# First-principles structural studies of polythiophene isomeric systems

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Recent experimental work has been reported for the synthesis of poly-ortho-thiophenes, in particular helical poly(5-alkyl-2,3-thiophene)s. These polythiophenes differ from the poly(3-alkyl-2,5-thiophene)s studied over for the past several decades as electroactive polymers similar to the polypyrroles, and which have had application in bulk heterojunction photovoltaics. We have carried out first-principles, density functional simulations for the electronic structure and total energy of a range of polythiophene systems using Gaussian-function-based orbitals in a band structure approach using helical symmetry. We have examined the hydrogen, methyl, ethyl, and propyl substituted poly(5-alkyl-2,3-thiophene)s and poly(3-alkyl-2,5-thiophene)s, optimizing the geometry as a function of twist angle in the helical backbone. We have also looked into other possible polymer conformations such as the poly(5-alkyl-2,4-thiophene)s.

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