

Detection of Two Glass Transitions on Triton X-100 under Confinement

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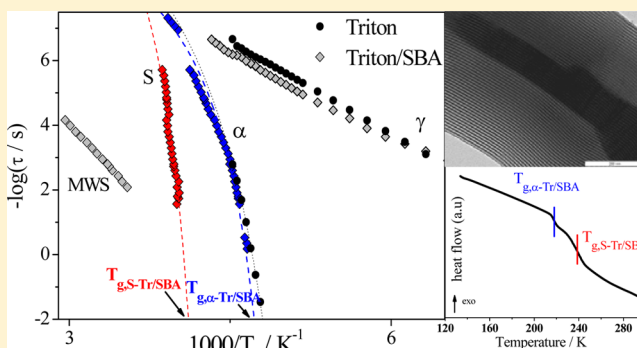
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ABSTRACT: Because of the strong tendency of Triton X-100 to crystallize, inclusion in a SBA-15 matrix of 5.7 nm in pore diameter was used as a means to suppress crystallization. Clear evidence that Triton X-100 exists under confinement in the amorphous and supercooled state is given by X-ray diffraction supported by differential scanning calorimetry and dielectric relaxation spectroscopy. From the thermogravimetric analysis, a loading degree of 50% (wt) was estimated; the decomposition of confined Triton X-100 follows a two-step profile, indicating that molecules are partitioned between bulklike and adsorbed, the latter fraction being in a higher proportion. This allowed the unequivocal detection by DSC of two well-resolved glass transitions (~ 20 K apart), which is a remarkable result obtained by conventional calorimetric analysis in confined systems. The two molecular populations have different mobilities giving rise to two different dielectric relaxation processes: an $\alpha_{\text{Tr/SBA}}$ bulklike process associated with molecules located more in the center of the pores, slightly slowed down relative to bulk α -relaxation, and an S-process due to molecules adsorbed at the walls with significantly hindered mobility. Moreover, an MWS process is detected due to interfacial polarization that builds up between the adsorbed Triton X-100 molecules and SBA pore walls whose temperature dependence seems to be correlated with the one of the S-process. The inclusion in SBA-15 revealed to be a good strategy to simultaneously avoid crystallization and achieve a long-term stabilization of the disordered form.



1. INTRODUCTION

Confinement studies emerged recently as an attractive means to explore fundamental concepts concerning condensed matter physics. In this context, particular attention is given to the influence of confinement on the glass transition:^{1,2} for polymer thin films, the studies concern mainly the thickness dependence of the glass transition temperature (T_g), whereas, for molecular guests confined to nanosized porous restricted geometries, the focus is given to the influence of the host pore dimensions (refs 1, 3, and 4, and references therein); recently, a correlation between the glass transition temperature and the interfacial free volume has been proposed.⁵

In systems exhibiting a distribution of the glass transition as multilayered polymer thin films, sophisticated techniques are needed, such as neutron reflectivity, to reveal multiple T_g 's,^{6,7} instead of thermal techniques as calorimetry. Even for glass formers confined to nanogeometries, which have been

extensively studied in the literature, the calorimetric detection of two glass transitions is not trivial. A few examples are provided as polystyrene/*o*-terphenyl solutions in controlled pore glasses (CPGs),⁸ salol in silica mesopores,⁹ propylene glycol in CPG,¹⁰ and acetaminophen in nanoporous Vycor glass.¹¹

In the present work, evidence of a bimodal behavior concerning the glass transition of the water-soluble, liquid surfactant Triton X-100 entrapped in a nanoporous matrix is investigated by differential scanning calorimetry (DSC) and dielectric relaxation spectroscopy (DRS). These techniques were employed in previous works by some of us^{12,13} to evaluate the temperature-driven phase transformations and dynamical

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