architecture, and spherulitic domains.
The main effects of vitrimer incorporation into HDPE can be summarized as follows:

1. Vitrimer addition leads to a decrease in the degree of crystallinity.
2. Vitrimers are primarily located in the amorphous domains, especially near the crystalline lamellae, in what is known as the restricted amorphous fraction (RAF).
3. Increased crystal thickening is observed at lower temperatures, suggesting enhanced mobility within the restricted amorphous phase.
4. The liquid-to-glass transition temperature of HDPE decreases, attributed to frustrated molecular packing.

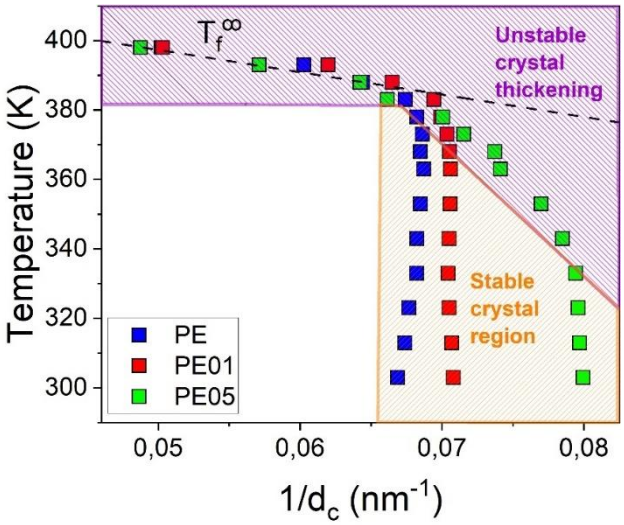

Figure 1: *Results from temperature-dependent SAXS experiments on PE neat (blue), PE m0.1 (red), and PE m0.5 (green) illustrate the relationship between crystallization temperature and crystalline lamellar thickness. The dashed line represents the behaviour of the curve as d_c approaches infinite. The region of the graph where the crystalline structure remains stable, and the lamella thickness does not change, is highlighted in orange. In contrast, the region marked in purple represents the state where, due to crystal instability, we have crystal thickening.*