Experimental report

22/07/2024

Proposal:	**TEST-2614**	**Council:**	4/2023
Title:	Local strctural dynamics of PFO		
Research area:			

This proposal is a new proposal

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Samples: PFO

Instrument	Requested days	Allocated days	From	To
IN6	4	7	09/06/2016 15/11/2016	13/06/2016 18/11/2023

Abstract:

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Dynamics of Polyalkylfluorene Conjugated Polymers: Insights from Neutron Spectroscopy and Molecular Dynamics Simulations

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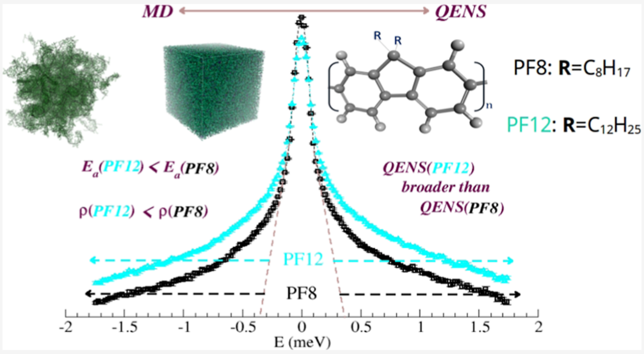

ABSTRACT: The dynamics of the conjugated polymers poly(9,9-dioctylfluorene) (PF8) and poly(9,9-didodecylfluorene) (PF12), differing by the length of their side chains, is investigated in the amorphous phase using the temperature-dependent quasielastic neutron scattering (QENS) technique. The neutron spectroscopy measurements are synergistically underpinned by molecular dynamics (MD) simulations. The probe is focused on the picosecond time scale, where the structural dynamics of both PF8 and PF12 would mainly be dominated by the motions of their side chains. The measurements highlighted temperature-induced dynamics, reflected in the broadening of the QENS spectra upon heating. The MD simulations reproduced well the observations; hence, the neutron measurements validate the MD force fields, the adopted amorphous model structures, and the numerical procedure. As the QENS spectra are dominated by the signal from the hydrogens on the backbones and side chains of PF8 and PF12, extensive analysis of the MD simulations allowed the following: (i) tagging these hydrogens, (ii) estimating their contributions to the self-part of the van Hove functions and hence to the QENS spectra, and (iii) determining the activation energies of the different motions involving the tagged hydrogens. PF12 is found to exhibit QENS spectra broader than those of PF8, indicating a more pronounced motion of the didodecyl chains of PF12 as compared to dioctyl chains of PF8. This is in agreement with the outcome of our MD analysis: (i) confirming a lower glass transition temperature of PF12 compared to PF8, (ii) showing PF12 having a lower density than PF8, and (iii) highlighting lower activation energies of the motions of PF12 in comparison with PF8. This study helped to gain insights into the temperature-induced side-chain dynamics of the PF8 and PF12 conjugated polymers, influencing their stability, which could potentially impact, on the practical side, the performance of the associated optoelectronic active layer.

INTRODUCTION

Conjugated polymer materials have received considerable attention over the last decades because they can be integrated in flexible and stretchable lightweight optoelectronic and bioelectronic devices[1−3] such as organic led emitting diodes (OLEDs),[4−7] organic solar cells (OSCs),[8−10] organic field effect transistors (OFETs),[11−14] and more recently, organic electrochemical transistors (OECTs).[15−17] These devices could be, in principle, fabricated at low cost using roll-to-roll solution processing techniques. Initially, the development of conjugated polymers has focused on engineering the π-conjugated backbone as it gives rise to the optoelectronic properties of the material with the flexible side chains, mainly alkyl side chains, being primarily used as necessary solubilizing groups. Two very common molecular donor units found in conjugated polymer backbones and used as model systems are the thiophene ring and the fluorene unit. The fluorene unit comprises, in comparison with the simple thiophene ring, two aromatic rings that are planarized through a carbon bridging atom.

Side chains have also been proven to have substantial impacts on the optoelectronic properties of conjugated polymers in the solid state. The solid-state morphology/microstructure is significantly influenced by the choice of side chains as the solvent solubility impacts the processing and, thus, the final packing. Also, it has been shown that different side chains can modify the miscibility of the polymer with other components in blends. The length of side chains can modify the glass transition behavior of the material. Often two glass transitions, one assigned to the backbone and one to the side chains, are observed,[18] either due to microphase separation between the backbone and side chains or decoupling of segmental dynamics between the backbone and side chains even without microphase separation.[19] This can affect the stability of the active layer, especially in blends where one component can diffuse through

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