Molecular simulation of side-chain liquid crystalline polymers

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Abstract

In our previous chapters more than 1800 polymers and copolymers have been simulated, but most of the research was concentrating on main chain polymers. This chapter presents a computational conformational study of side-chain liquid crystal polymers to predict the optical and liquid crystalline properties of a series of polyepichlorohydrin, polyacrylate, polymethylacrylate, and polystyrene-based side-chain liquid crystalline polymers using simulation method. Some of the simulated side chain polymers were synthesised by chemical modification.
and polymerisation. The predictive capability of the orientational order parameter has been utilised to predict the liquid crystalline-isotropic transition, isotropic temperature, of the investigated polymers, which was used to investigate the type of distribution in the synthesised polymers. The predictive possibilities of this criterion are explored in the estimation of the nematic-isotropic transition temperatures of the simulated polymers. Evidence is presented to suggest that for side chain liquid-crystalline polymer (SCLCP) molecules the nematic to isotropic transition occurs when the order parameter reaches a value of 0.43 according to Maier-Saupe mean field theory.

Introduction

In the last few years, scientific research has concentrated on the synthesis and characterisation of new polymers with special properties. Among these, side chain liquid crystalline polymers are distinguished by their properties as materials in a range of advanced electro-optical technologies, but also because they present a demanding challenge to our understanding of self-assembly in molecular systems. The main reason is that SCLCPs could combine the unique properties of low-molar mass liquid crystals and polymers together, which made it easier to form film during material processing. Although a large amount of experimental data has been available on the properties of side chain liquid crystalline polymers, the fundamental understanding of their behaviour at a molecular and atomic level is still limited. Molecular simulation is a technique capable of providing explanations that can supplement the data produced by experimental characterisation methods. Molecular simulation is considered as bridge between experimental and theoretical studies that can give important information on the expected behaviour of the polymers.

An important goal in the synthesis of SCLCPs is to design molecules with the necessary order to form a mesophase yet with sufficient chain flexibility so that the crystal melting temperature (Tm) is reached within the range of normal processing temperatures. One of the distinguishing structural properties of these polymers is the ease to form film during material processing. Therefore, SCLCPs offer potential solutions for problems that low-mass-molecular liquid crystals are unable to solve, and possible applications arise where the combination of these properties are basic requirements. These applications range from electrical-electronic components, chemical processing, transportation (including automotive and aerospace) and telecommunications, and more recently to optical and electro-optical display devices, optical computing and medical science as diagnostic aids. \(^{1-13}\)

Small molecule modified macromolecules (SMMM) have been used extensively to obtain functional polymers with special properties. This method is preferred due to the absence of side reactions that can induce the appearance of branched polymers. The synthesis by this method and molecular simulation
characterisation of polyesters, polyethers and copolymers was reported and discussed in our previous publications\textsuperscript{14-22}.

As with small-molecule liquid crystals, the appearance of a mesophase is associated with long-range organisation of the molecular orientations\textsuperscript{23-24}. For small molecules this order may arise from the packing requirements of the rod-like molecules, from anisotropic attractive forces or some combination of both. Models to predict orientational order in liquid-crystalline polymers are well known, the earliest being the lattice theory of Flory and co-workers\textsuperscript{25-26}. The lattice theory depends on aspect ratio of polymer chains (the ratio of length to diameter) as the only molecular parameter. In the particular treatment of Flory and Ronca, for example, it is predicted that the critical aspect ratio for a polymer to exhibit liquid crystallinity is 6.42.

This chapter presents an investigation of the most simple and effective parameter which, while describing the mesogenicity (i.e. tendency to form liquid crystalline phases) of a polymer, can also be derived from molecular simulations that include significant chemical and physical details. To this aim we explore the order parameter, in particular, test whether it has a critical value at the liquid-crystalline to isotropic phase transition temperature. In providing a measure of mesogenicity, the order parameter is useful for simulating polymers at different temperatures to provide signposts for molecular modelling and thus identify good candidate polymers for synthesis.

Some of the methods for calculating the conformational properties of polymer chains are based upon the rotational isomeric state (RIS) theory\textsuperscript{27}. However, there are difficulties preventing the routine and easy application of RIS in a reliable manner to polymers with complex monomeric structures, especially to polymers containing aromatic rings along the chain backbone.

As techniques for the atomistic simulation of polymer structures and properties have evolved the calculation of conformational properties by atomistic simulations has become an attractive and increasingly more feasible alternative. A new method, RIS Metropolis Monte Carlo (RMMC), was recently developed by Honeycutt\textsuperscript{28}. RMMC enables the direct conformational modelling of polymer chains by atomistic simulations, thus avoiding the pitfalls and technical difficulties involved with their calculation by RIS method. However, a comprehensive molecular simulation methodology that can explain or predict the liquid crystalline behaviour has not yet been established.

In this study molecular dynamics simulation of the polymers under consideration were performed. This was aimed to elucidate whether a correlation exists between polymer conformation and the mesophase character, and to analyse the structure-properties relationship of potential LCPs, thus aiding in the design of new materials. This chapter shows that it is possible to investigate LC properties of polymers by molecular simulation.
methods. In particular, the order parameter was calculated to estimate the liquid crystalline potential of the studied copolymers. In addition, the isotropisation temperature, \( T_i \), (clearing temperature) of the simulated polymers was derived from a diagram of calculated order parameter versus temperature. To our knowledge no molecular simulations have been reported in the literature on the isotropisation temperature of the side chain liquid crystalline polymers under consideration.

The results provide detailed quantitative information concerning the structural, orientational and liquid crystalline properties of the investigated copolymers as well as qualitative insights into the factors affecting the chain conformation.

**Polymers studied**  
*Figure 1* represents the monomer units of the polymers simulated in this work.

![Monomeric units of the simulated polymers](image)

*Figure 1.* Monomeric units of the simulated polymers (a) polymer-1, (b) polymer-2, (c) polymer-3, and (d) polymer-4.

**Computational methodology**  
Computer molecular modelling of the polymers, molecular mechanics (minimization), molecular dynamics simulations, and conformational analyses, were performed using molecular simulation software for materials science \(^{29}\), designed by Accelrys Inc, San Diego, CA, USA, and the program was run on a Silicon Graphics Computer. The models were prepared and energy minimised using the Open Force-Field (OFF). NVT and NPT molecular dynamics were performed to explore the conformations. Properties calculated form the simulated conformations were the orientation function, order parameter, and energy as a function of temperature from 0 to 500°C.
The Dreiding 2.21 force field described by Mayo et al.\textsuperscript{30}, and implemented in the OFF module was applied since it was found to be suitable and reliable for molecular simulation of aromatic polymers as evidenced by previous studies\textsuperscript{31-37}.

The Dreiding 2.21 force field provides a potential energy interaction function ($E_{\text{total}}$) that accounts for both bonded ($E_b$) and non-bonded ($E_{nb}$) interactions: $E_{\text{total}} = E_b + E_{nb}$. The bonded terms typically include harmonic bond stretching ($E_s$), harmonic angle bending ($E_a$), torsional ($E_t$), and inversion ($E_i$) energies: $E_b = E_s + E_a + E_t + E_i$. Non-bonded terms typically contain van der Waals (12-6 potential) ($E_{vdW}$), electrostatic (Coulomb) ($E_q$) and hydrogen bond (12-10 potential) ($E_{hb}$) interactions: $E_{nb} = E_{vdW} + E_q + E_{hb}$. Full details of the potentials can be found elsewhere\textsuperscript{31-38}.

In practice it is common to use a suitably large cut-off distance\textsuperscript{5-11}, and so for this study a cut-off distance of 100 Å was used for non-bonded interactions. The partial charge distribution on the atoms of the simulated polymer chains was obtained with the charge equilibration method described by Rappe and Goddard\textsuperscript{39}.

Single (non-periodic) chains and periodic unit cells of the polymers with degree of polymerisation (DP) equal to 20 have been used for these simulations. The initial conformations of the aromatic polymers were optimised and the energy minimised single chains were then used to construct the periodic unit cells of the studied polymers. Each energy minimisation cycle was continued until the total potential energy converged. The criteria of energy convergence were to obtain a residual root-mean-square (rms) force in the simulated polymer system that is less than 0.001 kJ mol\textsuperscript{-1}Å\textsuperscript{-1}. The minimisations were performed using the steepest descent and conjugate-gradient method described by Fletcher and Reeves\textsuperscript{40}.

The NVT and NPT molecular dynamics simulations were performed for a representative structure at 0, 50, 100, 150, 200, 250, 300, 350, 400, 450 and 500°C, for each constructed and energy minimised polymer system. For the NVT ensemble, employed for polymer isolated (non-periodic) chains, the number of molecules N, volume V and the temperature T of the system are kept constant, whereas for the NPT ensemble, employed for polymer periodic unit cells with 3-dimensional periodicity, the number of molecules N, pressure P and the temperature T of the system are kept constant. Full details of the MD algorithms can be found elsewhere\textsuperscript{31-38}.

The number of steps in NVE and NPT MD simulations was 50000000 (50 ns), and the output frequency was every 1000 steps. The time step of 0.0010 ps is taken for all the simulations of this study. In this study the model system exchanges energy with a heat bath in order to maintain a constant temperature. The non-canonical ‘T-damping’ thermostat described by Berendsen \textit{et al.}\textsuperscript{39}, was used for isothermal-isobaric NPT MD simulations. Polymer configurations saved over the MD simulations have been used for analysis of properties.
In particular, the order parameter, $S = 1/2 \left( 3\langle \cos^2 \theta \rangle - 1 \right)$, which is often difficult to measure, was calculated to characterise the degree of molecular orientation of the investigated LCPs. $\theta$ is angle between the structural unit vector of the polymer chain and the reference direction called director. The value of $\theta$ used for these simulations is restricted to the interval: $0 \leq \theta \leq 90$. The value $S = 1$ corresponds to the case of perfectly aligned mesogenic groups and $S = 0 \left( \langle \cos^2 \theta \rangle = 1/3 \right)$ for isotropic liquid.

The angular brackets around the cosine term denote an average of all of the unit molecules. Molecular orientation is a measure of the tendency of the molecules to align along the director, which is also known as optical axis. In this study the director was considered the longitudinal axis of the mesogenic group (monomer) perpendicular to the polymeric backbone (main chain) of the simulated SCLCPs. The results of NPT molecular dynamics simulations have been used to calculate the glass transition temperature, $T_g$, of the simulated polymers. The $T_g$ was determined from density versus temperature diagrams by analysing the trajectory file data generated by NPT-MD simulations. Trajectory file data generated from MD simulation was used in all the polymer property calculations and analyses presented in this chapter. The trajectory files were analysed by the Polymer Properties and Dynamics Analysis modules.

In order to predict the decomposition temperature the empirical correlation study based on QSPR (quantitative structure properties relationship) technique was performed. All the correlations used in QSPR technique are fully described by Bicerano 40.

Computer simulation experiments have both systematic and statistical errors, which, however, can be controlled and minimised. Applying MD simulation, the thermophysical, structural and dynamic properties of polymeric materials can be calculated with an accuracy that strongly depends on the reliability of the potential function: in other words, on the errors arising from truncation of the intermolecular forces, and statistical errors, arising from insufficient sampling.

For this study the reliability of the Dreiding 2.1 potential function has been proven and tested by previous molecular simulation studies of polymers 33-39. It was found that very accurate geometries and potential barriers for various organic polymers have been obtained employing the Dreiding 2.1 force field. The results of the molecular simulations will strongly depend on the way the molecular polymer system was originally prepared. One of the solutions to address this problem is to start from many, different initial conformations, and to make sure that the results obtained from them did not differ greatly. Therefore, in this study for each simulated polymer, several cycles of potential energy minimisations and MD simulations were performed to create a reasonable range of well equilibrated polymer conformations for averaging the calculated properties (QSPR) technique prior RMMC.
Molecular simulation of side-chain liquid crystalline polymers

Simulations. QSPR technique was also used in order to obtain an estimate of the glass transition temperature.

Experimental part
Details concerning the synthesis, characterization and thermal behaviour of the investigated polymers were reported previously. The polymers were synthesised by phase transfer technique. The phase transfer catalyst was tetrabutylammonium bromide (TBAB). TBAB catalyst is known from the literature to be more efficient in phase transfer reactions. The catalyst takes the sodium of mesogenic units into the organic phase and, at the same time, catalyses the nucleophilic substitution to attach the mesogenic units to the polymer backbone.

Results and discussion
All simulated polymers have the degree of polymerisation equal to 20 experimental results are likely to be much greater than 20. The simulations were performed for non-periodic and periodic molecular systems of the studied polymers. For LC structures the supramolecular ordering process takes place at chain and mesogenic group level (rod-like molecules). This superposition is based on varies chain flexibility, evidenced by the different Tg values.

The conformational analysis affected for polymers 1 to 4 (Figure 2 (a)-(d)) evidenced favourable conformations that can generate a mesophase.

The MD simulations were continued until the systems were equilibrated. The systems were evaluated after each in order to see whether the equilibrium has been achieved. In order to make sure that the simulated data are correct for each of the investigated copolymers we performed ran several MD simulations and have calculated the average value of each of the predicted properties presented in this research. The results show that the predicted properties were reproduced accurately by the simulation procedure.

To characterise the degree of orientation of the mesophase, the order Parameter, S, was calculated (see Computational Details section for more details). According to Maier-Saupe mean field theory for a polymer, it is possible to generate a stable mesophase if the order parameter is great than 0.6. The orientational order parameter decrease with the increase in temperature as a result of kinetic molecular motion, and a liquid crystalline-isotropic transition takes place. The theory indicates that the order parameter (S) in LC phases decreases with an increase in temperature until it reaches 0.43.

When the LC phase transform to isotropic phase. In practice, the critical value of S for SCLCPs varies is 0.43. During the heating processing, the side chain polymer will completely lose his orientational order when sample
Figure 2. Energy minimized structure of simulated (a) polymer-1, (b) polymer-2, (c) polymer-3, and (d) polymer-4.

Figure 3. Predicted order parameter vs temperature of polymer-1.

temperature reaches some value (shown as example in Figure 3 for polymer-1). The order parameter was calculated for all of the simulated alternating and random polymer samples. These data are present in Table 1 for single chain polymers and in Table 2 for unit cell of the simulated polymers.
Table 1. Simulated order parameter (S) for the investigated polymers (for single chain).

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Temperature, (°C)</th>
<th>0</th>
<th>50</th>
<th>100</th>
<th>150</th>
<th>200</th>
<th>250</th>
<th>300</th>
<th>350</th>
<th>400</th>
<th>450</th>
<th>500</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td>0.90</td>
<td>0.79</td>
<td>0.63</td>
<td>0.51</td>
<td>0.41</td>
<td>0.40</td>
<td>0.31</td>
<td>0.30</td>
<td>0.19</td>
<td>0.11</td>
<td>0.03</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>0.86</td>
<td>0.80</td>
<td>0.65</td>
<td>0.58</td>
<td>0.44</td>
<td>0.42</td>
<td>0.36</td>
<td>0.27</td>
<td>0.11</td>
<td>0.10</td>
<td>0.06</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>0.71</td>
<td>0.65</td>
<td>0.62</td>
<td>0.56</td>
<td>0.46</td>
<td>0.40</td>
<td>0.37</td>
<td>0.23</td>
<td>0.15</td>
<td>0.12</td>
<td>0.09</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td>0.69</td>
<td>0.89</td>
<td>0.83</td>
<td>0.67</td>
<td>0.43</td>
<td>0.39</td>
<td>0.29</td>
<td>0.23</td>
<td>0.11</td>
<td>0.07</td>
<td>0.005</td>
</tr>
</tbody>
</table>

Table 2. Simulated order parameter (S) for the investigated polymers (for unit cell of the simulated polymers).

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Temperature, (°C)</th>
<th>0</th>
<th>50</th>
<th>100</th>
<th>150</th>
<th>200</th>
<th>250</th>
<th>300</th>
<th>350</th>
<th>400</th>
<th>450</th>
<th>500</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td>0.77</td>
<td>0.71</td>
<td>0.59</td>
<td>0.48</td>
<td>0.40</td>
<td>0.39</td>
<td>0.34</td>
<td>0.32</td>
<td>0.20</td>
<td>0.10</td>
<td>0.06</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>0.63</td>
<td>0.61</td>
<td>0.58</td>
<td>0.52</td>
<td>0.43</td>
<td>0.34</td>
<td>0.31</td>
<td>0.27</td>
<td>0.22</td>
<td>0.19</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>0.61</td>
<td>0.57</td>
<td>0.52</td>
<td>0.49</td>
<td>0.44</td>
<td>0.42</td>
<td>0.39</td>
<td>0.25</td>
<td>0.17</td>
<td>0.09</td>
<td>0.01</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td>0.65</td>
<td>0.64</td>
<td>0.60</td>
<td>0.47</td>
<td>0.42</td>
<td>0.31</td>
<td>0.18</td>
<td>0.17</td>
<td>0.16</td>
<td>0.14</td>
<td>0.09</td>
</tr>
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</table>

Using the above criterion the calculated order parameter predicts that all of the simulated alternating polymers to exhibit LC properties. The glass transition and decomposition temperature determined by DSC and simulation was given in Table 3 for the studied polymers. The Tg was determined from density versus temperature diagrams by analysing the trajectory file data generated by NPT-MD simulations. It was found that the simulation results for polymers 1-4 are within, or very close to the experimental range. The difference between them is due to the slightly different DP.

The calculation was performed for 3-D models of amorphous cell structures of the studied polymers with DP equal to 20. As an example, the amorphous cell structure of the pure polymer corresponding to polymer-1 to polymer-4 is given in Figure 4. The predicted Tg andTd values of the simulated polymers are given in Table 3. The predicted values of Tg are in the range of 99-131°C and the predicted values of Td are in the range of 359-388°C. Initial observation of the data for all the studied polymers indicates that the values of Tg and Td increase with the increase of the rigidity of polymer backbone. This is easy to be understood. Figure 5 shows the TGA curves of
Table 3. The glass transition, isotropisation and decomposition temperature and density determined by DSC and simulation.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$T_g$, °C (theoretical)</th>
<th>$T_d$, °C (theoretical)</th>
<th>$T_g$, °C (DSC)</th>
<th>$T_d$, °C (DSC)</th>
<th>Density, g/cm$^3$ (theoretical)</th>
<th>$T_i$, °C (experimental)</th>
<th>$T_i$, °C (theoretical)</th>
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<tbody>
<tr>
<td>1</td>
<td>99</td>
<td>359</td>
<td>73</td>
<td>353</td>
<td>1.198</td>
<td>153</td>
<td>155</td>
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<tr>
<td>2</td>
<td>121</td>
<td>369</td>
<td>118</td>
<td>340</td>
<td>1.242</td>
<td>-</td>
<td>220</td>
</tr>
<tr>
<td>3</td>
<td>131</td>
<td>362</td>
<td>129</td>
<td>350</td>
<td>1.209</td>
<td>-</td>
<td>250</td>
</tr>
<tr>
<td>4</td>
<td>129</td>
<td>388</td>
<td>125</td>
<td>378</td>
<td>1.173</td>
<td>-</td>
<td>200</td>
</tr>
</tbody>
</table>

Figure 4. Computer-generated amorphous cell structure of the simulated polymers, X:Y = 1:1, DP = 20, snapshot of NPT-MD simulation at 25 °C: (a) Polymer-1, (b) Polymer-2, (c) Polymer-3, (d) Polymer-4.
polymer-1 as function of temperature during dynamic heating (10 °C/min, 30-800 °C) in an inert different environment. The thermal decomposition process under an inert atmosphere only involves the chain scission of polymers, and there is no interaction between the polymer and environment. The temperature at the maximum decomposition rate is around 353 °C (theoretical 359 °C).

The calculated $T_d$ of the simulated polymers predict and characterise these polymers as thermal stable because no theoretical $T_d$ below 359 °C. Initial observation of the data for all the studied polymers indicates that the values of $T_g$ and $T_d$ increase slightly with the rigidity of polymer backbone with the same mesogenic groups, which indicates that the polymer backbone rigid is not the main factors during their the processing.

**Conclusions**

The computer generated structures of the studied polymers have provided essential information about polymer chain conformation, including order parameter.

This research has revealed a valuable insight into the structure–property relationship at molecular and atomic levels for the investigated polymer sequences, it has also demonstrated a possibility to predict LC properties of polymers by molecular simulation methods. The MD simulations have produced the polymer chain conformations and their properties and through this a guide to a likely supramolecular order of the polymeric liquid crystalline structures. It is found that the ordering capacity of the studied polymer chains depends on chain rigidity, and it has revealed the interrelation between the conformational shape of the polymers and their LC behaviour.

It seems that MD simulations can be useful in determining the nematic isotropisation transition temperatures of liquid crystalline polymers.
The theoretically found Ti’s suggest a correlation between the backbone chain flexibility and liquid crystalline behaviour.

The understanding provided by the MD methodology can be useful for designing novel LCPs with desirable properties.

References

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