INTERMOLECULAR INTERACTIONS AND PROPERTIES
OF BULK POLYMERS

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The mechanical properties of highly ordered assemblies of rigid-rod macromolecules are among their most striking and relevant features. The modeling of such structures and their behaviour, most importantly the mechanical properties, is therefore of importance. However, while other densely packed macromolecular systems, such as crystals of flexible-chain aliphatic polymers [1-10] and amorphous glasses of some vinyl polymers [11-14] and polycarbonates [15], have received attention from atomistic simulations in the past, no such modeling efforts have been published, to our knowkledge, to date for packings of rigid-rod chains.

We report on a static atomistic modeling technique aimed specifically at the simulation of potentially pseudo-crystalline materials [16,17] without resort to the use of adjustable parameters [18]. We employ a conformation-dominated chain building technique and a packing method which is amenable to the inclusion of nonrational (or incommensurate) helices. Energy minimization is simultaneous with respect to both intramolecular and intermolecular degrees of freedom, a feature which is critical to the realistic modeling of the cooperative interactions between atoms in multichain systems. This method is then applied to the study of poly(para-phenylene terephthalamide) (PPTA) and simple structural modifications of this chain.

The application of these structure prediction procedures to the rigid-rod aramids reveals that, due to the convolution of the potential energy hypersurface, one may expect a multiplicity of viable candidates for stable geometries. In the presence of strong intermolecular packing forces, one encounters competing trends of similar magnitude, one driven by bonded interactions within a chain and the other by non-bonded interactions of the type commonly attributed to hydrogen bonds between chains. A detailed analysis indicates that one may expect the occurrence of several distinguishable polymorphs having comparable stability and capable of coexistence at the microscopic level.

These predictions have been tested in a set of experiments involving spinning of fibres by the dry-jet wet spinning technique and X-ray analysis of the fibres produced before and after annealing [19]. The combination of computation and experiment suggests that PPTA, depending on its process history, may consist of an agglomeration of crystalline polymorphs, the relative occurrence of which are process dependent and may be altered by annealing and other post-spinning techniques. The use of atomistic simulation techniques constitutes a convenient means to anticipate the natures of the several crystal structures possible and

provides one with suitable starting points for analyzing experimental X-ray data. In addition, analysis of the simulation yields insight into the details of interactions within the chain agglomerate and the source of structure formation.

Furthermore, the elastic response of the atomistic structures to imposed deformation has been addressed and the elastic constants of both the single crystal and the axially-symmetric polycristalline aggregate have been estimated for PPTA [20] as well as for the simple structural modifications, again without resort to adjustable parameters. Our computations suggest that the large intermolecular interactions present in rigid-rod aramid systems can have a significant effect on the longitudinal as well as the transverse moduli, resulting in considerable discrepancy between the results of single chain and packed chain estimation procedures. It also appears that, based on simple estimation procedures using the limited available experimental data, that entropic contributions to the elastic moduli at ambient temperature are significant; for the tensile modulus of a PTTA fibre they are roughly 15-30% of the total value. For the example of PPTA, the estimated values for the tensile and the torsional modulus are 220-290 GPa and 4-12 Gpa, respectively, in excellent agreement with experiment.

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