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Structural and Molecular Dynamic Studies of Poly(9,9-dioctylfluorene) Crystalline Phases

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Abstract – This article describes microstructures and dynamics in solid state of different structural phases of polyfluorene polymer, named, poly(9,9-dioctylfluorenyl-2,7-diyl) (PF8). It is well known that PF8 undergo phases transitions when is appropriated thermally treated. We prepared three different crystalline phases: β (as cast), α, and α´. In summary, this study intends to understand the influence of the structural characteristics on polymer conformation and molecular dynamics among the three different phases.

Polyfluorene-based polymers form a category of thermal and chemical stable polymers emitting from the blue to the red, depending on the chemical structures, substituent and side-chains[1]. These chemical modifications control the supramolecular structure and their optical properties[2]. The emission and the electrical conduction of polyfluorenes are modified by solid-state phase transitions and the related relaxation processes that involve segments of the polymer chains. In addition, depending on the thermal treatment or processing mechanisms they can crystallize in more than one crystalline phase and even to form molecular aggregates with mesomorphic phases[3]. In this sense, we prepared three different crystalline phases of PF8, using thermal treatments as reported by Chen *et al* [3]. Using Wide Angle X-Ray Diffraction (WAXD) it was possible to analyze differences of molecular packing and structure of the crystalline phases. By Dynamical-Mechanical Thermal Analysis (DMTA) we detected different activation energies for molecular relaxations, for example, the β relaxation – which is related to the molecular dynamics of the lateral chain. We also used High Resolution Solid-State Nuclear Magnetic Resonance (NMR) to investigate the molecular dynamics of individual segment of the molecule for several temperatures.

For films formed by cast procedure with very slow solvent-evaporation, we obtained β phase structures. However, a phase transition from β to α occurs by annealing for 40 minutes at 140ºC followed by subsequent quenching in liquid N_2. On the other hand, α´ phase is obtained if we anneal the sample at 160ºC for 20 minutes followed by cooling it down to room temperature. WAXD measurements showed differences on polymer structures as showed in figures 1 and 2. By solid-state NMR techniques was possible to observe and to quantify modifications in the dynamics for specific molecular segments among the three different phases.

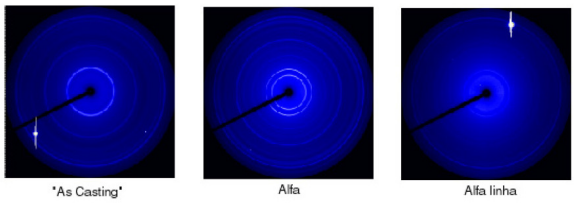

Figure 1: 2D-WAXD of the three crystalline phases.

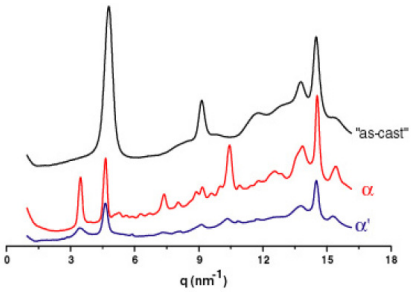

Figure 2: 1D-WAXD of the three crystalline phases.

References

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