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Prediction of liquid crystalline properties of poly(1,4-phenylene sebacate-oxybenzoate) by Monte Carlo simulation

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Abstract

A Monte Carlo simulation study was undertaken to predict the liquid crystalline potential of a group of poly(1,4-phenylene sebacate-oxybenzoate) polymers. Molecular modelling procedures have been used to determine statistical parameters of isolated chains, with the objective of achieving a description which defines the tendency of a polymer molecule to form a liquid-crystalline phase, its mesogenicity. Initial attention was focused on the persistence length parameter as the most promising in this context to provide a description of mesogenicity which is equally applicable to molecules that consist of rigid segments separated by flexible sequences. A range of known mesogenic molecules has been modelled using RIS Metropolis Monte Carlo (RMMC) method based on carefully determined bond-rotation potentials which enabled the direct estimation of several key structural properties of the polymer chains. Evidence is presented to suggest that for liquid-crystalline polymer (LCP) molecules the nematic to isotropic transition occurs when the ratio of the persistence length to diameter (the persistence ratio) reaches a value of 5. The predictive possibilities of this criterion are explored in the estimation of the nematic–isotropic transition temperatures of the simulated polymers. RMMC was also applied to a well known LCP (poly(*p*-phenylene terephthalate)) in order to confirm the validity of the simulations. 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.

Keywords: Monte Carlo simulation; Liquid crystalline copolymers; Persistence length

1. Introduction

In the last few years, scientific research has concentrated on the synthesis and characterisation of new polymers with special properties. Among these, aromatic polymers are distinguished by their excellent thermal stability and good mechanical strength, resulting from the special arrangement of the aromatic groups [1–10]. Many aromatic polymers have the potential to form a mesophase, because of the mesogenic character of their aromatic groups. Although a large amount of experimental data has been available on the properties of aromatic 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.

To a first approximation liquid-crystalline polymers (LCP) can be thought of as long rigid rods with little or no conformational freedom in the melt. This is far from representing the true picture. In fact, an important goal in the synthesis of LCP is to design molecules with the necessary order to form a mesophase yet with sufficient chain flexibility so that the crystal melting temperature (T_m) is reached within the range of normal processing temperatures. Due to their unique physical properties like high strength and modulus, good thermal endurance, small linear expansion coefficient (comparable with ceramics), high chemical resistance, significant attention has been devoted to these materials [9–15]. One of the distinguishing structural properties of these polymers is the ease in producing a uniform molecular orientation [16–17].

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Therefore, LCP offer potential solutions for problems that conventional materials 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, to high tensile strength polymeric fibres and components, thermography, holography and more recently to optical and electro-optical display devices, optical computing and medical science as diagnostic aids [18–25].

There has been much research on the synthesis of thermotropic polymers [26–28] with unique thermal and physical properties. Among them, the wholly aromatic thermotropic polyesters generally have high temperature crystal-to-mesophase transitions, T_m and are insoluble in most organic solvents [29–33]. The wholly aromatic polyesters are of particular commercial interest due to their potential application as high-performance engineering plastics. The poly(*p*-hydroxybenzoate), poly(*p*-phenylene terephthalate) and poly(*p*-phenylene naphthalene-2,6-dicarboxylate) polyesters have been known to have a liquid crystalline phase [34–38]. However, these cannot be processed in the molten state, because they have extremely high T_m.

To obtain polymers with considerably lower T_m, several chemical modifications including: (i) the introduction of bulky, or non-symmetrical substituents [39–40]; (ii) the use of flexible spacer; (iii) the use of non-linear or bent monomers [41–43]; and (iv) copolymerisation of different monomers [18–22,44–49] have been previously used. Here, the route of copolymerisation provides versatile ways to prepare new thermotropic copolyesters of low T_m through the use of conventional monomeric diacids and diols.

The copolymers consisting of *p*-hydroxybenzoic acid (PHBA), hydroquinone (HQ) and terephthalic acid (TPA) were reported [50], but the melting temperature proved to be too high for melt processing. With the development of copolymers with small mesogenic units and copolymers including flexible spacers, a substantial decrease in T_m has been obtained. In this contribution, we report on a thermotropic copolyester consisting of *p*-hydroxybenzoic acid (HBA), hydroquinone (HQ) and sebacic acid (SA) (HBA/HQ/SA copolyesters) that can be melt processed at moderate temperatures.

This paper 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 which include significant chemical and physical details. To this end, we explore the ratio of persistence length to diameter (persistence ratio) as a flexibility parameter and, 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 persistence ratio is useful for simulating polymers at different temperatures to provide signposts for molecular modelling and thus identify good candidate polymers for synthesis.

As with small-molecule liquid crystals, the appearance of a mesophase is associated with long-range organisation of the molecular orientations [51]. 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 also well known, the earliest being the lattice theory of Flory and co-workers [52–53]. 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. The lattice theory of Flory is similar to the persistence ratio approach we apply in this study.

Some of the methods for calculating the conformational properties of polymer chains are based upon the rotational isomeric state (RIS) theory [54]. 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 [55]. 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 RMMC 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 paper shows that it is possible to investigate LC properties of polymers by molecular simulation methods. In particular, the geometric parameters, such as persistence length (q), diameter (d), and persistence ratio (q_r), $q_r = q/d$, were 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 persistence ratio versus temperature. To our knowledge no molecular simulations have been reported in the literature on the isotropisation temperature of the copolymers 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.

2. Model systems

The comonomeric units used in constructing the model polymer chains are shown in Fig. 1. The candidates for potential liquid crystalline formulations are presented in Table 1. There is a limited number of ways the 4-hydroxybenzoic acid (HBA), hydroquinone (HQ), and sebacic acid (SA) can be polymerised given their functionality. These are designated in the order shown in Table 1 as (111)*n*, (211)*n*, (311)*n*, (122)*n*, (222)*n* and (322)*n* where *n* is the degree of polymerisation (DP) considered in this work.

First, a repeat unit for each of the studied polymers was built and its energy was minimised, then a polymer chain was built with head-to-tail connection. As an example, the monomeric unit corresponding to copolymer (311)*n* is presented in Fig. 2. Each model chain was terminated by a hydrogen atom at each end. The number of rotatable backbone bonds in a model system, N_{bbrot}, is the number of single bonds along its backbone. The model systems had 99 to 599 backbone bonds, depending on the DP which ranged from 9 to 90.

3. RMMC method

The closest method to RMMC that has been published was developed by Dodd and Theodorou [56]. As in traditional RIS methods, only torsional degrees of freedom are considered in determining a chain's conformation; bond length and angles are fixed. Unlike these methods, RMMC allows torsion angles to vary continuously; it does not impose the assumption of discrete rotational states. RMMC is Metropolis Monte Carlo method [57–58]. It can be contrasted to the Markovian approach used in a RIS MC calculation to build independent polymer chains. In a Metropolis simulation of a polymer, one begins with a chain in an arbitrary conformation. A Monte Carlo step consists of making a small change to that conformation, e.g., by rotating a bond and then deciding whether or not to retain that change, based on the temperature and the energy of the new conformation relative to the old one. This process is repeated many times in order to yield a set of conformations characteristic of that chain at the specified temperature.

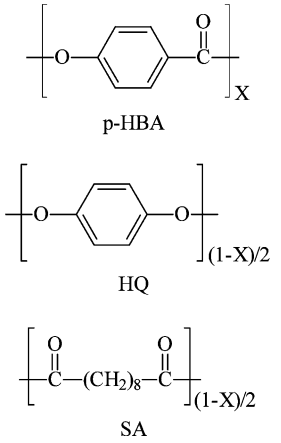

Fig. 1. Monomeric units of the simulated copolymers.

In outline, a RMMC simulation proceeds as follows:

1. Perform an energy minimization on the molecule.
2. Randomly select a rotatable backbone bond.
3. Select a random torsion value for this bond between −180 and +180°.
4. Rotate the bond to its new torsion value and compute the new energy of the chain.
5. Generate a random number, R, between 0 and 1. If $\exp[-(E_{new}-E_{old})/kT]>R$, keep the new torsion value. Otherwise, restore the old value.
6. After enough steps have been performed so that the chain is equilibrated: compute the properties of the chain conformation and update the running averages of these properties.
7. Repeat from step (2) until the desired number of iterations has been performed.

It should be noted that in a RMMC simulation, bond lengths and bond angles are constrained. For this reason, 'pre-minimization' is necessary in order that the bond lengths and angles adopt reasonable values. Unlike RIS and RIS MC calculations, RMMC does not use statistical weights. Instead, it uses the energy as computed from a forcefield in order to calculate chain conformational properties. The only energy terms considered in a RMMC calculation are: torsion, van der Waals, and Coulombic (electrostatic) terms.

There are two main parameters, Min Bonds and Max Bonds, that determine the interacting pairs of atoms for the purpose of calculating nonbond (van der Waals and Coulomb) energies. Nonbond energies are not computed for atoms closer than Min Bonds bonds away from each other. The usual value for Min Bonds is 3. Nonbond energies are also neglected for atoms further than Max Bonds bonds away from each other. Reasonable values for Max Bonds range from 4 to about 7 for polymer chains in theta conditions. Larger values of Max Bonds may greatly increase CPU and memory requirements.

A number of other parameters can affect the outcome of a RMMC simulation. These include the following: temperature, forcefield, charges (whether on or off), dielectric constant, rigidity or flexibility of articulated side groups, and energy scaling factor. The temperature determines the Boltzmann factor that is used to determine whether to accept or reject a conformation. The forcefield provides the

Table 1
Copolymer formulations

Copolymer sequences	DP, *n*, modelled	Number of comonomeric units		
		HBA	HQ	SA
(111)*n*	5–90	1	1	1
(211)*n*		2	1	1
(311)*n*		3	1	1
(122)*n*		1	2	2
(222)*n*		2	2	2
(322)*n*		3	2	2

parameters for the torsion and nonbond energy calculation. The inclusion or exclusion of atomic partial charges and the dielectric constant determines the calculated Coulomb energy.

In principle, it is more realistic to treat side groups as flexible rather than rigid. However, doing so increases the computation time and might not be necessary if the groups are small.

Therefore, in this study RMMC was also applied to a well known LCP (poly(*p*-phenylene terephthalate)) in order to confirm the validity of the simulations by changing the most relevant simulation parameters.

4. Computational details

As stressed above, for the RMMC simulations, instead of the statistical weights necessary in the conventional RIS methods, a forcefield is required to generate the polymer conformations. In this study the simulations were carried out using complete atomistic models with the analytical form of the potential energy expression given by the polymer consistent force field (PCFF) from Accelrys [57–60].

The dielectric constant, used in calculating the electrostatic energy, was estimated by the quantitative structure–property relationships (QSPR) technique prior RMMC simulations. QSPR technique was also used in order to obtain an estimate of the glass transition temperature (T_g), of the investigated copolymers. The QSPR technique is fully described by Bicerano [61] and implemented into Accelrys molecular simulation software for material science.

The number of RMMC steps was set proportionally to the degree of polymerisation (DP) of the simulated polymer chains. In most calculations, 5,000,000 steps were used in the equilibration portion and 3,000,000–5,000,000 steps were used in the production portion of the RMMC simulations. The snapshots for calculating the average chain properties were taken at 1000-step intervals.

Temperature effects were estimated by performing calculations at temperatures ranging from $T=300$ to 600 K in intervals of 50 K.

There are two ways to treat cut-off for nonbonded interactions in the RMMC method: use of a maximum number of bonds between the interacting atoms, or use of a distance dependent cut-off. Honeycutt discusses the choice of the Max Bonds value, and concludes that typical values range from 4 to 6 depending on the polymer chain architecture [55]. A value of 4 neglects interactions beyond the ‘pentane effect’. However, as mentioned by Honeycutt, in polymer chains with side groups or with closed loops or with specific interactions between adjacent repeat units, larger values may be needed to take the necessary interactions properly into account. Therefore, for the polymer chains simulated in this study the Max Bonds value of 7 was chosen. The program calculates two different values of persistence length (q); namely, a value calculated from the projection of the chain vector on the first bond along the chain, and another value calculated from its mean projection on all bonds along the chain. The second value is statistically more representative of the true q of the polymer, and was therefore preferred in this study.

In future studies, snapshot conformations generated by RMMC method here will be used as initial structures to perform molecular dynamics simulation in order to

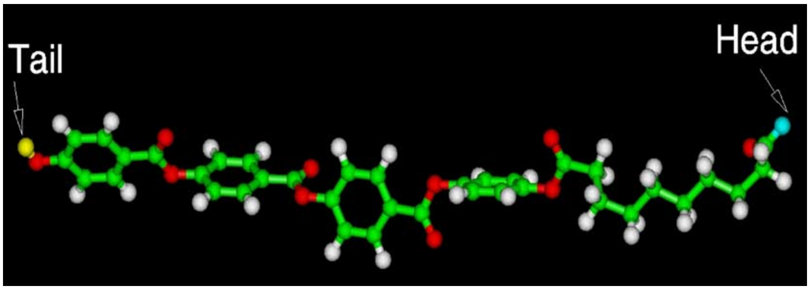

Fig. 2. Energy minimized structure of monomer used for modelling of liquid crystalline copolymers (311)*n*.

investigate the orientational (order parameter) and dynamic properties of the simulated copolymers.

Commercial molecular simulation software for materials science, designed by Accelrys, Inc., implementing RMMC within Insight II, was used on a Silicon Graphics Origin 2000 workstation.

5. Results and discussion

First of all, we calculated the dielectric constants of the polymers which are presented in Table 2. The values were used in subsequent RMMC calculations to estimate the Coulomb energy.

The RMMC simulations were continued until the systems were equilibrated. The systems were evaluated after each run 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 ran several RMMC 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 explore the change of the chain conformations and dimension we investigated the structural properties of the simulated polymers. The most important prerequisite for liquid crystallinity in a polymer is the straightness, also known as rectilinearity, of its chains. The parameter which describes chain straightness in polymers is the persistence length, q. Persistence length is a key parameter of semi-flexible polymer chains. If the persistence length of a candidate polymer is approximately five times its average chain diameter it can be predicted to form a liquid crystalline phase.

In order to check the reliability of the methodology utilised during this study we have performed a trial RMMC simulation for poly(p-phenylene terephthalate), (PPT), a well characterised common polymer. During this study, it was found that the q of PPT is 753.5 Å which demonstrates its rigidity and LC behaviour. A previous simulation for PPT reports [62–64] the value of $q = 751$ Å which is in a good agreement with the result obtained using the parameters proposed for this study.

Polymers listed in Table 1 were simulated and the relationship between the persistence length and the chain's degree of polymerisation (DP) determined. The calculated persistence lengths as a function of DP are presented in Fig. 3. The values of the persistence lengths are smaller than the contour lengths of the polymer chains (sums of the bond lengths in the chains), which is an indication of chain semi-flexibility due to the sebacic acid (SA) monomeric units in the copolymer chain.

Table 2
Dielectric constants predicted by the QSPR method

Copolymer sequences	Dielectric constant
111	2.98
211	3.02
311	3.05
122	2.95
222	2.98
322	3.00

The values of q increased with increasing DP from 9 to about 80, and then it remained constant for all of the simulated copolymers for DP higher than 80. During this study, it was found that the chain stiffness of copolymers 111, 211 and 311 is significantly higher than the chain stiffness of copolymers 122, 222 and 322. The copolymers 111, 211 and 311 have a much higher value of q, ranging from 162 to 186 Å, (Fig. 3), than the copolymers 122, 222 and 322 with values of q ranging from 45 to 78 Å (Fig. 3). The lower value of q for the copolymers 122, 222 and 322 is explained by a higher content of SA monomeric unit (see Table 1), which is a flexible aliphatic spacer, within the copolymeric chain (see Fig. 1). The highest value of q, and consequently the highest chain stiffness, was calculated for copolymer 311 which contains the highest number of aromatic rings within the copolymer chain. Then the value of q decreases from copolymer 311 to copolymer 211 and to copolymer 111, with the decrease of the number of aromatic rings within the copolymer chains and increasing the content of SA spacer.

For the second group of copolymers (122, 222 and 322), with a higher content of SA monomeric unit, the value of q decreases from copolymer 122 (78 Å), to copolymer 222 (51 Å), to copolymer 322 (45 Å). Contrary to copolymer 311, which has the highest value of q, the copolymer 322 has the lowest value of q. So, increasing the contents of SA comonomer from 20%, in the case of copolymer 311, to ~30%, in the case of copolymer 322, reduces significantly the chain stiffness, and at the same time the liquid crystalline potential.

In order to determine the nematic to isotropic transition temperature, the relationship between the persistence ratio ($q_r = q/d$) and temperature was investigated. For this we simulated the copolymers at temperatures ranging from 300 to 600 K. Using the generated equilibrium chain conformations, the average diameter (d) was estimated from the maximum polymer width perpendicular to the longest chain direction, i.e., a diameter of a hypothetical cylinder accommodating the polymer chain in this direction [62]. The calculated values of q_r as a function of temperature of the simulated copolymers for DP = 80 are depicted in Fig. 4. In this paper, the DP = 80 was chosen for investigation of q_r versus temperature since q has been shown to remain constant for DP higher than 80 for all of the simulated copolymers (Fig. 3). However, a separate study on possible DP effects on transition temperature is currently under way and will be presented separately.

A critical value of q_r of 5 suggests a nematic isotropic transition temperature [62–64] (T_i). During this study it was observed that at high temperature the molecules adopt, on

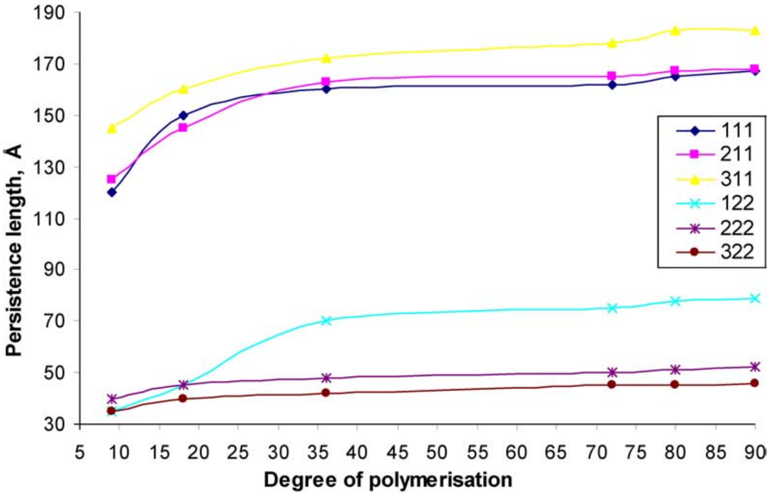

Fig. 3. Persistence length versus degree of polymerisation for simulated copolymers (111, 211, 311, 122, 222, 322).

average, a coiled conformation with a low persistence length but on reducing the temperature the width of the distribution about the straight conformation narrows and the persistence length increases.

Fig. 4 shows that for DP = 80 all of the simulated copolymers at 300 K have a q_r higher than 5, however, for the copolymers 122, 222 and 322 the persistence ratio drops below 5 at temperature between 380 and 400 K which is very close to the predicted glass transition temperature. The predicted T_g of sequences 122, 222 and 322 is ranging from 360 to 375 K. Although the simulations predict an isotropisation temperature for these copolymers the real copolymers will not exhibit a liquid crystalline behaviour as liquid crystalline phase is not within the processing temperature window. It is found from these results that the liquid crystalline properties were lost when the incorporated SA content is higher than 30%.

For the sequences 111, 211 and 311 the simulations predict a liquid crystalline isotropic transition at a much higher temperature which is in the range of 510–535 K (see Table 3). Sequences 111, 211 and 311 show a nematic transition matching the processing temperature window of many conventional thermoplastics.

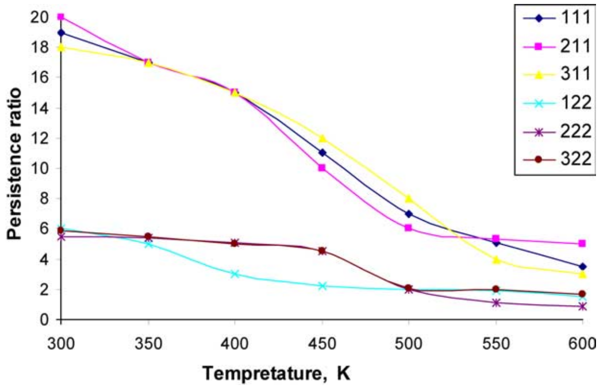

Fig. 4. Persistence ratio versus temperature for simulated copolymers (111, 211, 311, 122, 222, 322).

A comparison of the simulated and experimental data [65] was also performed and the results are presented in Table 3. The T_i for the simulated polymers was determined for q_r value of 5 from the diagrams of temperature versus q_r (Fig. 4). It was found that the simulation results for the first group of copolymers (111, 211 and 311) are within, or very close to the experimental range.

Furthermore, a comparison of the persistence ratio approach to predict the LC behaviour with Flory's lattice theory (axial ratio, $x = L/d$) was performed. As the lattice theory of Flory states, an axial ratio greater than 6.42 is sufficient for the occurrence of a mesophase [53–54]. The values of the polymer chain length (L), its diameter (d) and axial ratio (x) of the simulated copolymers for DP = 80 and at 300 K are presented in Table 4. The average (over the equilibrium conformations) chain length was estimated from the length of a hypothetical cylinder accommodating the RMMC generated polymer chain, as used for the calculation of the diameter [62]. According to Flory theory, all the simulated copolymers exhibit a mesophase. This demonstrates a reasonable to excellent agreement between the predictive capability of persistence ratio and axial ratio methods for the simulated copolymers with DP = 80 at 300 K.

The theoretically found T_i values correlate well with the

Table 3
Comparison of computational and experimental isotropisation temperature of the simulated copolymers

Copolymer sequences	T_i (K) computational	T_i (K) experimental
111	530	468–533
211	510	
311	535	
122	350	
222	390	
322	380	

Table 4
Calculated length, diameter and axial ratio of the simulated copolymers for DP = 80 at 300 K

Copolymer sequences	L (Å)	d (Å)	x = L/d
111	210	8.1	26
211	203	8	25
311	240	10.3	23
122	94	13	7.2
222	83	9.2	9
322	65	7.6	8.5

backbone chain flexibility, therefore, the results illustrate the predictive capability of the approach and open up the possibility for providing an indication of relative ranking of transition temperature of polymers yet to be synthesised. This study, using the sequences of monomers, demonstrated that within a main chain LCP some parts of the chain are more likely to form LC than others depending on the sequence of monomers.

6. Conclusions

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 RMMC 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. In particular, the geometric parameters, such as persistence length (q), diameter (d), and persistence ratio (q_r), $q_r = q/d$, were calculated. The polymers (311, 211, and 111) present, from a conformational point of view, the persistence ratios necessary for mesophase formation. The liquid crystalline properties were lost when the incorporated SA content was more than 33%.

The predictive capability of the q_r parameter has been utilised to estimate nematic isotropic transition temperature, which was derived from the diagram of calculated q_r versus temperature for a chosen DP. It seems that RMMC simulations can be useful in determining the nematic isotropisation transition temperatures of liquid crystalline polymers. The theoretically found T_i values suggest a correlation between the backbone chain flexibility and liquid crystalline behaviour.

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

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