

Molecular Dynamics Simulations in Investigating the Liquid Crystalline Behavior Found in Biodegradable Polyarylates

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Statement of Purpose:

Materials formed from polymers that show long-range ordering in the fluid state because of the organization and conformational preference of the chain frequently demonstrate unusual mechanical properties. Since late 80s these so-called liquid crystalline polymers (LCPs) are being increasingly utilized in specialty and high performance applications. Recently Jaffe and coauthors investigated selected representatives of combinatorial library of biodegradable polyarylates by means of Wide Angle X-ray Scattering (WAXS) and thermal analysis (DSC) [1,2]. It was reported that polymers, which possess eight-carbon atoms (and longer) aliphatic diacid component exhibit a highly layered mesogenic structure with long-range ordering similar to that observed in smectic or discotic liquid crystals. The authors carried out energy minimization and suggested that in bulk material polymer molecules are aligned along the backbone axis and stabilized by hydrogen bonding through the amide linkage with the pendant chains situated in layers normal to the main chain axis [1,2]. In the present work we utilized the results of Molecular Dynamics simulations to develop realistic model for polymers as bulk materials and to provide more accurate interpretation of WAXS measurements.

Methods:

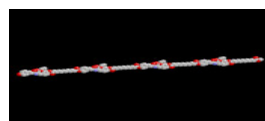
Two representatives of the combinatorial library of polyarylates, namely DTE-dodecanedioate and DTD-dodecanedioate (naming convention from Ref. [1]) were chosen for the present study. Repeat units of these polymers have same chemical composition for diphenol and diacid components but they differ significantly in the length of aliphatic pendant R. Numerical estimates of the side chain separations were performed using experimental data from WAXS. Molecular Dynamics simulations of polymer chains consisting of twenty repeat units in the presence of implicit solvent (water) were carried out using MacroModel simulation package (Schrodinger [2]). Bulk materials were modeled using module Amorphous Cell of Materials Studio (Accelrys [3]).

Results / Discussion:

It has been noted that some of the characteristics of polyarylates (e.g. molecular weight, rigidity of the backbone) noticeably deviate from those known from the literature for LCPs [6]. To understand and explain this phenomenon long-chain models were simulated in aqueous surrounding (Fig.1b) and the side chain spacing was estimated by measuring distances between ester oxygens in the backbone and carbon atoms of carbonyl in the pendant chain (average over 20 monomers in 10 sampled structures). Results were compared with theoretical estimates of the side chain separation for the

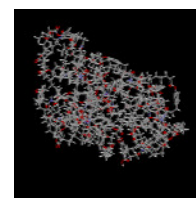
polymer in extended conformation (Fig.1a) and experimental data extracted from WAXS.

Figure 1. Side chain spacing, d , for DTE-dodecanedioate in extended conformation (a) is compared with that in final conformation from the of 1.5ns MD run (b).



$d=31$ A

(a)



$d=25.1\pm 0.4\times 10^{-4}$ A

(b)

The value of 20.5 ± 1.2 A for side chain spacing was extracted from WAXS measurements of DTE-dodecanedioate (wet film at 296K). If the model of intermolecular assemblage of unfolded chains linked by H-bonds on amide groups proposed in [1] is true then the experimental side chain spacing has to be much larger than that observed in folded, *globular-like* model structure (Fig1b). From the data shown above one can see that the trend is opposite.

Conclusions:

Occurrence of long-range (more specifically smectic-like) ordering is investigated for two polymers from the library of biodegradable polyarylates by means of MD technique. Experimentally determined side chain and main chain separations are used as essential aid for modeling of bulk materials and as criteria to evaluate quality of modeling approximations (e.g. long-chains in aqueous surrounding vs. penta- or tetramers layered in the simulation cell). Comparison of experimental side chain separations with those obtained from globular-like structures do not confirm the alignment of polymers suggested in Ref. [1]. The modeling possibilities for packing of polyarylates in bulk materials, which reflect the real dynamics of molecules at different temperatures, are discussed.

References:

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