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Investigating the Influence of Morphology in the Dynamical Behavior of Semicrystalline Triton X-100: Insights in the Detection/Nondetection of the α'-Process

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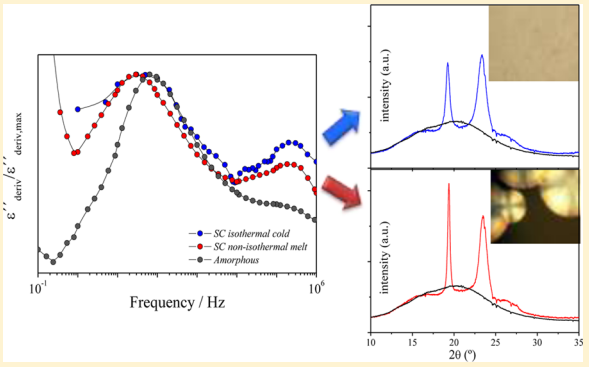
ABSTRACT: The paper investigates the influence of the crystalline structure in the dynamical behavior of semicrystalline Triton X-100 allowing enlightening the reason for the detection/nondetection of the α'-process. The work was preceded by the study of the full amorphous material for which dielectric relaxation spectroscopy (DRS) identified multiple relaxations: the α-process associated with the dynamical glass transition and two secondary relaxations (β- and γ- processes). To evaluate how crystallinity affects the detected relaxation processes, different crystallizations were induced under high and low undercooling conditions. While the secondary relaxations are unaffected by crystallization, the mobility of the cooperative bulk α-process is sensitive to the distinct morphologies. The distinct semicrystalline states were structurally characterized by X-ray diffraction and polarized optical microscopy (POM). Differential scanning calorimetry (DSC) was used as a complementary tool. Depending on the extension of undercooling, large and well-defined shperulites or grainy-like structure emerge, respectively, for low and high undercooling degrees, as monitored by POM. In the two crystalline structures, X-ray diffraction patterns detected the amorphous halo meaning that both are semicrystalline. However, no differences between the amorphous regions are indentified by this technique; the distinction was done by means of dielectric measurements probing different mobilities in each of those regions. When the large spherulites evolve, the bulk-like α-process never goes to extinction and slightly shifts to low frequencies increasing the associated glass transition by 2−3 K, as confirmed by DSC; the slight change is an indication that the dimensions of the persisting amorphous regions become comparable to the length scale inherent to the cooperative motion that determines the glass transition in the full amorphous material. For the grainy-like structure, the α-process becomes extinct and an α'-process evolves as revealed by isochronal plots of dielectric measurements, with the features of a glass transition as confirmed by temperature modulated differential scanning calorimetry; both techniques indicate a 10−12 K displacement of the associated hindered glass transition toward higher temperatures relative to the amorphous glass transition. It is concluded that the detection of the α'-process in Triton X-100 is greatly determined by the high degree of constraining of the amorphous regions imposed by the grainy crystalline structure disabling the occurrence of a bulk-like α-process. Triton X-100 can be taken as a model for understanding low molecular weight materials crystallization, allowing correlating the observed dynamical behavior with the achieved crystalline morphology.



1. INTRODUCTION

Recently, the temperature driven phase transformations of the water-soluble liquid surfactant Triton X-100, with the molecular formula $C_{14}H_{22}O(C_2H_4O)_n$ (n = 9−10), were investigated by some of us,[1] mainly by using dielectric relaxation spectroscopy (DRS); differential scanning calorimetry (DSC) and polarized optical microscopy were used as complementary tools.

Due to its high dielectric response and ability to crystallize from both molten and glassy states (melt-crystallization at ∼255 K at 1 K·min^{-1}; cold-crystallization at ∼232 K), Triton

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