

# Structure and Dynamics of Poly(9,9'-dioctylfluorene-co-benzothiadiazole) (PF8BT) as revealed by Solid-State NMR, Dynamic Mechanical Thermal Analysis and Wide Angle X-Ray Diffraction.

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**Abstract:** We present an extensive characterization of the molecular dynamics and structure of PF8BT as a function of temperature using X-Ray, NMR, and DMTA. We showed that the backbone is quite rigid, but executes small angle librations with reorientation angles in the range of 5-20° at 300 – 373K. In contrast the side chains are very mobile, executing local rotations with activation energies of 25 kJ/mol. Besides the dynamics aspects, the polymer structure also changes considerably with the temperature, evolving from a lamellar phase to a 3D crystalline phase, which melts at 523 K to a liquid crystalline phase.

Poly(9,9'-dioctylfluorene-co-benzothiadiazole) (PF8BT), is currently one of the most promising material for use as active layers in polymeric electronic devices, such as polymer light-emitting diodes (PLEDs) and the polymer field effect transistor (P-FET) [1]. The chemical structure of PF8BT, which has a rigid backbone and a flexible side-chain, make possible the formation of different crystalline or mesomorphic phases, in which the polymer chains have distinct dynamic behavior. Both polymer structure and dynamics affects the luminescence and transport properties of the material, making worthwhile to investigate them.

In order to investigate possible temperature induced structural modification Wide-angle X-Ray Diffraction (WAXD) measurements as a function of temperature were carried out. The results revealed that, for as cast films, at low temperature, the molecular structure is not so well organized essentially constituted by a lamellar phase, formed by the packing of the phenyl rings. As the temperature increases, this lamellar phase transforms into a more complex crystalline structure, probably with the backbone forming a helix structure similar to that formed by other polyfluorene polymers. At 523 K, the crystalline phase melts and the polymer structure become liquid crystalline.

The dynamical aspects of PF8BT were first investigated by Dynamical Mechanical Thermal Analysis (DMTA) measurements. The results revealed the presence of two main relaxation process, which occurs at about 223 K ( $\beta$  relaxation) and 348 K ( $\alpha$  relaxation). The  $\beta$  relaxation showed Arrhenius behavior with activation energy of 26 kJ/mol. The  $\alpha$ -relaxation does not present Arrhenius like behavior, which point to the attribution of this relaxation as a glass-transition like process. In order to understand the molecular dynamics of different segments of the polymer molecule, solid-state NMR techniques were used. To study the molecular dynamics with correlation time in the range of  $10^{-4}$  –  $10^{-6}$  seconds – we used a NMR method called Dipolar Chemical Shift Correlation (DIPSHIFT). The results showed that in the temperature range of 223 to 373 K the lateral chain execute molecular rotations with average correlation times ranging from  $10^{-4}$  –  $10^{-7}$  seconds. The average activation energy (EA) obtained from the DIPSHIFT experiments was about 25 KJ/mol, which is in very good agreement with the DMTA results. This is an expected result since the  $\beta$  relaxation of polymer is usually attributed by dynamics of side chains. The DIPSHIFT experiments revealed that there is no molecular motion with correlation times in the range of  $10^{-4}$  –  $10^{-7}$  seconds in the polymer backbone, but slower motions cannot be ruled out. To investigate the presence of slow dynamic in the backbone (correlation times in the range of  $10^0$  –  $10^{-3}$  seconds) we used a NMR methods named Constant Time Recoupling of the Anisotropies Method – CONTRA. The results showed that from 300 to 350K the backbone carbons executes slow libration motions with reorientation angles that increases as a function of temperature.

In summary, we will present an extensive characterization of the molecular dynamics and structure of PF8BT as a function of temperature. In a second step we also will associate these modifications with variation in their opto-electronic properties, which are currently under investigation.

[1] M. Grell, D. D. C. Bradley, G. Ungar, J. Hill, K. S. M. Whitehead, *Macromolecules* 32 (1999) 5810-5817.