THE JOURNAL OF PHYSICAL CHEMISTRY B

ARTICLE

pubs.acs.org/JPCB

Phase Transformations Undergone by Triton X-100 Probed by Differential Scanning Calorimetry and Dielectric Relaxation Spectroscopy

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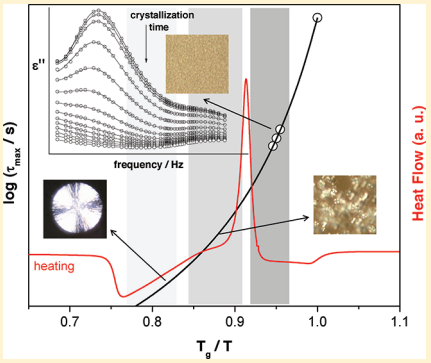
ABSTRACT: The phase transformations of the surfactant Triton X-100 were investigated by differential scanning calorimetry (DSC), polarized optical microscopy (POM), and dielectric relaxation spectroscopy (DRS). In particular, crystallization was induced at different cooling rates comprised between 13 and 0.5 K min^{-1}. Vitrification was detected by both DSC and DRS techniques with a glass transition temperature of ~212 K (measured on heating by DSC) allowing classifying Triton X-100 as a glass former. A fully amorphous material was obtained by cooling at a rate ≥10 K min^{-1}, while crystallization was observed for lower cooling rates. The temperature of the onset of melt-crystallization was found to be dependent on the cooling scan rate, being higher the lower was the scan rate. In subsequent heating scans, the material undergoes cold-crystallization except if cooled previously at a rate ≤1 K min^{-1}. None of the different thermal histories led to a 100% crystalline material because always the jump typical of the glass transformation in both heat flux (DSC) and real permittivity (DRS) is observed. It was also observed that the extent/morphology of the crystalline phase depends on the degree of undercooling, with higher spherulites developing for lower undercooling degree ($24\ K \le T_m - T_{cr} \le 44\ K$) in melt-crystallization and a grain-like morphology emerging for $T_m - T_{cr} \approx 57$ K either in melt- or cold-crystallization. The isothermal cold- and melt-crystallizations were monitored near above the calorimetric glass transition temperature by POM (221 K) and real-time DRS (T_{cr} = 219, 220, and 221 K) to evaluate the phase transformation from an amorphous to a semicrystalline material. By DRS, the α-relaxation associated with the dynamic glass transition was followed, with the observation that it depletes upon both type of crystallizations with no significant changes either in shape or in location. Kinetic parameters were obtained from the time evolution of the normalized permittivity according to a modified Avrami model taking in account the induction time. The reason the isothermal crystallization occurs to a great extent in the vicinity of the glass transition was rationalized as the simultaneous effect of (i) a high dynamic fragile behavior and (ii) the occurrence of catastrophic nucleation/crystal growth probably enabled by a preordering tendency of the surfactant molecules. This is compatible with the estimated low Avrami exponent ($1.12 \le n \le 1.6$), suggesting that relative short length scale motions govern the crystal growth in Triton X-100 coherent with the observation of a grainy crystallization by POM.



1. INTRODUCTION

The factors that govern the interconversion between amorphous and crystalline states and their stability are fundamental aspects of several areas of science and technology gaining special importance in pharmaceutical[1−3] and food[4] industries. Indeed, significant molecular mobility can persist in the glassy state enabling, for instance, the occurrence of phase transitions such as crystallization.[5−7] In this context, understanding key questions such as under what conditions an amorphous leads to crystal formation and the relation between temperature and crystallization pathways is most relevant in materials preservation.[1,2,8,9]

In this work, the water-soluble, liquid surfactant Triton-X 100, the molecular formula of which is $C_{14}H_{22}O(C_2H_4O)_n$ (with $n = 9-10$), was chosen to explore the different aspects concerning temperature-driven phase transformations because it is able to undergo both vitrification and crystallization. This nonionic detergent is widely used in industrial and pharmaceutical formulations and in biological applications such as solubilization of membrane proteins without losing their activity[10] and isolation of membrane rafts,[11] and it also forms transparent microemulsions capable of dissolving both water and oil in relatively large amounts.[12] Because of its high dielectric response and ability to crystallize

Received: March 25, 2011
Revised: August 5, 2011
Published: September 19, 2011