A molecular modelling study of 2,3-exo-disyndiotactic polynorbornene

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The present contribution reports a detailed molecular modelling study of the peculiar crystalline structure of the 2,3-exo-disyndiotactic polynorbornene (dsPNB) obtained by polymerization with a TiCl4 based catalysts. Molecular mechanics and dynamics have been used together with quantum mechanical methods specific for solid crystalline phases. Using the low energy models obtained and data from X-ray diffraction experiments, the stereochemistry was proved revealing macromolecular chains, in the crystalline state, with an unusual tubular helical (constituted by 12 units) conformation [1]. Interestingly, the estimated coherence length (obtained by X-ray diffraction analysis) along the backbone axis is higher than the value predicted by the average degree of polymerisation of the system thus suggesting that a single chain is plausibly a sequence of oligomers. Moreover, the hexagonal packing of the helices generates an empty accessible core in which guest molecules (toluene or iodine molecules) and also chain terminals can be easily hosted by reversible processes. Experimental study demonstrated that a guest like iodine influences very substantially the relative intensities of the diffraction patterns while leaving peak positions unchanged as expected for a unique polymer conformation in which iodine replaces molecular guests inside dsPNB channels [2]. Molecular modelling methods confirmed the stability of empty and host-guest crystalline structures. In particular, molecular dynamics simulations rationalises both the guest exchange mechanism and the key role of chain tails in the crystalline structure [3].

References

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