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Conformational study of substituted *p*-phenylene terephthalates with molecular mechanics and Metropolis Monte Carlo methods

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Abstract

The conformation of substituted poly(*p*-phenylene terephthalate)s has been studied with molecular mechanics and Metropolis Monte Carlo methods. It was shown that substitution lowers the *trans–gauche* energy difference of the most important dihedral angle of the backbone more when the substituent is attached to the hydroquinone residue (HQ) than when it is attached to the terephthalic acid residue (TA). The substitution also lowers the *trans–gauche* energy barriers for both HQ and TA, but the *gauche* states are more stable in HQ. The *trans* region is wider for HQ compared with the unsubstituted monomer and TA. The mean squared radius of gyration, the mean squared end-to-end distance and the persistence length were calculated with the Metropolis Monte Carlo method for polymers with octyloxy side chains, when the side chain was attached either to the hydroquinone unit (PHQ8) or to the terephthalic acid unit (PTA8). In PHQ8 the side chains are oriented mainly parallel to the backbone; in PTA8 they are oriented more randomly. The main chain of PTA8 is more extended than that of PHQ8, owing to the wider *trans* minimum in PHQ8 than in PTA8. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Modelling; Aromatic polyester; Substitution

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1. Introduction

Rigid rod molecules are of considerable interest because of their highly anisotropic properties [1]. However, the processing of these materials is difficult as a consequence of their high melting temperatures. Decomposition prevails before the polymer melts. To lower the melting point and increase the solubility of such polymers, the attachment of flexible alkyl side chains has proved to be successful [2–11]. Iannelli et al. recently reported the properties of monosubstituted aromatic polyesters that included a flexible segment also along the main chain [12]. They found that both the melting temperature (T_m) and the isotropic transition (T_i) were lowered considerably and that the liquid crystalline behaviour was perfectly enantiotropic. It has been shown not only that the melting temperature decreases as the length of the side chain increases, but also that these polymers are able to form novel layered mesophases [2,5]. In the molten state the side chains act in much the same way as a ‘bound solvent’, decreasing the steric and attractive interactions between the main chains in a systematic fashion [1].

Typically, liquid crystalline polymers are highly aromatic and incompatible with aliphatic polymers. The attachment of flexible alkyl side chains should improve the compatibility of liquid crystal polymers with cheaper aliphatic polymers like polyethylene. This is a way to combine the desired properties of both polymers: good mechanical properties and profitability.

Poly(*p*-phenylene terephthalate) is an aromatic polyester that has a melting point at 600°C, as measured by differential scanning calorimetry at a heating rate of 80°C min^{-1} to minimize degradation [13]. Monosubstitution in the hydroquinone residue lowers the melting temperature more than monosubstitution in the terephthalic acid residue [14]. We have studied how the substitution affects the conformation of the polymer and the correlation between the orientation of the side chains and the main chain. The studies were concentrated on the effect of the substitution site on chain stiffness. The systems studied were poly(*p*-phenylene terephthalate) (PPT), 2-alkoxy-1,4-phenylene terephthalate with octyloxy (PHQ8) and 1,4-phenylene-2-alkoxy terephthalate with an octyloxy side chain (PTA8). Polymers that are monosubstituted in the hydroquinone moiety with alkoxy side chains had not, to our knowledge, been synthesized before the work done in our laboratory

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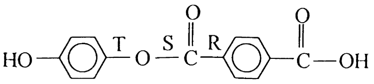


Fig. 1. Model system for repeat unit for poly(*p*-phenylene terephthalate) showing the torsional angles T, S and R.

[15]. Thus, it is possible to compare modelling results with some experimental results concerning these PHQ polymers.

2. Calculation methods

2.1. Choice of force field

All calculations were performed with the molecular modelling package InsightII of MSI (release 400) and a Silicon Graphics Indigo 2 workstation. The results of any mechanics or dynamics calculation depend directly on the quality of the force field. PCFF (polymer consistent force field) and CVFF (consistent valence force field) force fields were tested in order to find the optimal force field for PPT-based polymers. Analysis by the molecular mechanics method was done for 4-hydroxyphenyl monoterephthalate, which represents the repeat unit for poly(*p*-phenylene terephthalate) (Fig. 1). Rotational barriers for bonds T, S and R were calculated. It was shown that the dihedral angle T has the lowest energy barrier and therefore the rotation around this bond is free compared with rotation around other bonds of the polymer backbone. We found that our results obtained on the basis of the PCFF force field are in good agreement with the results of Saebo et al. [16], who performed a theoretical analysis by means of ab initio calculations for the same molecule, as can be seen from Table 1. The value of torsion angle T differed by only 1.5° and the energy barrier by only 0.4 kcal mol^{-1}, when ab initio calculations and values obtained from PCFF calculations were compared. For CVFF, the differences were essentially larger. According to this analysis the PCFF force field is better suited to model poly(*p*-phenylene terephthalate) than the CVFF force field.

Table 1
Torsion angles and energy barriers for bonds T, S and R in hydroxyphenyl monoterephthalate, see Fig. 1

	CVFF	PCFF	Ab initio [16]
Torsion angle (°)			
T	− 90	− 113	− 114
S	0	0	—
R	± 180,0	± 180,0	—
Energy barrier (kcal mol^{-1})			
T	3.4	1.6	2.0
S	9.3	10.8	—
R	17.0	5.4	—

2.2. Conformational analysis

The energy contour maps for the alkoxy-substituted monomers were calculated for ST and SR pairs of dihedral angles T, S and R (Figs 2 and 3). The effects of the methoxy substituent on the energy barriers and energy minima of the main chain were also studied. The substituent was either in the hydroquinone residue (HQ) or in the terephthalic acid residue (TA). Varying two torsions leads to a potential-energy surface which is essential in trying to understand correlations between various conformations of neighbouring dihedral angles. The energy surface was scanned every 10° from −180° to +180°. During generation of the energy contour, the rest of the molecule was minimized by the conjugated gradient method until the energy derivatives were less than 0.001 kcal mol^{-1} Å^{-1}. Torsion forcing of 1000 kcal mol^{-1} was used to force a torsion systemically to a grid of angles.

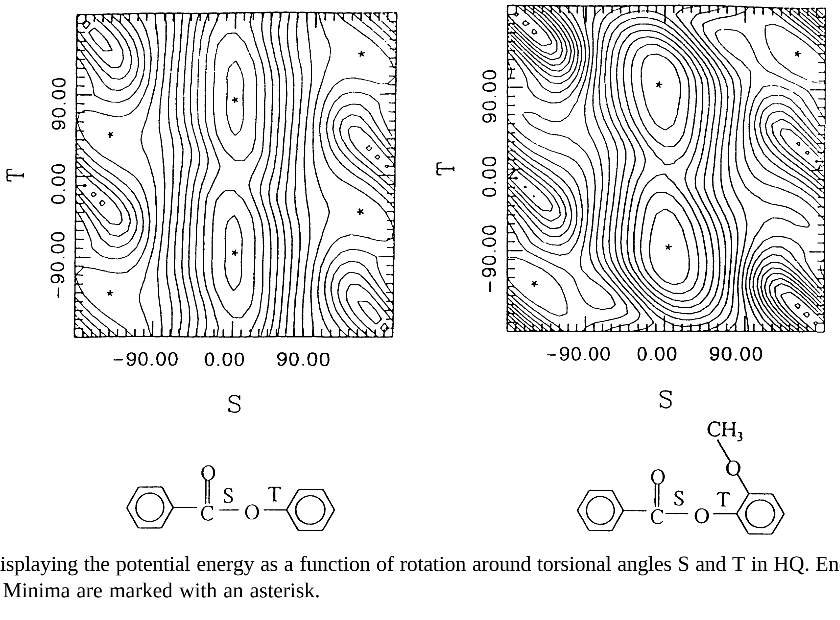


Fig. 2. Energy contour map displaying the potential energy as a function of rotation around torsional angles S and T in HQ. Energy differences between the graph plots are 1 kcal mol^{-1}. Minima are marked with an asterisk.

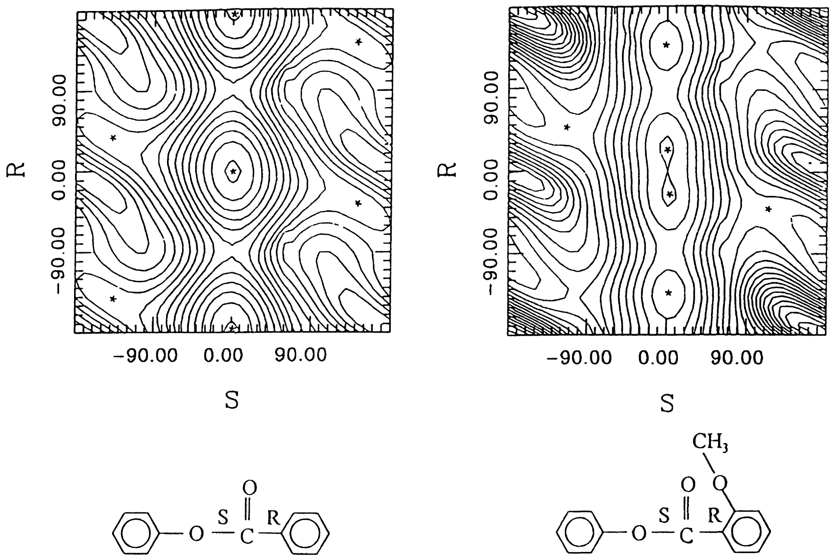


Fig. 3. Energy contour map displaying the potential energy as a function of rotation around torsional angles S and R in TA. Energy differences between the graph plots are 1 kcal mol^{-1}. Minima are marked with an asterisk.

2.3. Metropolis Monte Carlo methods

Metropolis Monte Carlo (MMC) is a method for calculating the conformational properties of polymers. As in traditional rotational isomeric state (RIS) methods, only torsional degrees of freedom are considered in determining the conformations of a chain; bond lengths and angles are fixed. Unlike traditional RIS methods, MMC allows torsion angles to vary continuously; it does not impose the assumption of discrete rotational states. The method is based on relative energies of the new and the old conformation [17].

In MMC it is possible to use a bond-based cutoff or a distance-based cutoff to determine the interaction range of the potential. In the distance-based cutoff MMC uses the spatial distance between atoms rather than the number of bonds along the chain, as is the case in the bond-based cutoff. The distance-based cutoff is usually used to simulate a bulk system. The bond-based cutoff method is used for simulation of a single polymer chain in a Θ solvent or at conditions near the Θ state. In the first stage of our work we studied the behaviour of single polymer molecules by the MMC method and used the bond-based cutoff.

In the bond-based method parameters n_{min} and n_{max} affect the way van der Waals' and Coulomb energies are evaluated in an MMC simulation. The nonbond energies are not computed for atoms which are closer than n_{min} bonds away along the chain from each other. The usual value for n_{min} is 3. The nonbond energies are also neglected for atoms further than n_{max} bonds away from each other. That is, only interactions for atoms between n_{min} and n_{max} apart are computed. Use of n_{max} to limit the range of nonbond interactions is a way of mimicking Θ conditions. Reasonable values for n_{max} range from 4 to about 6 for linear polymer chains in Θ conditions. Because of the branched and ring-containing structures of the polymers studied here, n_{max} should have a larger value in order to include the interactions of some neighbouring monomers and also the side chains of the neighbouring repeating units in the energy evaluation. Coulombic interactions between partial charges were calculated by the charge-group-based method [18]. A charge group in this method is a small group of atoms, close to each other, which have a net charge of zero or almost zero.

The n_{max} value was determined so that the ends of the neighbouring side chains would 'see' each other. This is important especially in the case of longer substituents (PHQ12, PHQ18), which are currently being simulated in our laboratory. In these polymers the side chains are long and the density of the side chains is so high, that there would most probably be overlaps of the side chains if the n_{max} value was too small. Our aim is to compare polymers with different lengths of the side chain. Therefore the n_{max} value had to be nearly the same for all simulations and chosen according to the polymer with the longest side chains, PHQ18. Taking into account the principle that the neighbouring side chains should be interacting and the determination of charge groups, the n_{max} value was chosen to be 48. Four repeating units along the main chain were included in the energy evaluation when such a definition of n_{max} was taken into account.

MMC simulations were done for polymers with 20 repeating units at room temperature. The molecules were preminimized by Discover [18] before the simulation. The number of equilibration steps was 7000 for each rotatable bond. This stage is necessary to bring the polymer chain from its initial conformation to a conformation typical for the chain in solution or melt at the desired temperature. The number of simulation steps was 20 000 for each rotatable bond. This parameter specifies the number of Monte Carlo simulation steps to be performed after the equilibration stage. The block-averaged values of the mean squared

Table 2
The results of Metropolis Monte Carlo calculations

	Mean squared end-to-end distance (Å^2)	Mean squared radius of gyration (Å^2)	Persistence length (Å)
PPT	37 112 ± 218	3810.6 ± 5.14	75.03 ± 0.26
PHQ8	33 773 ± 280	3626.5 ± 3.57	68.11 ± 0.17
PTA8	37 572 ± 194	4067.9 ± 2.56	79.50 ± 0.13

end-to-end distance and energy were plotted as functions of the simulation step number in order to see whether the system was fully equilibrated. There was no evidence of any long-term drift in mean squared end-to-end distance or energy over the course of simulation, which indicated that the chains had reached a steady state. The following properties were determined for PPT, PHQ8 and PTA8: mean squared end-to-end distance, mean squared radius of gyration and persistence length. The equilibrated results are shown in Table 2. The structures of PPT, PHQ8 and PTA8 were studied by dihedral distribution analysis (Figs 4–6). The actual occurrences of (R), (S) and (T) are shown in Fig. 4 and the distributions of (S,T) and (S,R) are shown in Figs 5 and 6. Additionally, the structures of PHQ8 and PTA8 were studied by the distribution of orientations between the end-to-end vectors of monomer and side chain (Fig. 7), where is Θ the angle in rad between two vectors **i** and **j**. The radial distribution function (RDF) between the tail of the side chain and the oxygen atoms of the ester bond was calculated, see Fig. 8. The definitions of the end-to-end vectors of monomer and side chain and the atoms included in the radial distribution function used in these analyses are illustrated in Fig. 9. The methyl carbon is represented with an asterisk; the oxygen atoms are marked with 1 and 2 for PTA8 and 1′ and 2′ for PHQ8, respectively. Some examples of resulting structures are shown in Fig. 10.

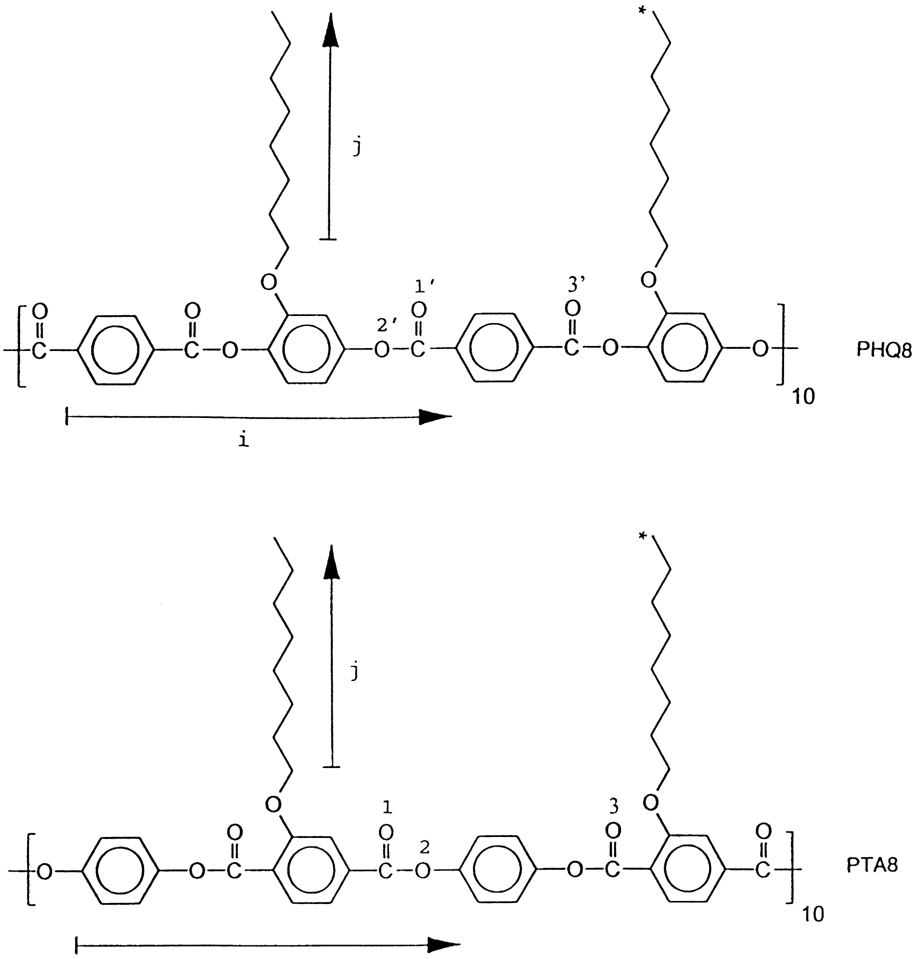


Fig. 4. Results of dihedral distribution function analysis of side chains and dihedral angles R, S and T.

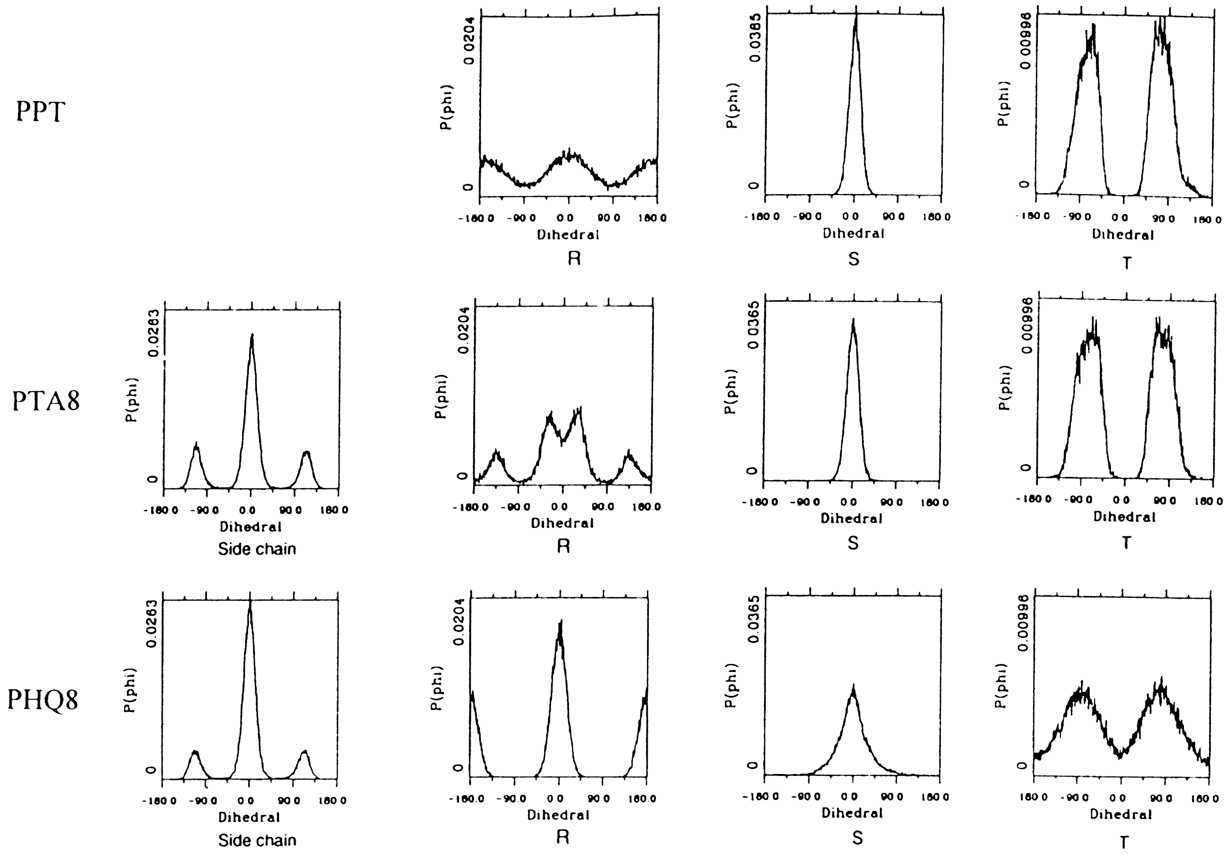


Fig. 5. Distribution of dihedral angles (S,T) for PPT and PHQ8.

3. Results and discussion

In the case of HQ, our conformational analysis shows that the dihedral angles S and T have six minima, as can be seen in Fig. 2, which shows the contour map for a structure with a methoxy substituent compared with an unsubstituted unit. For the monomer without the substituent the local minima are at (S,T) = (−130°,−130°), (−130°,50°), (130°,−50°) and (130°,−130°) and the global minima are at (0°,±90°). For the monomer with a substituent the global minima are the same as without substituent, but the local minima are at (−145°,−130°) and (145°,130°), respectively.

The contour maps shown in Fig. 3 display the energy as a function of dihedral angles S and R for a structure of TA

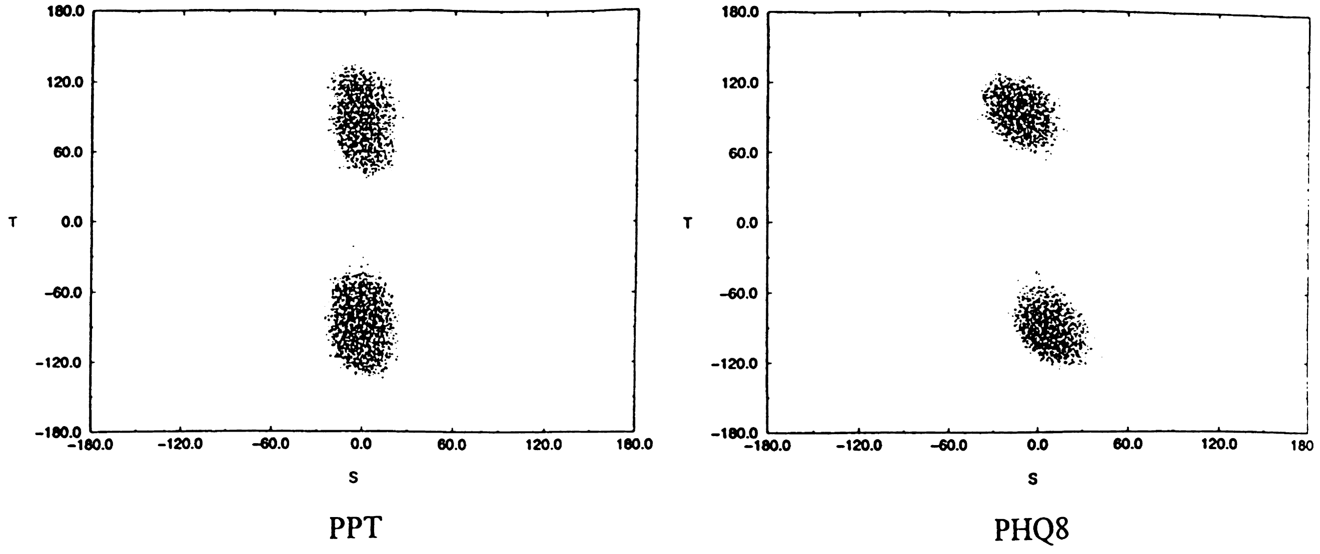
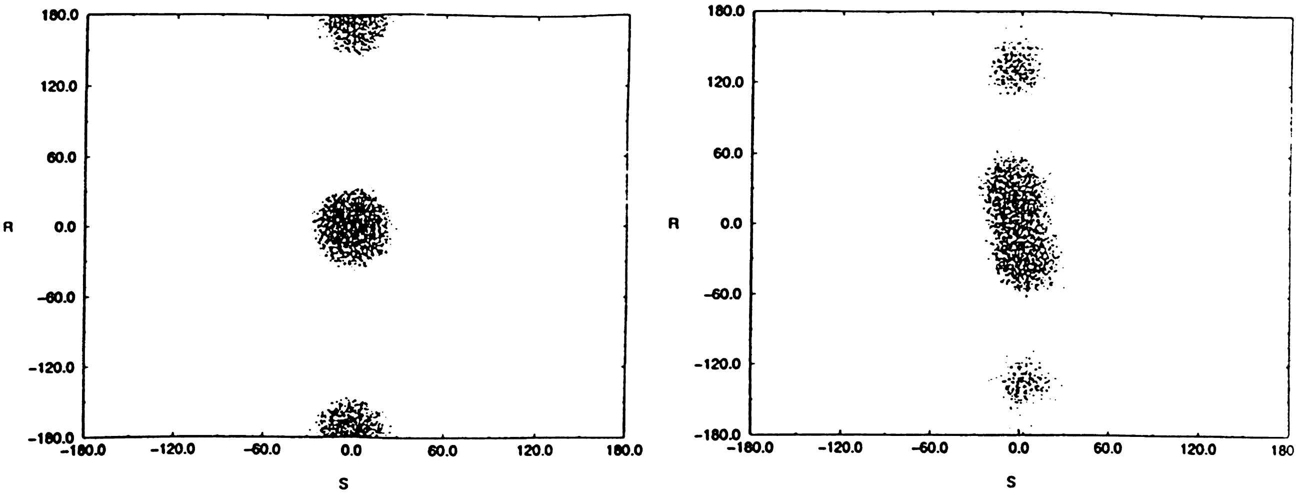


Fig. 6. Distribution of dihedral angles (S,R) for PPT and PTA8.



PPT

PTA8

Fig. 7. Distribution of orientations $p(\Theta)$ for PTA8 (1) and PHQ8 (2). Θ is the angle in radians between the end-to-end vectors of the monomer and the side chain.

without a methoxy substituent. There are two global minima for S and R. They are at (S,R) = (0°,0°) and (0°,±180°). The local minima are at (−140°,−140°), (−140°,40°), (140°,−40°) and (140°,140°). The number of global minima rises from two to four when the methoxy substituent is attached to the terephthalic acid residue. The global minima are at (S,R) = (0°,±140°) and (0°,±20°) and the local minima are at (±180°,±90°).

Rotations around the S bond change the shape of the chain. Therefore the torsional behaviour of the S bond is the most important from the viewpoints of liquid crystalline behaviour and processability. It can be noted from the contour map of the molecule without the substituent (Figs 2 and 3) that there are two symmetrical *gauche* minima at about ±130°, with energy about 10 kcal mol^{-1} higher than the *trans* minimum. The *trans–gauche* energy barrier is about 10 kcal mol^{-1}. The *gauche–trans* barrier is very low, less than 1 kcal mol^{-1}. Substitution lowers the *trans–gauche* energy difference by 7 kcal mol^{-1} in HQ and by 3–4 kcal mol^{-1} in TA. This means that the backbone is stiffer in PTA polymers than in PHQ polymers. The substitution also removes two of the four *gauche* minima in HQ, but in TA the effect is quite small. Also the *trans–gauche* barrier of bond S decreases from 10 kcal mol^{-1} to 7 kcal mol^{-1} for

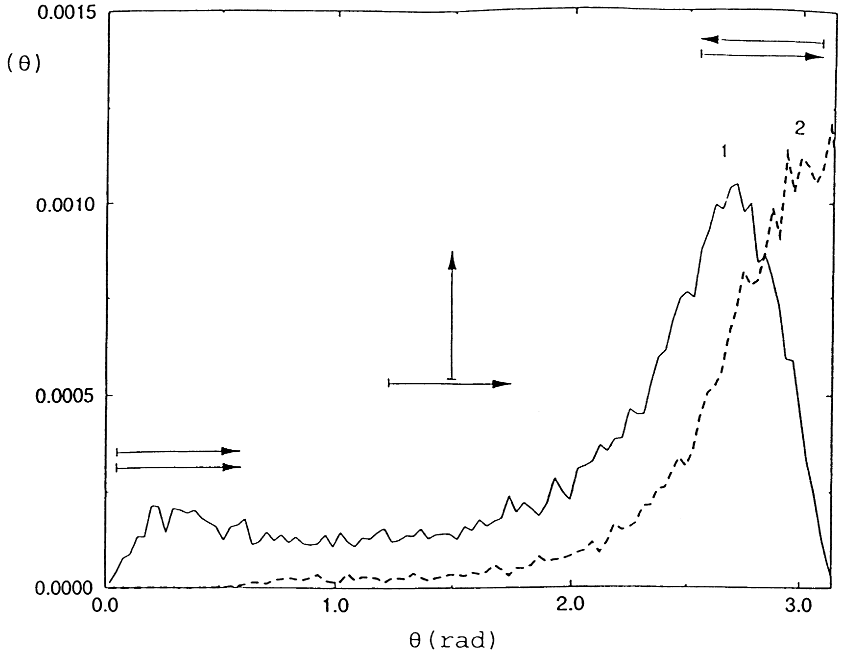


Fig. 8. Radial distribution function $g(r)$ as a function of distance (Å) between the methylene carbon at the end of the side chain and the oxygen atoms in the ester bonds; 1 and 2 for PTA8 and 1′ and 2′ for PHQ8, respectively.

HQ and to 8 kcal mol^{-1} for TA, which means that substitution facilitates the accessibility of the *gauche* state in both cases. The *gauche–trans* barrier increased to 4 kcal mol^{-1} for HQ, but only to about 1 kcal mol^{-1} for TA. This means that it is essentially easier for the bond S in TA to be transferred from the *gauche* state to the *trans* state compared with HQ. Our analysis shows that substitution facilitates the availability of *gauche* states in both HQ and TA, but in HQ the *gauche* state is more stable.

It is well known that there are two main mechanisms which may be responsible for the flexibility of a polymer chain. The first is based on rotational isomerism and the other on small libration near the minimum. The appearance of *gauche* states is essential only if the flexibility of the polymer is based on rotational isomerism. The energy difference between *trans* and *gauche* states is $\Delta E = 3$ kcal mol^{-1} in PHQ polymers. This means that the probability of finding *gauche* states at room temperature, which is proportional to $\exp(-\Delta E/kT)$, is only 0.65% according to the Boltzmann factor. The probability increases with increasing temperature so that at 493 K (mesophase temperature) it is 4.7%. The same probabilities for PTA polymers are 0.0008% (300 K) and 0.08% (493 K), respectively. This means that the rotational isomerisation mechanism of flexibility does not contribute much to the flexibility of PTA8 and PHQ8 until at rather high temperatures.

MMC has been used in this work to study the structure and conformational properties of the polymers. The mean squared end-to-end distance, the mean squared radius of gyration and the persistence length were calculated for PPT, PHQ8 and PTA8. The dihedral angle distributions (Figs 4–6), the distribution of orientations $p(\Theta)$ between the backbone and side chains (Fig. 7) and the radial distribution function $g(r)$ of distances between the tail of the side chain and the oxygen atoms of the ester bond (Fig. 8) were calculated in order to study 1000 structures of each polymer. An important observation is that results of molecular mechanics (MM) and Monte Carlo (MC) calculations are qualitatively similar despite different lengths of the substituent in our MM and MC calculations. The forms of the *trans* minima look alike, upon comparison of Figs 2 and 5 or Figs 3 and 6, respectively. The *trans–gauche* energy differences of S are smaller for PHQ polymers and PTA polymers compared with PPT. However, there is practically no appearance of *gauche* states of S in equilibrated conformations of our MMC calculations, even in the case of PHQ8 where the energy difference is the lowest (3 kcal mol^{-1}). This can be seen from the distribution of dihedral angles (S,T) of PHQ8 (Fig. 5) and also from Fig. 4, where the distribution of S only is represented. The distribution of dihedral angles (S,R) of PTA8 is shown in Fig. 6. Because of the absence of *gauche* states in our MC simulations, the flexibility of the chain is not based on rotational isomerism in our simulations at room temperature but on librations near the *trans* minimum. The reason for the shorter persistence length of PHQ8 than for PTA8 is in the form of the *trans* minimum. This can be seen best from Fig. 4, where a difference in dihedral distributions of S is seen; PHQ8 has a wider dihedral distribution near the *trans* minimum than PTA8 and this results in the smaller polymer size and

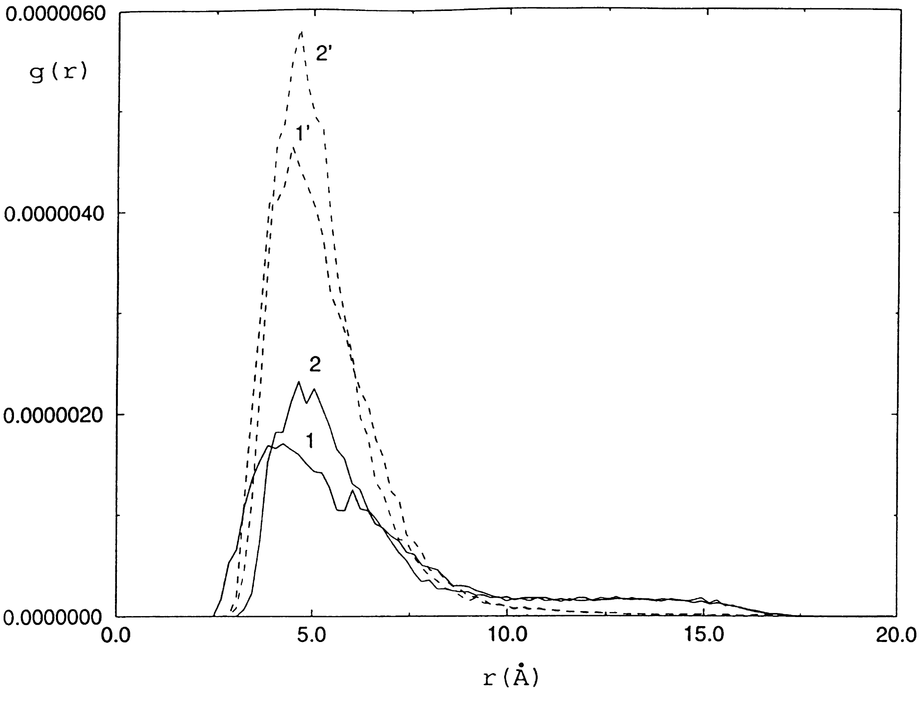


Fig. 9. Definition of the end-to-end vectors of monomer and side chain for PHQ8 and PTA8. The distances, which were used for the radial distribution function, were calculated between the methylene carbon (marked with an asterisk) and the oxygen atoms of the ester bond (marked with 1 and 2 for PTA8 and 1′ and 2′ for PHQ8).

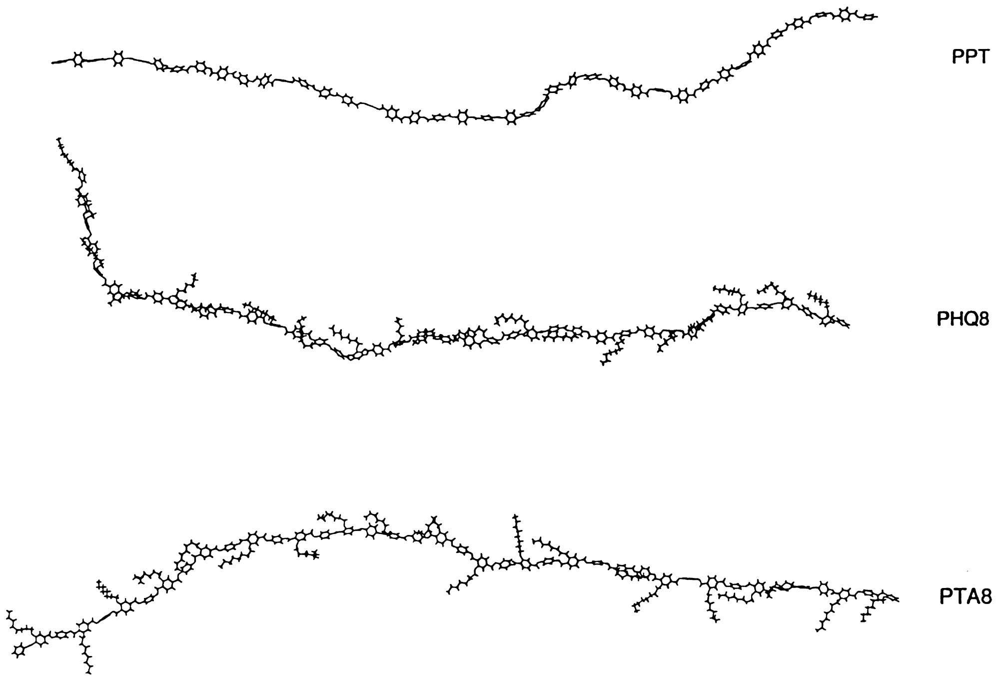


Fig. 10. Examples of structures resulting from Metropolis Monte Carlo calculations.

persistence length. Furthermore, PPT has a narrower minimum than PHQ8. PTA8 has the narrowest potential well and therefore it is the stiffest polymer. The larger radius of gyration in PTA8 can also be partly explained by the more random orientations of the side chains in comparison with PHQ8. This can be seen from Figs 7 and 8. According to the distribution of orientations between the backbone and the side chains, PHQ8 has the greatest number of conformations in which the side chains are oriented along (antiparallel) the backbone. Many of the side chains in PTA8 are also oriented almost antiparallel to the backbone, but there is also a large portion of side chains more randomly oriented, as can be seen from Fig. 7. Orientations both close to perpendicular and parallel can be seen, which is not the case in PHQ8. The results for radial distribution functions confirm these results, see Fig. 8. The methyl carbon at the tail of the side chain is close to the oxygen atoms 1′ and 2′ in PHQ8 more often than it is close to 1 and 2 in PTA8. The reason for this behaviour could be steric repulsion near the attachment point of the side chain and van der Waals' and Coulombic attraction of the end of the side chain with the main chain. There is steric hindrance between the oxygen of the closest C=O group (atom 3 in Fig. 9) and the first methylene group of the side chain in PTA8. This practically hinders tilting of the side chain parallel to the backbone in PTA8. In the case of PHQ8 this tilt is unhindered. This is the main reason why the orientations of the side chains in PTA8 are more random than in PHQ8.

4. Conclusions

The PCFF force field was chosen and used to calculate rotational barriers of 4-hydroxyphenyl terephthalate, which represents the repeat unit for poly(*p*-phenylene terephthalate). Substitution of alkoxy chains of various lengths into the HQ (PHQ polymers) or the TA (PTA polymers) moiety had an influence on the energy barriers and minima regions of the repeat unit.

Results obtained from molecular mechanics calculations with short substituents and from Monte Carlo calculations with longer substituents are qualitatively similar. Our modelling results show also that the PTA polymers are stiffer than the PHQ polymers in both the following cases: (1) when the flexibility is based on rotational isomerism and (2) when the flexibility is based on libration near the minimum area. This can explain why substitution in the HQ unit decreases the melting temperature of the liquid crystalline polymer more than substitution in the TA unit.

Further simulations of PHQ and PTA polymers are in progress in order to study the structures and conformational properties of these polymers as the length of the side chain increases. Additionally, modelling the structures in the bulk material is in progress.

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