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RMMC simulations of the chain properties of polyester homopolymers from 1,4-cyclohexanedimethanol and 2,2,4,4-tetramethyl-1,3-cyclobutanediol

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Abstract

Conformational properties of polyesters based on terephthalate and cyclohexylene dicarboxylate with 1,4-cyclohexanedimethanol and 2,2,4,4-tetramethyl-1,3-cylcobutanediol are studied using RIS Metropolis Monte-Carlo simulations. The polyester single chains investigated have two different configurations, one with an all *trans* linkage of 1,4-cyclohexanedimethanol and 2,2,4,4-tetramethyl-1,3-cylcobutanediol, and the other in which both *trans* and *cis* linkages of these rings in the diol units were present. Incorporation of *cis* isomers results in a decrease in the chain dimensions, and reduces the influence of the repeat unit chemical structure on the overall conformationally averaged chain dimensions. The trend in the variation in chain dimensions with increase in temperature is found to be dependent on the structure of the polyester along with the isomer constitution of the chains. In the all-*trans* isomer chains, the polyester containing cyclobutylene groups were much more rigid than those with cyclohexylene groups in the backbone, as evident from the characteristic ratios and the persistence lengths. The effect of temperature, isomer linkage, nature of the aliphatic ring in the backbone and its content, on the overall chain dimensions and the persistence length, is brought out by this study. © 2002 Published by Elsevier Science Ltd.

Keywords: Polyester; Cycloaliphatic; Monte-Carlo

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1. Introduction

Conformational properties of polymer chains are of fundamental as well as practical importance in the area of polymer science. The chain structural properties, which are derived from conformational statistics, depend on the conformational states at specific bond pairs of the repeating unit as well as on the interdependence between the repeat units and are controlled by the excluded volume, which avoids the segmental overlaps along the chain. RIS theory has been used over the past four decades to comprehend the conformational statistics and chain properties of polymers [1]. Since the inception of the RIS Metropolis Monte-Carlo (RMMC) method [2], inspired by the existing discrete RIS method, this approach has been used to calculate the statistical properties of polymer chains. Even though in principle this method is not used to obtain bond level conformational states, which can be obtained otherwise by conformational energy analysis and the use of conformational energies that are obtained experimentally in moieties similar to the ones constituting the repeat unit into the discrete RIS formalism, RMMC simulations provide an effective method to the calculation of the overall chain dimensions such as the mean-squared end-to-end distance ($\langle R^2\rangle$), the mean-squared radius of gyration ($\langle S^2\rangle$), the persistence length (L_p) and the characteristic ratio (C_n). The discrete RIS formalism is superior to the RMMC formalism when accurate conformational energies are available from experiments, obviating the need for a force-field based continuum Monte-Carlo simulation of conformationally averaged unperturbed single chain properties. However, the RMMC method, employed with a reasonably well-parameterized force-field, is especially useful for implementation on complicated polymer structures containing rings in the backbone for which formulation of the RIS model can some times not be straightforward to perform (depending upon the situation, stereochemical dispositions, etc.).

The general advantages offered by the RMMC method over the conventional RIS method are: (1) derivation of the statistical weights for novel polymer structures and new

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polymers are not required for use in RMMC simulations, (2) use of the RMMC method for polymers with any type of architecture is possible in a more tractable manner without extensive parameterizations. The RMMC method was first implemented by Honeycutt [2] for polyethylene, poly(dimethylsiloxane), poly(ethylene oxide), bisphenol A polycarbonate, poly(ethylene terephthalate), and, poly(ethylene) stars with three and four arms, with the use of the COMPASS force-field. Around the same time, using RMMC simulations, Bicerano [3,4] reported the characteristic ratio, persistence length, radius of gyration and intrinsic viscosity of novel liquid crystalline polymers containing dihydroxy-α-methylstilbene, and made comparisons with experimental data. The values of the calculated radius of gyration of these compounds and their variation with the weight-averaged molecular weight were comparable to the experimentally observed values. The calculated intrinsic viscosity showed a similar exponential variation with molecular weight as experimentally observed, but were larger than the observed values by roughly a factor of 6 over the entire M_w range.

Several reports have appeared in the recent literature on the implementation of RMMC method for simulation of linear polymers with a variety of different structural moieties in their repeating units. Sundholm and co-workers [5] studied the rigid-rod polymers of *p*-phenylene terephthalates. Lee et al. [6] have looked at the conformational statistics of the polycarbonate of bisphenol A using the PCFF force-field and they found, from the comparison of the calculated and experimentally observed intrinsic viscosities, that the calculated radius of gyration was closer to the experimentally derived value from measurements in either chloroform at 293 K or *p*-dioxane at 303 K. Blomqvist et al. [7] have studied the chain properties of polyesters with isolated carboxyl groups, as well as for poly(methyl acrylate), poly(methyl methacrylate), poly(vinyl acetate) and for some aliphatic main-chain polyesters having alkyl chains of various lengths between the carboxyl groups. Their calculated characteristic ratios, using torsional states from ab initio calculations on small fragments into the reoptimized PCFF force-field, agreed well with the experimental values. Also, the dependence of the calculated characteristic ratios for PMMA with different tacticities followed the experimentally observed behavior. In a later work, Blomqvist [8], performed studies on chain properties of poly(L-lactic acid), poly(L,D-lactic acid) and poly(glycolic acid) which have strongly interacting polar carboxyl groups, by using the modified PCFF force-field from ab initio calculations of the torsional potentials.

Amorphous polyesters, in comparison to predominantly crystalline polyesters, are more amenable to statistical studies using single chain conformations with an aim of discerning molecular structure–macroscopic property relationships. Amorphous polyesters containing aliphatic rings in the backbone have emerged as an interesting class of polymers, which can exhibit useful thermal and mechanical properties in their condensed phase as we are aware from studies in the recent literature [9,10]. Yee and co-workers [9] have performed extensive studies on polyester co-polymers formed from 1,4-cyclohexanedimethanol, such as poly(1,4-cyclohexylenedimethylene terephthalate) [PCT], poly(1,4-cyclohexylenedimethylene cyclohexylenedicarboxylate) [PCC] and poly(1,4-cyclohexylenedimethylene 2,5-dimethylterephthalate) [DMPCT]. Another class of amorphous polyesters, which has emerged as interesting polymers with high ductility, is the copolyesters of rigid 2,2,4,4-tetramethyl-1,3-cyclobutanediol [CBDO] with flexible diols [10,12]. The interesting properties of these polyesters essentially arise from the conformational transitions and the molecular structure of their repeat units containing such cyclic moieties. Therefore, such polyesters have been chosen in the present paper, to understand their overall chain conformational statistics as well as compare these chain properties with other simpler synthetic polyesters which have been investigated in literature prior to the present work. The set of homopolyesters PCT, DMPCT, PCC, and CBDO also form a structurally variant set wherein a fruitful molecular structural comparison of the effect on the chain properties can be made between the effect of (i) cyclohexylene and the cyclobutylene rings, (ii) one of the two rings in the polyester repeat unit being an aliphatic ring versus both the rings being aliphatic, while still maintaining the same number of bonds in the rings, and (iii) the effect of methyl substituents on the phenylene ring in DMPCT. Such polyesters have not been studied in terms of chain conformational statistics prior to the present paper, and thus the work presented here is motivated by the lack of systematic computational studies on such polymer chains.

In this paper, we present a first study of the conformational statistics of the homopolyesters of PCC, PCT, DMPCT, and CBDO. The structures of the repeat units in the *trans*-configuration are provided in Fig. 1. The paper is organized as follows: Section 2 describes the computational methods and the simulation parameters and details; next, the results of this work are presented in terms of the energetics, chain statistics, and comparison of such properties for these polymers with other structurally different polyesters that have been reported in literature. There is a separate section devoted to the calculation of dipole moments of the repeat unit fragments as well as the polymer chains for the polyesters studied here, and a fruitful comparison of the dipole moments for our compounds with the values experimentally reported for other polyester fragments and chains in the literature. Finally, the conclusions of this work are summarized.

2. Simulation methodology and parameters

RMMC simulations were performed using Cerius^2 [13] on a Silicon Graphics Octane workstation. All calculations were performed with the PCFF force-field [14]. 50 repeat

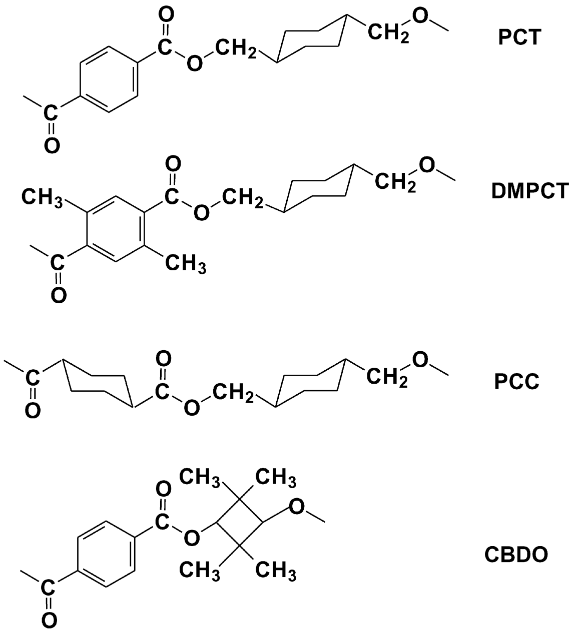

Fig. 1. Geometry of the repeat units of the polyesters in the *trans* configuration.

units were used for construction of the polyester chains. For the polyesters the single chains generated had two different *configurations*, for the bonds flanking the cycloaliphatic rings, which were generated initially itself and which do not change with conformational transitions and relaxations of the polymers. In one set of chain samples, the cyclohexylene groups of the *diol* part (in PCT, DMPCT and PCC) and the tetramethylcyclobutylene groups of the diol part in CBDO, were all in the *trans-configuration* (*the 100% trans isomer, trans–trans*). For cyclohexylene units, the *trans* substitution corresponds to equatorial–equatorial, and the axial–axial substitution was not considered because of its much higher energy and very low probability of existence. For the other set of chain samples, in the second configuration, the chains had a constitution in which both the *cis* and *trans* configurations (isomers) of the diol (1,4-cyclohexanedimethanol or 2,2,4,4-tetramethyl-1,3-cyclobutanediol) were present according to experimental conditions reported earlier in literature [9–12]. The cyclohexylene groups of the *acid* part in PCC were kept at the *trans* configuration. For PCT, DMPCT and PCC, the ratio of the *trans* to *cis* configuration of the cyclohexylene groups was 70:30 [9]. For CBDO, the *trans* to *cis* ratio was 50:50 [12]. The optimized conformations of the repeat units of the polyesters in the *trans* and *cis* conformations are depicted in Fig. 2.

For each polyester, five chains were generated corresponding to the *trans–trans* (*tt*) and *cis–trans* (*ct*) configurations. These were optimized by steepest descent and conjugate gradient methods. In the case of CBDO, more chains had to be generated, to get single chains of lower energy. 20 ps of molecular dynamics simulation (NVT) was performed on three of the lower energy chains corresponding to each polyester, at 300 K. The lowest energy snapshot from the MD run was then further minimized using conjugate gradient method, which enabled the proper optimization of the single chains so that the bond lengths and bond angles are in their equilibrium values. The root-mean-squared force (calculated as the gradient of the potential energy as sum over all interatomic interactions), during the steps of the minimization procedure, on all the optimized chains was less than 0.1 kcal mol^{-1} Å.

RMMC simulations were performed on the optimized single chains, three each for the *trans–trans* configurations and one for the *cis–trans* configurations for each of the polyesters. In the simulations, the bond lengths and bond angles of the chains are kept constant and the dihedrals are varied in a continuous fashion. The equilibrium geometric parameters (bond lengths and angles) are shown in Table 1 for the polyester repeat units. The details of the method are described elsewhere [2]. A bond-based cutoff was used to determine the interaction range of the potential. The number of maximum bonds which is defined as the maximum number of rotatable bonds separating two atoms, within which both electrostatic and van der Waals interactions are included in the energy calculation during the RMMC simulation, is an important parameter and a value of 8 was felt sufficient and suitable and was used in our calculations [2]. The dielectric constant (used in calculating the electrostatic energy) was estimated using quantitative structure–property relationships. The values were 2.82 (CBDO), 2.88 (PCT), 2.80 (DMPCT) and 2.70 (PCC) and were determined via the QSPR method incorporated in Cerius^2 [13,15]. During the RMMC simulation, the chains were first equilibrated for 3 000 000 steps and then the sampling was performed for 6 000 000 steps. Data collection during sampling was carried out after every 200 steps. The RMMC simulations were performed at two different temperatures, 300 and 483 K. The higher temperature was chosen to represent the chain behavior at temperatures well

Table 1
Geometrical parameters of the polyester chains

	PCT	DMPCT	PCC	CBDO
Bond length (Å)				
C_c–C_p	1.491	1.499		1.487
C_c–O	1.360	1.363	1.356	1.362
O–C	1.419	1.420	1.425	
C–C_{cyx}	1.539	1.541	1.541	
C_c–C_{cyx}			1.524	
O–C_b				1.423
Bond angle (°)				
O–C_c–C_p	110.7	110.5		111.6
C_c–O–C	120.8	120.9	119.3	
O–C–C_{cyx}	107.2	107.3	108.9	
C_c–C–O			109.3	
O–C_c–C_{cyx}			110.2	
C_c–O–C_b				119.2

C: alkane carbon; C_c: carbonyl carbon; C_p: phenyl ring carbon; C_{cyx}: cyclohexyl carbon; C_b: cyclobutanediol carbon.

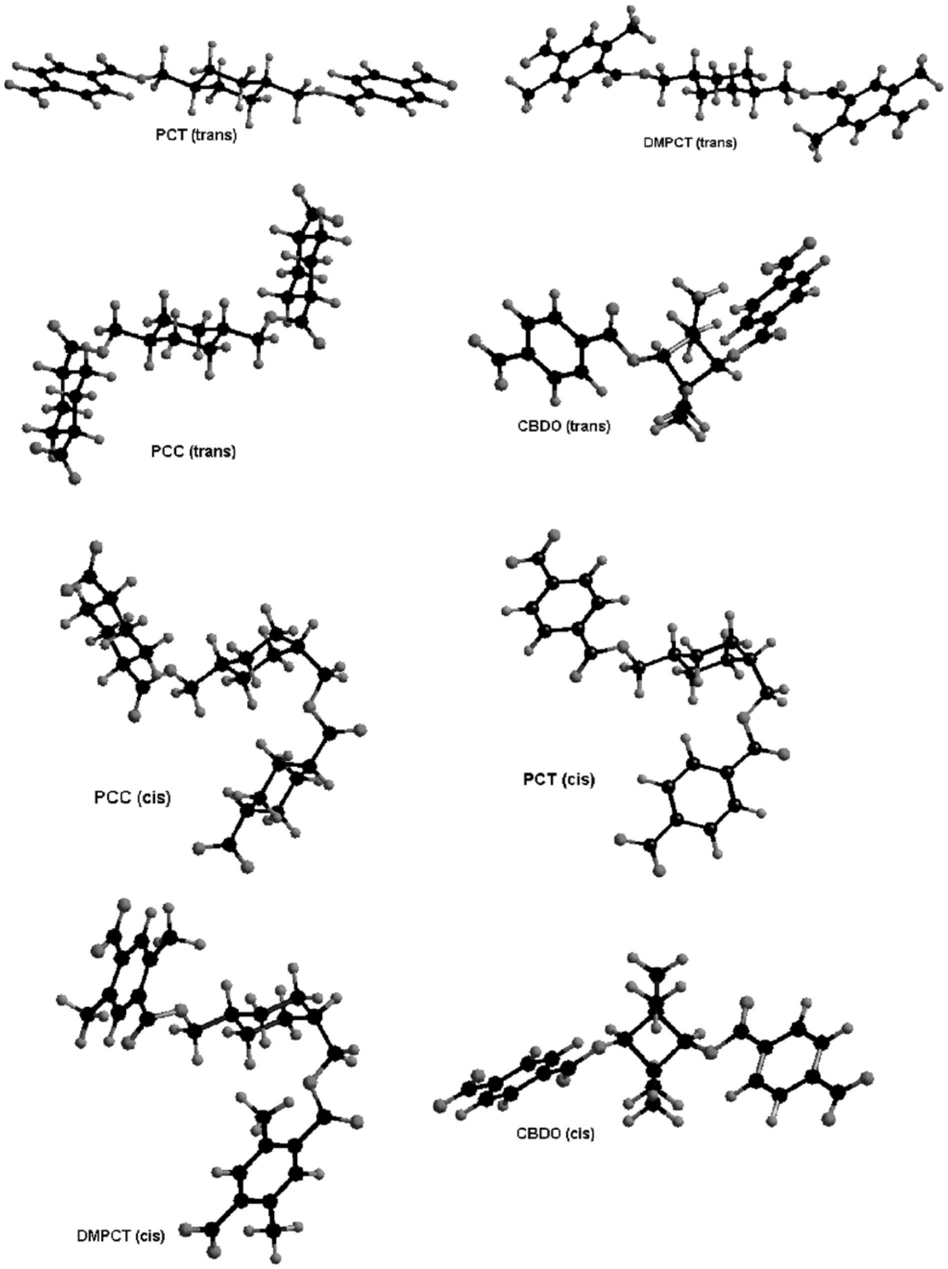

Fig. 2. Geometry optimized conformations of the repeat units of the polyesters with *cis* and *trans* configurations of the aliphatic ring in the diol.

above the glass transition temperature of these polyesters. CBDO has the largest T_g among these polyesters, with a value of 457 K for 60% of the *trans* diol [12]. There was no evidence of any long-term drift of energy during the simulation, which indicated that the chains were fully equilibrated at the end of 3 000 000 steps.

3. Results and discussion

3.1. Energetics

The potential energies of the polyesters during the sampling stage of the RMMC simulations were almost constant. The results are presented in Table 2. Standard deviation in potential energies during the simulation was less than or equal to 3% for the polyesters, for example, 2% (CBDO), 3% (DMPCT), 1.77% (PCC) and 1.3% for PCT, in the *trans* configuration at 300 K. The standard deviation in mean van der Waals energy is less than 1% and for Coulomb energy it is less than 2%, except for PCC, where the deviation in coulomb energy is 5%. The standard deviation in mean torsional energy is less than 6%, except for PCC where the value is 17%. Coulomb energy is negative (attractive) for both configurations of DMPCT at 300 and 483 K, whereas this contribution is positive in the case of

Table 2
Mean energies for PCT, DMPCT, CBDO and PCC polyesters

Polyester	300 K				483 K			
	E_{total}	E_{vdw}	E_{coul}	E_{tor}	E_{total}	E_{vdw}	E_{coul}	E_{tor}
trans (tt)								
CBDO	524.4 ± 10.4	891.4 ± 7.2	298.4 ± 1.1	−665.5 ± 11.3	637.0 ± 15.9	911.9 ± 10.2	298.7 ± 1.4	−573.6 ± 16.8
DMPCT	355.4 ± 11.2	996.5 ± 16.1	−84.5 ± 2.0	−556.6 ± 20.2	560.6 ± 15.7	1028.6 ± 20.5	−81.0 ± 2.2	−387.1 ± 24.4
PCC	628.5 ± 10.8	730.9 ± 7.1	45.2 ± 2	−147.6 ± 7.7	751.2 ± 17.1	782.5 ± 10.7	44.4 ± 2.2	−75.8 ± 13.1
PCT	760.0 ± 10.0	933.8 ± 8.5	330.2 ± 2.0	−503.2 ± 11.9	860.7 ± 15.5	938.6 ± 11.9	331.7 ± 2.4	−409.6 ± 18.1
cis–trans (ct)								
CBDO	483.8 ± 10.5	860.2 ± 7.1	297.0 ± 1.4	−673.4 ± 10.8	587.6 ± 16.2	873.0 ± 10.1	301 ± 1.8	−586.3 ± 16.8
DMPCT	406.1 ± 10.9	1020.8 ± 17.3	−114.0 ± 4.4	−500.7 ± 20.3	519.6 ± 16.1	1014.8 ± 21.0	−105 ± 5.6	−390.0 ± 24.8
PCC	568.7 ± 11.2	703.4 ± 7.1	9.4 ± 3.9	−144.1 ± 7.8	698.6 ± 17.9	754.2 ± 10.7	17.8 ± 5.4	−73.4 ± 13.0
PCT	690.6 ± 10.3	895.8 ± 8.5	298.6 ± 4.1	−503.8 ± 11.6	797.2 ± 15.9	901.9 ± 11.8	307.2 ± 5.3	−411.8 ± 18.2

other polyesters. Contribution due to van der Waals energy is positive and repulsive for all polyesters at both temperatures.

Comparison of the total energies of the polyester chains in the two different configurations (isomers) is as follows. In the case of PCT, the chains which had 70:30 constitution of the *trans* and the *cis* orientation of the cyclohexylene groups (*ct*) were of lower energy than the one in which all the cyclohexylene groups were in *trans* orientation (*tt*). The higher energy of the *tt* configurations of the PCT chains is due to the higher van der Waals and electrostatic energy values when compared to the *ct* chains. This is true at 300 K as well as at 483 K. For DMPCT, the *tt* chain is at a lower energy than *ct* chain at 300 K, but at 483 K the reverse holds true. At 300 K, this behavior is due to significantly lower values of the van der Waals and torsional energies for *tt* in comparison to *ct*. However, at 483 K, the van der Waals and electrostatic energies are significantly lower for the *ct* chain, when compared with the *tt* chain, with similar contributions of the torsional energies for *ct* and *tt* chains. For the CBDO polyester, the *ct* chain (in which the population of the cyclobutane diol is 50:50 for *trans* and *cis* orientations) is of lower energy than *tt* chain at 300 and 483 K. Here, the factors responsible for the higher energy of the *tt* chain are the higher values of the van der Waals and torsional energies, with the electrostatic energies remaining fairly similar in both these types of chains. The relative energetics for CBDO, therefore, does not change with temperature below T_g as well as above T_g. Thus, for PCT, PCC and CBDO, the *ct* chains are of lower energy than the *tt* chains at 300 and 483 K. For DMPCT, at 300 K the *tt* chain is energetically favored over the *ct* chain and the reverse holds true at 483 K.

The energy contribution due to van der Waals interactions is seen to be much higher in the case of DMPCT, for both *tt* and *ct* chains when compared to the other polyesters. This is reasonable because the presence of the methyl groups on the phenylene rings increases the steric hindrance and strain, which in turn enhances the repulsive van der Waals interactions. Van der Waals energy of PCC chains is lower than that of PCT and CBDO. The intramolecular repulsive interactions within the chain are well separated in PCC due to the presence of two cyclohexylene groups than in PCT and CBDO (the spatial length of the cyclohexyl group is higher than that of the phenyl and cyclobutyl groups). The variation in van der Waals energy, with temperature, for all the polyesters is the same, wherein the energy increases with temperature, except for the case of *ct*-DMPCT. For PCT (*tt*) there is only a slight increase in van der Waals energy with temperature. Electrostatic energies of the single chains are not much affected by temperature changes and the energy is found to be the lowest for DMPCT at both temperatures and for both chain configurations *ct* and *tt*. The electrostatic contribution, which is effectively repulsive in nature for three out of four polyesters, in both the *tt* as well as *ct* configurations, is greatest for PCT.

Curves representing the torsional distributions of the *ct* configurational polyester chains are given in Fig. 3. In all cases, the dihedral angle distribution, taken as cumulative of all rotatable bonds in the chain, is centered around torsions of 0 and ±120° with maximum probability for the 0° torsion. For PCT, DMPCT and CBDO, the torsional value of zero is due to the planar ester linkage of the terephthalate unit and the *trans* (*t*) conformations of the CH_2–O and CH_2–cyx linkages where cyx refers to the cyclohexyl group. The torsional values of ±120° are due to the g^+ and g^- conformations of the CH_2–O and CH_2–cyx groups. In the case of PCC, a torsional value of 0° is contributed predominantly from the *t* conformations of the CH_2–O and CH_2–cyx bonds. The preferred conformation for the cyclohexylene dicarboxylate linkage is around 120°, where the g^+ and g^- conformations of CH_2–O and CH_2–cyx bonds are also populated. As expected, the probability of the occurrence of the torsional values of ±120° is higher for PCC when compared to other polyesters (for example, probability of the torsion 120° is 7.9×10^{-3} for PCC against 4.1×10^{-3} for PCT at 300 K). The planar conformation of the carboxylate group of the cyclohexylene linkage is highly strained and is unfavorable. These

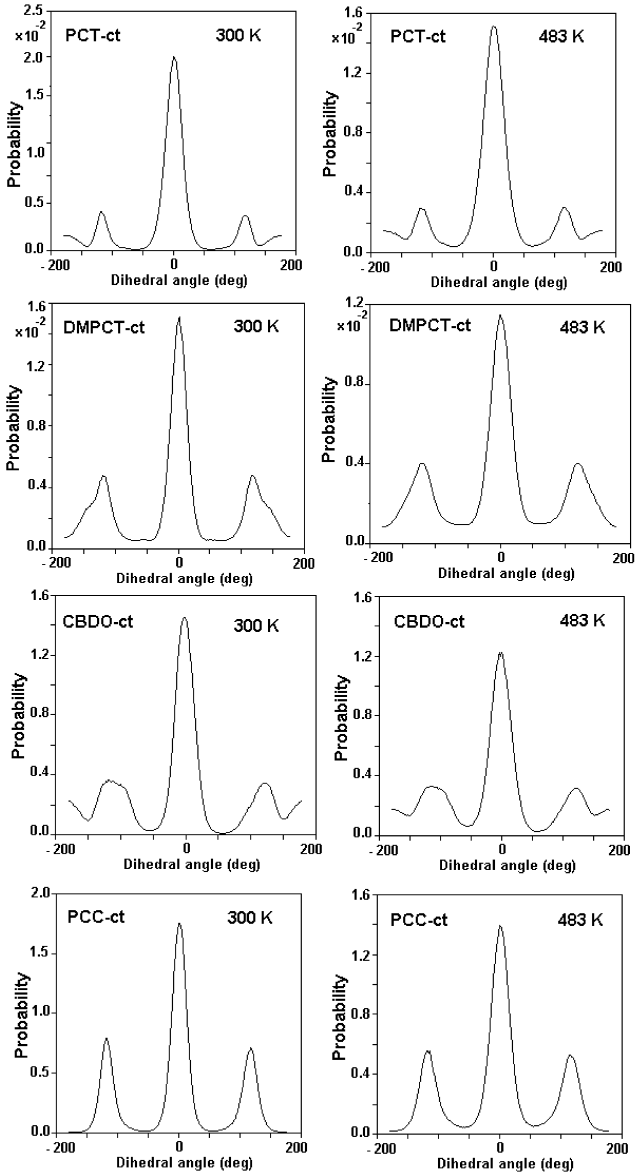

Fig. 3. Torsional distributions of the *cis–trans* (*ct*) configurations of the polyesters from RMMC simulations.

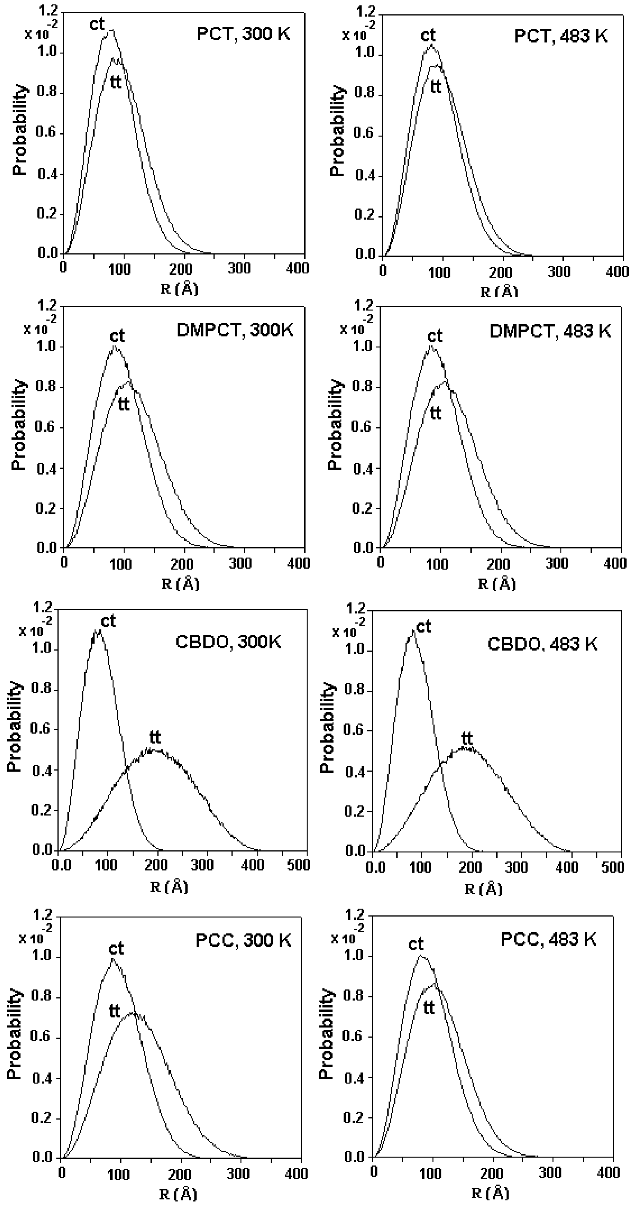

Fig. 4. End-to-end distance distributions of the polyesters in the *trans* (*tt*) and *cis–trans* (*ct*) configurations at 300 and 483 K.

torsional probabilities of the various bonds in the polyester single chains obtained from our RMMC simulations are well in agreement with those reported for analogous fragments in polyesters [20,26].

3.2. Chain structural properties

The chain dimensions derived from the RMMC simulations for both configurations of the polyester single chains at two different temperatures 300 and 483 K are given in Table 3. For the *tt* chains the values given in Table 3 are averaged over the results obtained from simulations performed on three different randomly and independently generated chains. The probability distribution of the end-to-end distance of the *tt* and *ct* chains at 300 and 483 K of the four polyesters studied are given in Fig. 4. In Fig. 5, the end-to-end distance distribution for all the four polyesters is given (for each polyester the *tt* and *ct* separately at different temperatures). For all the polyesters, clearly the *tt* chains are more extended than the *ct* chains as clearly observed from the higher chain dimensions of the former. For CBDO, large reduction in the chain dimensions are obviously observed while incorporating 50% of the cyclobutanediols in the *cis* conformation. Mean-squared end-to-end distance changes from 47 885 Å^2 for the *tt* chains to 8915 Å^2 for the *ct* chain at 300 K. Overall, the chain dimensions of the *tt* chains of CBDO were considerably higher than the *tt* chains of other polyesters in terms of $\langle R^2\rangle$, $\langle S^2\rangle$, C_n and L_p. The higher values of C_n and L_p point towards a rather rigid backbone in the CBDO chain with *trans* orientation of the

Table 3
Chain dimensions for CBDO, PCT, PCC and DMPCT polyesters from RMMC simulations

Polyesters	300 K				483 K			
	$\langle R^2 \rangle$ (Å^2)	$\langle S^2 \rangle$ (Å^2)	C_n[a]	L_p (Å)	$\langle R^2 \rangle$ (Å^2)	$\langle S^2 \rangle$ (Å^2)	C_n	L_p (Å)
trans (tt)								
PCT	11 083 ± 214	1825 ± 5.3	7.4 ± 0.1	6.2	11 495 ± 188	1898 ± 5.5	7.7 ± 0.1	6.4
DMPCT	15 710 ± 331	2558 ± 7.3	10.5 ± 0.2	8.5	13 430 ± 241	2198 ± 6.2	9.0 ± 0.2	7.3
CBDO	47 885 ± 935	6812 ± 15	41.8 ± 0.8	40.8	42 226 ± 744	6086 ± 14.4	36.9 ± 0.6	29.6
PCC	20 255 ± 413	3219 ± 9.0	12.9 ± 0.3	10.7	14 134 ± 240	2305 ± 6.6	9.0 ± 0.1	7.7
cis–trans (ct)								
PCT	8284 ± 162	1389 ± 4.0	5.5 ± 0.1	4.8	9497 ± 158	1576 ± 4.6	6.3 ± 0.1	5.4
DMPCT	10 479 ± 224	1714 ± 4.8	7.0 ± 0.2	5.7	10 839 ± 198	1790 ± 5.2	7.2 ± 0.1	5.9
CBDO	8915 ± 201	1368 ± 3.5	7.8 ± 0.2	6.1	9154 ± 180	1395 ± 3.6	8.0 ± 0.2	6.3
PCC	10 946 ± 228	1966 ± 5.6	7.0 ± 0.2	6.3	10 266 ± 178	1763 ± 5.2	6.5 ± 0.1	5.8

[a] C_n from the simulations represents the limiting value C_∞ (50 repeat units are sufficient to derive the limiting characteristic ratio as well as other chain dimensions).

cyclobutanediol groups. Among the *trans* chains, PCT exhibited the lowest chain dimensions followed by DMPCT and PCC. While comparing the *ct* chains, the chain dimensions of PCT are lower in this case also. The trend observed for the dimensions of the *ct* chains is PCT < CBDO < DMPCT < PCC.

The effect of temperature on chain dimensions is now discussed. The trend observed for the change in chain dimensions with temperature is the same for both *tt* and *ct* chains. The *tt* polyester chains except for PCT showed reduction in chain dimensions with increase in temperature. The dimensions increase with temperature for PCT in the case of both *tt* and *ct* chains. This suggests that PCT chains become more extended with increase in temperature. The increase in the chain dimensions with temperature is higher for the *ct* chain when compared to the *tt* chain of PCT, for example, $\langle R^2 \rangle$ increases from 11 082 Å^2 (300 K) to 11 495 Å^2 (483 K) for the *tt* chain, which essentially is about 400 Å^2 increase for $\langle R^2 \rangle$. But in the case of *ct* chain, $\langle R^2 \rangle$ increases from 8284 Å^2 (300 K) to 9497 Å^2 (483 K), which means $\langle R^2 \rangle$ increases by about 1213 Å^2. Among the *ct* polyester chains, the chain dimensions increases with temperature except for PCC. Thus for PCT, chains become more expanded, whereas for PCC the chains become more compact with increase in temperature irrespective of the chain constitution. For CBDO and DMPCT, the *tt* chains become contracted and *ct* chains tend to expand with increase in temperature. In the case of all the *ct* chains, at higher temperatures especially as noted from the results at 483 K well above the T_g, the variation in the chain dimensions among the four polyesters is lower than at 300 K and the chain dimensions almost become similar as shown in Fig. 5.

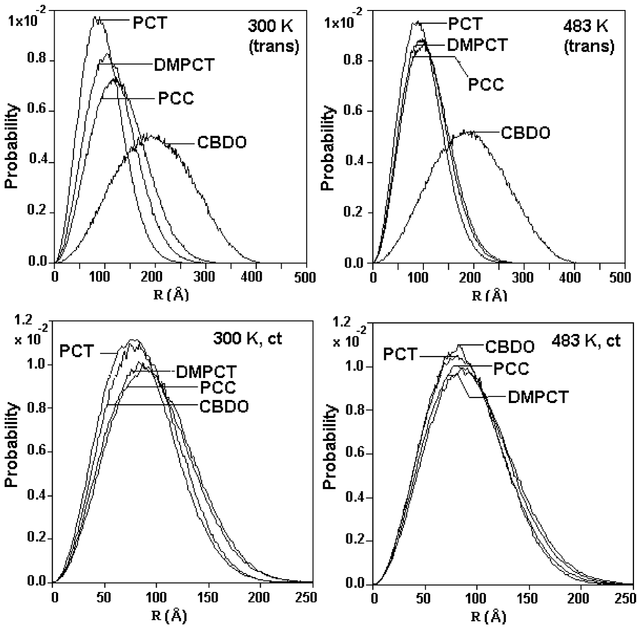

Fig. 5. End-to-end distributions of the polyesters in the *trans* (*tt*) and *cis–trans* (*ct*) configurations at 300 and 483 K.

The characteristic ratio (C_n) and persistence length (L_p) of *tt* CBDO are exceptionally higher than for the rest of the polyesters. These are similar in their behavior and the results are similar to those reported from RMMC simulations of rigid polyesters [3] and the RIS calculations for poly(*p*-hydroxybenzoic acid) by Jung and Schurmann [16]. But these values for CBDO in the *ct* chains were significantly lower and comparable to the other polyester chains used in the present study. Among the cyclohexyl containing polyesters, for the *tt* chains, the highest values of C_n and L_p were observed for the case of PCC, indicating that the absence of a cyclohexyl group in the main-chain increases the chain flexibility.

The characteristic ratio consistently is found to increase with temperature for all polyesters in their *ct* configuration as seen from Table 3. While comparing the *ct* chains of all the four polyesters, CBDO showed the highest value of C_n and L_p. C_n values for the *tt* chains at 300 K were 7.4 (PCT), 10.5 (DMPCT), 12.9 (PCC), 41.8 (CBDO) and the values for the *ct* chains were 5.5, 7.0, 7.0 and 7.8, respectively. L_p values of the polyesters at 300 K were 6.2 Å (PCT), 8.5 Å (DMPCT), 10.7 Å (PCC) and 40.8 Å (CBDO) for the *tt* chains and 4.8, 5.7, 6.3 and 6.1 Å, respectively, for the *ct* chains. Thus the *tt* chains are found to be more extended and rigid than the *ct* chains. With incorporation of more of cyclohexylene and cyclobutylene groups in the *cis* conformation the C_n and L_p values are lowered which leads to compact chains. In a configuration where all the cycloaliphatic rings are in the *trans* orientation all along the polymer chain, a presence of cyclobutylene ring results in far greater rigidity compared to a cyclohexylene ring.

The above results suggest that incorporation of cyclobutylene rings in the backbone tend to increase the chain dimensions including the C_n and L_p thus imparting rigidity to the single chains. Comparing *tt* configurations of CBDO and PCT, the difference in the chain dimensions due to the incorporation of the cyclobutylene rings is evident. Higher values of chain dimensions as shown by CBDO-*tt* chains are due to the conformational preferences of the various bonds in the repeat unit of CBDO. The terephthalate linkage always prefers a planar conformation, which is extended and the probability of the ester groups being *trans* or *cis* with respect to each other is similar [26]. Now, by analyzing the torsional distributions about the oxy-cyclobutylene linkage, it is noted that this bond prefers a conformation corresponding to a torsional value of about 5 and 95°, wherein the steric interactions due to the proximity of carbonyl oxygen and the methyl groups on the cyclobutylene ring is minimal. Other conformations about this linkage are energetically unfavorable. Hence, it is understood that the torsional flexibility of the various bonds constituting the repeat unit of CBDO is limited and the preferable conformations possible for the constituting linkages are extended and/or planar. This leads to a highly extended chain for the *tt* configuration and high C_n and L_p values, relative to those for the cyclohexyl ring containing polyesters, as is seen from RMMC simulations here.

In the case of cyclohexyl containing polyesters, inspection of the dihedral distribution about the CH_2–cyx and O–CH_2 linkages suggests that 0° (*trans*), 120°(*gauche* $^+$) and -120°(*gauche* $^-$) torsions are populated. Thus more compact conformations like the g^+ and g^- are also accessible about the CH_2–cyx and O–CH_2 linkages and hence the chain dimensions of these polyesters in the *tt* configuration are much lower than CBDO-*tt* chain. For *ct* configurations, the reduced dimensions are due to inclusion of compact *cis* configurations about the cyclobutylene or cyclohexylene rings of the diol. It should also be noted that in the case of *ct* configurations of CBDO, the percentage of *cis* and *trans* cyclobutylene rings is equal (50%) as compared to the 30% of *cis* cyclohexyl groups of the diol part in cyclohexyl containing polyesters. Torsional distributions about the oxy-cyclobutylene groups remain almost the same in CBDO-*ct* chains as in the corresponding *tt* chains. Since the amount of cyclobutylene groups in the *cis* configuration is higher, the chain dimensions are considerably reduced and are of the same order as *ct* chains of the cyclohexyl containing polyesters.

The mean-squared averaged chain dimensions, scaled by the molecular weight $\langle R^2\rangle/M$ and $\langle S^2\rangle/M$ are given in Table 4. As discussed before, among the *tt* chains of cyclohexyl containing polyesters, PCT chains are compact. Chains containing partly *cis* configurations of the cycloaliphatic rings for all the four polyester have comparable values of $\langle R^2\rangle/M$ and $\langle S^2\rangle/M$. The number averaged molecular weights reported for the polyesters used in the present study correspond to 57, 64 and 82 repeat units, respectively, for PCT, PCC and DMPCT [9]. In the present simulations the number of repeat units in the chain is 50 for all the polyesters. Our RMMC simulations for 82 repeat units (limiting value for high polymer chain properties) for DMPCT gave exactly the same values for $\langle R^2\rangle/M$, $\langle S^2\langle/M$, and C_n as the results for 50 repeat units. For the case of PCT and PCC the 50 repeat units used for our simulations pertain to the chain lengths for the high molecular weights for these polymers wherein the dimensions attain their limiting values. For the case of CBDO, the limiting molecular weights are not mentioned in the experimental reference [12], and we assume that 50 repeat units would be sufficient for attainment of the limiting values of the chain dimensions. In general for polyesters, including the ones in the present work, a chain length of 50 repeat units is sufficient for calculation of the limiting values of the chain dimensions and shape of the chains.

3.3. Comparison with other homopolyesters

We now compare our results with those available in the literature for other polyesters, especially for $\langle R^2\rangle/M$, $\langle S^2\rangle/M$, C_n and L_p. The unperturbed dimensions of poly(ethylene terephthalate) (PET) has been studied both experimentally and by RIS methods [17]. From the work of Williams and Flory [17], the experimental $\langle R^2\rangle/M$ was found to be 0.93 Å^2 mol g^{-1} and the value obtained from RIS method was 1.05 Å^2 mol g^{-1}. For the polyesters studied in our work, the $\langle R^2\rangle/M$ values at 300 K, for the all *trans* structures comes out to be in the range 0.81–1.44 Å^2 mol g^{-1} for the cyclohexylene polyesters while it is 3.48 Å^2 mol g^{-1} for

Table 4
Scaled chain dimensions of polyesters from RMMC simulations

Polyesters	$\langle R^2\rangle/M$ (Å^2 mol g^{-1})		$\langle S^2\rangle/M$ (Å^2 mol g^{-1})	
	300 K	483 K	300 K	483 K
trans (tt)				
PCT	0.81	0.84	0.13	0.14
DMPCT	1.03	0.89	0.17	0.14
CBDO	3.48	3.07	0.50	0.44
PCC	1.44	1.01	0.23	0.17
cis–trans (ct)				
PCT	0.60	0.69	0.10	0.12
DMPCT	0.69	0.72	0.11	0.12
CBDO	0.65	0.67	0.10	0.10
PCC	0.78	0.73	0.14	0.13

CBDO, indicating that CBDO is much more extended and stiffer compared to the other polyesters, as is also seen from the persistence length for all *trans* configurations. This trend among the polyesters is maintained at the higher temperature of 483 K as well. For the *cis–trans* case, $\langle R^2\rangle/M$ is very similar for all the polyesters, at 300 K, and is in the range 0.6–0.78 Å^2 mol g^{-1}. The range at the higher temperature is 0.67–0.73 Å^2 mol g^{-1}, which is much smaller than the range for the *trans* isomers at the higher temperature. So the *trans* isomers of cyclohexyl containing polyesters, which is the correct set for comparison with structurally similar non-cyclohexyl containing polyesters, show a smaller value of $\langle R^2\rangle/M$ compared to PET, and the scaled dimensions increase with increasing content of cyclohexylene groups in the main-chain. The *cis–trans* isomers, however, show a smaller value of $\langle R^2\rangle/M$, which is due to the nature of the *cis*-linkage that leads to a compaction of the end-to-end distance of the chain.

Mendicutti and Mattice [18] have reported fluorescence and conformational studies on polyesters based on the terephthalate group and diols derived from cyclohexane. The various diols were *cis*-1,2-cyclohexanediol, *trans*-1,2-cyclohexanediol, a 1:2 mixture of *cis* and *trans*-1,3-cyclohexanediols, a 1:2 mixture of *cis* and *trans* 1,4-cyclohexanediols, and a 1:3 mixture of *cis* and *trans* 1,4-cyclohexanedimethanols. Conformational studies indicated that spacers most conductive to excimer formation are 1,3-*cis*-cyclohexanediol and 1,4-*cis*-cyclohexanedimethanol. However, chain dimensions for the 1:2 mixture of *cis* and *trans* 1,4 cyclohexanedimethanol based polyesters are not available from their work for a comparison and the present work brings out these properties.

There are other reports in the literature pertaining to the conformational properties of polymers with cyclohexane rings incorporated in the main chain [19–22]. Experimental measurements and RIS calculations were performed on polyformals synthesized from *trans*-1,4-cyclohexanedimethanol and paraformaldehyde to determine the mean-square dipole moment and its temperature coefficient [19]. The values obtained from RIS calculations were in good agreement with the experimental results. Thus the unperturbed dimensions of these polyesters exhibit negative temperature dependence and its absolute value is slightly larger for the *trans* than the *cis* isomer. Our results for some of the polyesters in the present study show the same observation from RMMC simulations.

The value of the temperature coefficient of $\langle R^2\rangle$ was available only for the cross-linked polyesters of *cis* and *trans* isomers of 1,4-cyclohexanedimethanol and sebacic acid (PCCS and PTCS) [20], for the closest comparison with structurally similar polyesters as the ones in the present work. The coefficient $10^3\ \mathrm{d}(\ln\langle R^2\rangle)/\mathrm{d}T$ from their thermoelastic experiments was found to be -0.93 ± 0.25 and -1.26 ± 0.34 K^{-1} for the *cis* and *trans* isomers based polyesters. Our simulations here give the temperature coefficients for the *tt* isomer polyesters and *ct* isomer polyesters in the range -0.86 to -1.97 K^{-1} and 0.15–0.74 K^{-1}, respectively. With the exception of PCT, the rest of the polyesters based on the fully *trans* isomer show negative temperature coefficient, while for the *cis–trans* chains by using the experimentally available isomer ratio as synthesized, the RMMC simulations show that PCC is the only polyester showing a negative temperature coefficient. Negative temperature coefficient is observed in the case of both *trans* and *cis* configurations of polyester based on cyclohexanedimethanol and sebacic acid [20]. The reason for this behavior in these polymers could be hypothesized to be due to the increase in the population of the *gauche* states of the CH_2–CH_2 groups of the sebacoyl residue with increase in temperature and thus leading to a reduction in the chain dimensions. In the case of polymers in our study the trend in the temperature coefficient of the chain dimensions is dependent on the polymer structure along with the configuration (whether *tt* or *ct*). These interesting observations need more detailed investigations based on the variation of the local torsional minima and rotational states at the bond pairs and how they propagate to affect the overall chain properties in such polyesters. The distribution of the torsional states across the RMMC chains here, do not show any significant differences in order to rationalize or quantify these observations. Such an information can be more suitably derived from RIS calculations of the chain properties for the specific distribution of the *cis* and *trans* linkages, based on conformational analysis about bond pairs. Three out of four polyesters, when in their *cis–trans* isomers combination chain, at experimental conditions as synthesized, show a positive temperature coefficient of $\langle R^2\rangle$ from the results of the RMMC simulations presented here. This signifies the unusual influence of the *cis*-linkage and its fraction in the polymer chain. A possible hypothesis for the positive temperature coefficients in some of the polyesters in our work in their *cis–trans* linkages configuration (for PCT, DMPCT, and CBDO), could be the differences in the variations of the populations of the torsional states across the bonds flanking the cyclohexyl ring and the O–CH_2 bond between the carboxyl group and the cyclohexyl ring, especially in the *cis*-linkage which are present along the chain, as compared to the bonds in the conventional polyesters. Thus, this effect possibly leads to higher repeat unit dimensions (*trans* conformations favored at higher temperatures relative to *gauche* conformations) than in the usual case of the other conventional polyesters. Probably also the reason why PCC *cis–trans* chains shows a negative temperature coefficient could be the fact that it has the cyclohexanedicarboxylate group (which has always the *trans*-linkage) and its effect on the neighboring carboxylate group, which could be responsible for the contraction of the chain with temperature, as that is the only structural moiety which is different in the case of PCC as compared to the PCT and DMPCT. All the fully *trans*-linkage configuration chains, except for the case of PCT, uniformly show negative temperature coefficients similar to the behavior of other polyesters in literature which are either some what structurally similar or are very different from the structures in the present study. For the case of the polyesters made from cyclohexanedimethanol and sebacic acid reported by Riande and co-workers [20], PTCS (*trans*-linkage chain) and PCCS (*cis*-linkage chain), even though the same O–CH_2 flanking the cycloaliphatic ring and the cycloaliphatic ring itself are present as in PCT, DMPCT and PCC here, the presence of a significant amount of alkyl CH_2–CH_2 bonds leads to chain compaction at higher temperatures and thus the negative temperature coefficients.

3.4. Dipole moments of polyesters

In order to understand the effect of the force-field parameters on the electrostatic properties of the polyester chains used in our study, we calculated the root-mean-squared dipole moments of the repeat units and their corresponding single chains using the PCFF force-field via RMMC simulations. The dipole moments which are calculated for the repeat units as well as the polymer chains, using the PCFF force-field and the RMMC method, for several types of polyesters, were also compared with the available information on some of the polyesters for which experimental data have been reported in the literature.

Dipole moments were also computed for the 50 repeat unit chain of poly(diethyleneglycol terephthalate), PDET, and some of the ester fragments for which experimental data is available in literature. The values of $(\langle\mu^2\rangle)^{0.5}$ are given in Table 5. The computed dipole moments are 10.43, 9.76, 7.95 and 15.24 Debye (D) for PCT, DMPCT, PCC and CBDO single chains, respectively. The values corresponding to their respective repeat units are 2.99, 2.60, 2.48 and 3.41 D. The lowest value of the dipole moment is obtained for PCC, which is reasonable due to fully aliphatic nature of the chain. The trend observed for the repeat unit is also the same as that for the single chains. The calculated values here, for the repeat unit of PDET, using the dielectric constant of the bulk polymer ($\varepsilon = 3.18$) and of benzene (solvent used for the experimental data reported in literature [23], $\varepsilon = 2.27$) are 2.80 and 2.60 D, respectively. The calculated value is in good agreement with the experimental value of 2.55 D in benzene. The computed dipole moments for the polyester repeat units in the present study are in the same range as that for the PDET repeat unit. The value for the PDET chain with 50 repeat units is 20.28 D using PCFF force-field at the bulk dielectric constant ($\varepsilon = 3.18$) of the polymer. When a dielectric constant of benzene ($\varepsilon = 2.27$) is employed the dipole moment of the chain is 16.91 D. The experimental value corresponding to this polyester in benzene solution is 18.05 D [23]. This brings out a very good comparison between calculated and experimental mean dipole moments (error is approximately 5.6%).

Also given in Table 5 are the values of the dipole moments for some of the other ester fragments such ODB (diethylene glycol benzoate) [24], DEB, TEB and HEB (di, tetra and hexaethylene glycol benzoates) [25], and DMT (dimethyl terephthalate) [26] for which experimental dipole moments (in benzene) are available. In our calculation of the dipole moment for these ester fragments, using PCFF force-field, the dielectric constant corresponding to benzene was used. It is found that the calculated values for TEB, HEB and DMT are in agreement with the corresponding experimental values. The agreement is unsatisfactory in the case of ODB.

For the compounds in the present study (PCC, PCT, DMPCT, and CBDO), the root-mean-squared dipole moments of the polyesters and the corresponding repeat units are of the same order as that reported directly from experiments on PDET in the literature. CBDO exhibits the highest value of the dipole moment among these compounds, while PCC which has a fully aliphatic backbone,

Table 5
Comparison of root-mean-square dipole moments, $\langle\mu^2\rangle^{1/2}$ (Debye) of polyesters

Polyesters	PCFF[a]			Repeat unit/ester fragments	
	Single chain (DP = 50)	Repeat unit		Experimental	PCFF[b]
PCT	10.43 ± 0.025	2.99 ± 0.020	ODB	2.737	4.47 ± 0.015
DMPCT	9.76 ± 0.023	2.60 ± 0.015	DEB	2.753	1.93 ± 0.020
PCC	7.95 ± 0.019	2.48 ± 0.014	TEB	2.683	2.40 ± 0.011
CBDO	15.24 ± 0.033	3.41 ± 0.024	HEB	2.782	2.62 ± 0.012
PDET	20.28 ± 0.047[c] 16.91 ± 0.040[d] (18.05)[e]	2.80 ± 0.023[c] 2.60 ± 0.022[d] (2.55)[e]	DMT	2.250	2.350 ± 0.02

ODB is $C_6H_5COO(CH_2)_2O(CH_2)_2OCOC_6H_5$ [24]; $C_6H_5COO(CH_2)_mOCOC_6H_5$, $m = 2, 4, 6$ corresponds to DEB, TEB and HEB, respectively [25]; DMT is dimethyl terephthalate [26].

[a] The calculations for polyester single chains and repeat units of PCT, DMPCT, PCC and CBDO were performed with the respective bulk dielectric constants.

[b] Dipole moments for ester fragments were simulated with the dielectric constant of benzene in which the dipole moments were experimentally measured.

[c] Calculated using bulk dielectric constant 3.18.

[d] Calculated using dielectric constant 2.27 of benzene as solvent.

[e] The value in brackets is the experimental root-mean-square dipole moment of PDET in benzene [23].

shows the lowest dipole moment. The enhancement in the dipole moment in the case of CBDO is due to a stronger correlation between the dipole moments of the ester groups, than in the other three polyesters, due to a fewer number of bonds separating the ester groups in CBDO (only a cyclobutyl group separates the neighboring ester groups). In the case of the cyclohexyl ring containing polyesters, the aliphatic bonds between the successive ester groups tend to reduce the correlation between the ester dipoles, which leads to much lower dipole moments than for CBDO. A comparison of the repeat unit structures of PCT and DMPCT shows that the two methyl groups on the phenyl rings in DMPCT are oriented *para* to each other. If this were the only effect controlling the dipole moment, then in effect their contribution towards the repeating unit fragment dipole moment should cancel each other and the dipole moment of PCT should in principle be the same as that for DMPCT. But from a conformational point of view, due to the steric overlap of these methyl groups with the carbonyl oxygen of the ester groups, the ester linkages in DMPCT can also take up the out of plane conformation (skewed, in the range 20–40°) with respect to the phenyl rings. These conformations would lead to a lower value of the dipole moment than in a conformation wherein the ester linkages are in plane with the phenyl groups (which is the case for PCT). The dipole moments for PCT, PCC and DMPCT repeat units calculated here, are similar to the experimental values for ester fragments ODB [24], DEB, TEB, and HEB [25].

4. Summary and conclusions

Conformational properties of polyesters have been derived using RMMC simulations at two different temperatures. Simulations were carried out on single chains with two different constitutions of the diol units viz. *cis* and *trans* 1,4-cyclohexanedimethanol and 2,2,4,4-tetramethyl-1,3-cyclobutanediols. Torsional distributions of the polyesters indicate a planar ester linkage (C_p–C_c) for the terephthalate group and a torsional value of 120° for the cyclohexylenedicarboxylate group (C_{cyx}–C_c), which agrees with the reported conformational studies on these fragments. Chain dimensions of the *cis–trans*, *ct* linkage chains are lower than those of the corresponding fully trans linkage *tt* chains. CBDO (*tt*) showed exceptionally high chain dimensions compared to other polyesters (*tt* and *ct* and CBDO in the *ct* form) suggesting a rather rigid backbone. These results are similar to those reported from RMMC simulations of rigid polyesters. The chain dimensions of the CBDO-*ct* chain were comparable to the other polyesters. The *tt* polyester chains except for PCT showed reduction in chain dimensions with increase in temperature, whereas for the *ct* chains the chain dimensions decreases except for PCC. PCT chains become more extended and the PCC chains become more compact, irrespective of the chain constitution, with increase in temperature. Incorporation of more of cyclohexylene and cyclobutylene groups in the *cis* conformation leads to lower values of C_n and L_p values. In a polyester single chain configuration where all the cycloaliphatic rings are in the *trans* orientation, backbone rigidity is enhanced considerably by presence of cyclobutylene ring as compared to a cyclohexylene ring. The dipole moments calculated for the repeating unit as well as the chain of these polyesters are comparable to values reported for some of the polyesters in literature, while differences which emerge with respect to some other polyesters structures in reported literature are rationalized through basic understanding of the structural features that control the dipole moments in polyesters.

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