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Structural Properties of Poly-alkylthiophenes Studied by Computer Simulation Methods

Abstract

Studies of new materials that look for interaction between atomic, molecular and macro-molecular properties are mainly investigated by experimental methods. Nowadays, how-ever, simulation methods appear useful for that purpose, and it has become obvious to us that the molecular dynamics method can be applied to any polymer aggregation.
We have chosen poly-alkylthiophenes molecules for two reasons; first, because they are widely studied by experimental methods at our faculty, and second because of its non-trivial structure, that allows molecules of gradually increasing complexity to be simulated.
We will present a comparison of the structures, the reasons for the differences between them, and suggestions for solution of poly-3-alkylthiophene structure.

Key words: *poly-alkylthiophene, molecular dynamic simulations, X-ray analysis.*

Introduction

The relation between the physical properties of materials and their atomic, molecular and macromolecular structure are traditionally investigated by advanced experimental methods. Nowadays, however, computer simulations are becoming valuable tools that may accompany other methods, especially if we consider the constantly expanding area of nanotechnology. One such computer method is classical molecular dynamics, which is commonly used for the simulation of molecule systems important for biological science, such as DNA chains, lipid bi-layers and proteins. The similarity between such systems and polymers decided us in favour of using molecular dynamics. The article covers preliminary results from simulations of poly-3-alkylthiophenes.

A genealogy of poly-alkylthiophenes

Poly-alkylthiophenes are molecules that have been well-known since the early 1990s. Its structure has been resolved mainly by means of X-ray scattering experiments, although some questions related to the disorder of parts of poly-alkylthiophenes have been opened. This family of molecules is therefore good material for testing the new concept and methods that we intend to use.

The direct predecessor of poly-alkylthiophenes is the well-known, first-discovered conjugated polymer, polythiophene. It is built up from thiophene rings connected to each other in an anti-syn configuration, as illustrated in Figure 1. Poly-alkylthiophenes (PATs), a derivative of polythiophene substituted with alkyl chains, arose while the technical processing of conjugated polymers was considered. PATs were good material for chemists, who developed methods that allow an almost ideal substitution of polythiophene. As a result, regioregular poly-3-alkylthiophenes (Figure 1) were synthesised and become good material for our research.
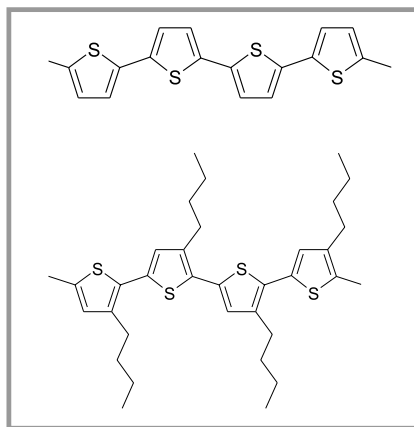

Figure 1. *Polythiophene and example regio-regular poly-3-butylthiophene.*

As soon as such promising polymers were developed, X-ray investigations of their structure were performed. During several years of developments in this area, increasingly complicated models of unit cell for the polymers were introduced. A common feature of early models was the stiffness of PAT molecules [1], especially alkyl chains. This was actually not expected, and questions about the role of disorder of alkyl chain arose: however, the models were simpler with fewer degrees of freedom. The next step was taken by Winokur [2] who introduced the so-called inverse comb model that contained additional parameters responsible for the overall rotation of alkyl chains. Other attempts were also performed to prove the assumption of the flat main/thiophene chain [1]. Among the articles in literature that deal with molecular simulations of PATs, one finds tentative attempts to use molecular dynamics to describe the structure of poly-3-alkylthiophenes. These still restrained the freedom to build the structure by assuming specific and small unit cells. The direction of our approach is different. We intend to obtain as much information as possible from simulations while making as few assumptions as is rational.

Simulation methodology

Our simulations were conducted with a molecular dynamics package of simulation programs as well as analysis tools called GROMACS [3]. Several other tools were considered for these experiments; however, this one appeared to be the most flexible of those available, most of which are mainly focused on biological systems. After all GROMACS is one of the fastest tools that can be run on an average PC computer, and allowed high time- and size-scales of simulations to be attained.

mMolecule systems s consist of conceptual layers that accurately model them. They are as follows:
- the co-ordinations of atoms
- the topology of molecules
- the force field attached to every atom

The topology of the molecule comes directly from the covalent model of the molecule. This can be expressed in the form of a graph made of atom-sites and

Table 1. *Density and enthalpy of vaporisation for thiophene liquid.*

Source of data	Density, g/l @ T=293K	DH, kJ/mol @ T=356K
Simulation	1070	30
Experiment	1083	32

bounds between atoms. Additional topological relations between atoms, such as angles and different kinds of torsional angles, are derived from the graph. It is essential for successful managements of molecules to synchronise the topology and geometry of molecule, as is especially visible in the case of polymers that are constructed from repeatable units. It should be possible to easily build a polymer of any length, if the building units as well as the connections between them are known. To our knowledge no freely available tool for the purpose exists, although a few plain programs focused on DNA and RNA manipulation are available. We developed tools that fulfil the tasks described in a very flexible way (they are not available yet).

The third layer – a force field – was assigned with the help of PAT genealogy. We could assign step by step parameters for thiophene and poly-alkylthiophene while checking whether interaction parameters are good. The results from the checkout are placed in Tables 1 and 2. Standard functional representation containing harmonic bonds, angles, dihedrals and Lennard-Johnes & coulomb interactions from an OPLS-AA force-field was used [4]. A set of parameters designed for furan with the help of X-ray data [1] was adapted for thiophene, standard parameters for alkyl chains were used, and the height of the torsional barrier for the anti-syn connection between rings was equal to 5.5 kJ/mol [5].

The simulated systems were poly-3-hexyl, octyl and decylthiophene with 6, 8 and 10 carbon atoms in alkyl side chains respectively. Periodic boundary conditions were applied, yielding effectively to infinitely long polythiophene chains, which restricts the available range of fluctuation frequencies. There were 16 thiophene rings in main chains, and between 24 to 30 chains were placed in parallel into the simulation triclinic box in such a way that none of the chains interacts with itself in a direction perpendicular to the main chains (Figure 2).

The configuration does not allow a whole set of molecular movements in phase space; for example, due to the alkyl chains' interaction, any translation of molecules along the main chains is rarely possible. The remedy is to provide a different starting structure and compare the simulation results. Two kinds of structure were considered: the ideal crystal of PATs

and the distorted crystal; each polymer chain of the ideal crystal was translated by a small, random vector (of a few Angstroms) in three dimensions.

The prepared structures were simulated at a constant temperature (293K) and pressure (1atm) over 900ps. A part of the simulation time was used for equilibration, and the remaining trajectory (usually 300ps) was used for averaging.

◼ Simulation results

The structures obtained from the simulations (an example is given in Figure 2) are in good agreement with diffraction data, see Table 3. Both the characteristic dimensions and the tendency in the density of the PAT system are reproduced. It should be stated that our simulations are applicable for the crystal part of real PAT samples which are not crystallised com-

Table 2. *Density of simulated poly-alkylthiophene systems versus experimental density for crystalline and distorted starting structures.*

Compound name	Density, g/l		
	PHT	POT	PDT
Crystal	1218	1182	1139
Distorted	1168	1076	1112
Experiment [2]	1103	1052	1034

Table 3. *Unit cell parameters from our simulations(for ideal crystal as the starting structure) and experiment.*

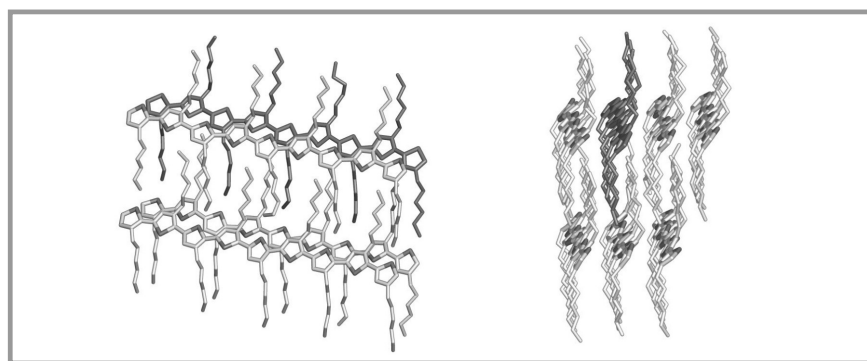|	a, Angstr		b, Angstr	
	Simulation	Experiment [1]	Simulation	Experiment [1]
PHT	16	16,7	3,6	3,7
POT	20	20,5	3,7	3,8
PDT	23	23	3,7	3,8

Figure 2. *Example parts of the resulting structure of PHT obtained from the initial crystal configuration, front and side view. One chain is marked by a darker colour, as are the sulphur atoms in all the presented chains.*
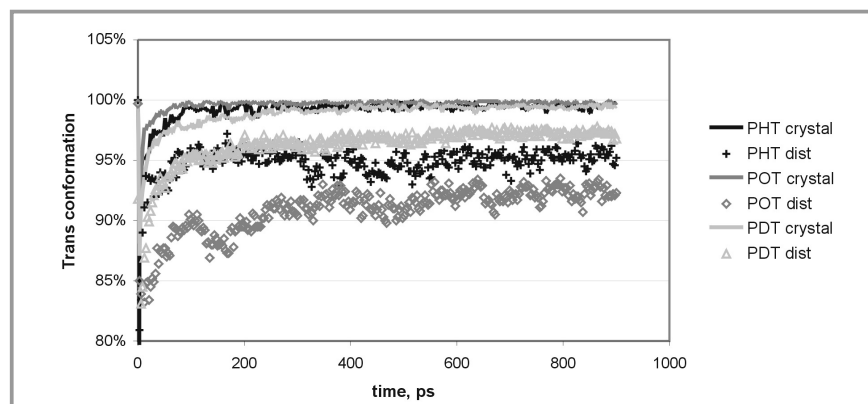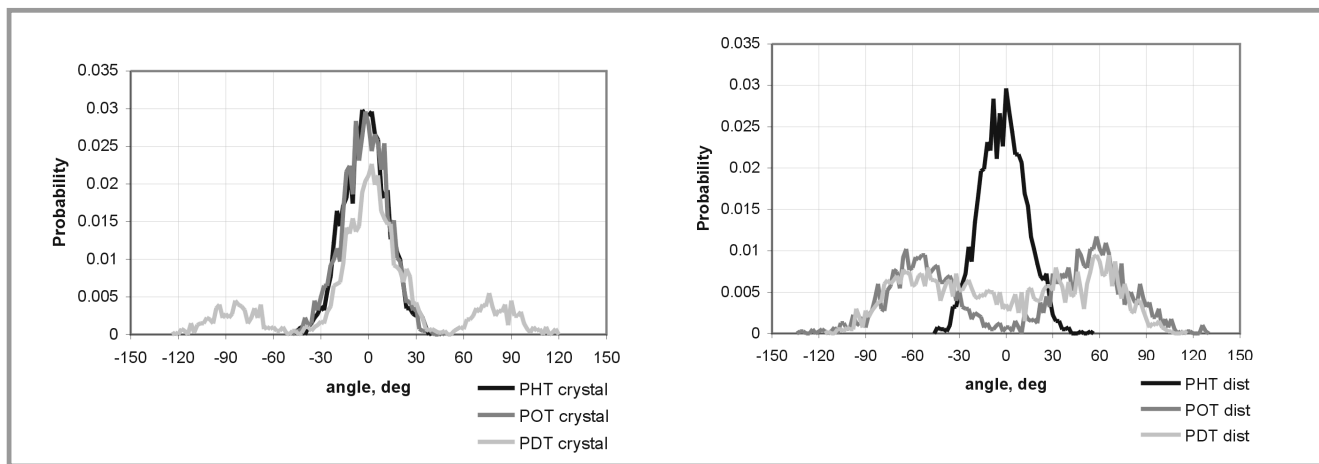

Figure 3. *Probability of trans conformation for alkyl sidechains.*

Figure 4. a) Twist angle for main poly-3-alkylthiophene chain (starting from crystal structure); b) Twist angle for main poly-3-alkylthiophene chain (starting from distorted structure).

pletely, and so their density is expected to be less than obtained from our simulations (Table 2).

Interesting properties are related to the alkyl side chains' disorder. It can be seen in the averaged histograms of torsional angle that develop a trans or gauche conformation as well as the radius of gyration of such fastened chains. It was shown that trans conformations are favourable for crystal samples (Figure 3). However, the percentage of trans conformations decreases slightly when alkyl chains become longer, as well as for distorted structures. For simulations based on distorted structure, the alkyl chains' disorder is greater (Figure 3).

The side chain's influence on the main chain structure is clearly visible in the histogram of twist angle between consecutive thiophene rings in Figures 4a, 4b. Its fluctuations are surprisingly large as for a conjugated system; these are respon-

sible for the thermochromism effect reported for poly-alkyltiophenes [1].

The results show that PAT molecules are not stiff molecules as a whole. The backbone chain can be significantly twisted due to interaction between alkyl chains. The longer the chains, the greater the possibility of obtaining large twist angles (as shown in Figure 4a). It is remarkable that the structure of the PAT molecules is strongly affected for simulations that start from a distorted structure. The starting point does not well describe the crystal structure of poly-3-thiophenes.

The simulations agree that alkyl chains may be treated as stiff objects. However, they rotate within a few angstroms along the directions perpendicular to them (Figure 5) and interact with each other. Nor do the chains intercalate in 3 dimensions, although from the front, 2-dimensional cast (Figure 4a) they seem to.
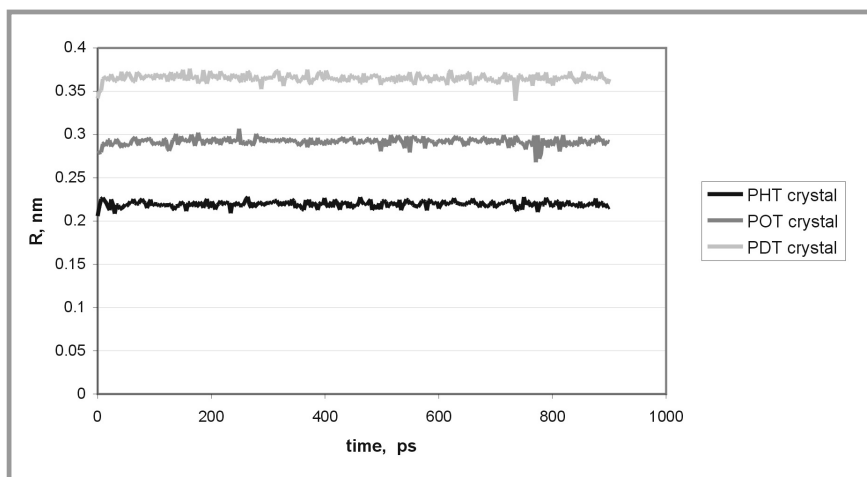
Conclusions

We have shown that simulations of polymer poly-3-alkylthiophenes by means of molecular dynamics can be performed, and can give valuable results for the interpretation of their structure. Appropriate tools for preparation and manipulation of the structure were developed with further exploitation in mind. We plan to use the methodology described in the article to investigate more demanding and challenging mixtures of conjugated polymers and dopants as well as solvents.

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Figure 5. Radius of gyration for chosen alkyl sidechain.