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EFFECT OF THE POLY (ϵ -CAPROLACTONE) CRYSTALLINITY ON THE MOLECULAR MOBILITY IN TRIBLOCK COPOLYMERS AND BLENDS

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Poly(ϵ -caprolactone), PCL, is a biodegradable and semicrystalline polymer very often used in triblock copolymers and polymeric blends. Its crystallinity is an important factor in improving the mechanical properties and therefore the potential applications of the block copolymers or blends based on PCL. PCL is dielectrically active and suitable for thermally stimulated depolarization currents, TSDC, and broadband dielectric spectroscopy, BBDS experiments. Triblock copolymers poly(styrene)-*b*-poly(butadiene)-*b*-poly(ϵ -caprolactone), SBC were synthesized by successive anionic polymerization, the resulting material formed by the association of immiscible components is made of highly organized morphologies. The segregation of mesophases depends on the polymerization degree and the segment-segment interaction. The ordered state is characterized by long range order in the composition and by segregated zones with sizes in the range of tens of nanometers.¹ The PCL segregated mesophase is made of crystalline zones with 3D order and amorphous regions which mobility may be constrained by the complex environment made by the lamellae and the other segregated components of the copolymer. In the case of blends, e.g. poly(carbonate)/poly(ϵ -caprolactone), PC/PCL, the system has been found miscible in the amorphous phase when studied by calorimetric techniques as a single heat capacity step at intermediate temperatures exists. Also the PC phase usually amorphous, becomes semicrystalline depending on the PCL content and thermal history of the blend.² TSDC records the depolarization current caused by the return to random orientation of the previously oriented dipoles due to the application of an intense electric field at a temperature where the dipolar segments are mobile. This oriented state is frozen-in by a rapid quenching to LN₂ temperature. The spectrum recorded as the temperature increases at a constant rate is made of secondary γ and β relaxations due to localized motions of short

segments and of a main relaxation or α peak associated with the glass-rubber transition of the material.

The triblock $S_{57}B_{27}C_{16}$ was studied in the quenched state and after a thermal annealing that optimizes the phase segregation as observed by transmission electron microscopy (TEM). A polygonal core-shell morphology in a PS matrix is observed. PCL is confined in flattened nanotubes with cross-section around $30 \times 13 \text{ nm}^2$ surrounded by a soft PB shell. Also, the PCL crystallinity degree increases from 4% to 18% after annealing as determined by WAXS. The TSDC spectrum for the quenched sample is shown in Fig.1 where the glass transition of the PB and PCL components are clearly visible at 178K and 211 K, respectively. The more crystalline annealed sample shows a remarkable shift and broadening of the segmental relaxation to higher temperature that indicates a reduction of the molecular mobility when the phases are better segregated and the crystalline lamellae coexist in higher proportion in the nanotubes. The confinement effect is affecting the number of mobile entities that cause the low and high temperature peaks.

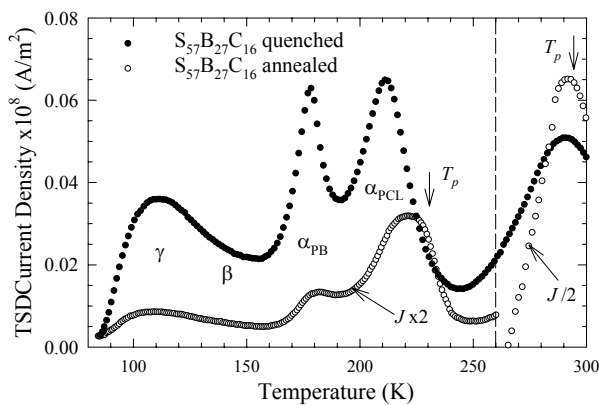


Figure 1. TSDC spectrum of Triblock copolymer $S_{57}B_{27}C_{16}$

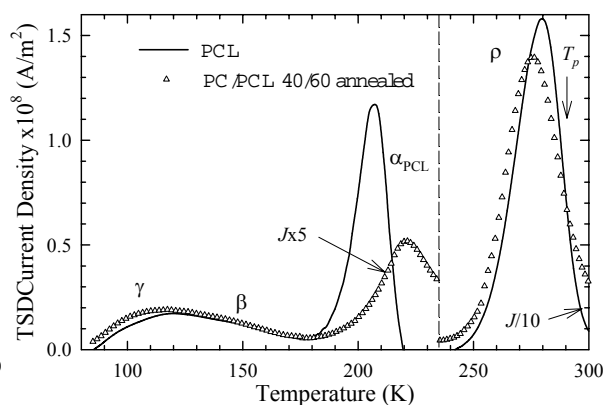


Figure 2. TSDC spectra of PC/PCL 40/60 blend and PCL

In Fig. 2 the TSDC spectrum of the 40/60 PC/PCL blend annealed which is the blend with the higher PC crystallinity degree together with an important PCL one (22% and 37%). The recorded signal is very weak and does not scale with the amount of amorphous phases present in the sample. This shows that there exists a large amount of amorphous chains which are rigidified by the presence of the PC lamellae and which are unable to orient and contribute to the TSDC signal.

¹ E. Laredo, M.C. Hernández, A. Bello, M. Grima, A.J. Müller, V. Bálsamo, Phys. Rev. E **65**, 21807 (2002).

² M.C. Hernández, E. Laredo, A. Bello, P. Carrizales, L. Marcano, V. Bálsamo, M.Grimau, A. Müller (in press Macromolecules).