

RIS Metropolis Monte Carlo studies of some aliphatic main chain and side group polyesters

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Abstract

Structure related single chain properties of polyesters with isolated carboxyl groups have been studied to test the performance of the RIS Metropolis Monte Carlo (RMMC) method. The mean square end-to-end distances, radii of gyration, characteristic ratios and persistence lengths have been calculated 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. The PCFF force field, modified by the authors in a recent study on some model molecules for the polyesters in question, has been used in the generation of chain conformations. The effect of the choice of run parameters (i.e. the cut-off limit for nonbonded interactions and chain length) on the results is discussed in more detail. The characteristic ratios calculated with the RMMC method using the PCFF force field with the refined torsion potentials agree well with the experimental values. The dependence of the calculated characteristic ratios on the tacticity of the chain in poly(methyl methacrylate) is found to follow experimental behavior. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

The Rotational Isomeric State (RIS) method is a powerful tool to predict conformational properties of polymer chains when statistical weight matrices are known [1–4]. However, in many cases they are not readily available. Typical examples comprise copolymers and branched polymers. Also polymers with unsymmetric and flexible side groups cause problems, since statistical weight matrices should be derived for each orientation and conformation of the side group.

Recently, a variation of the RIS method, which can also treat these systems, has been developed by Honeycutt [5]. In this new procedure, called the RIS Metropolis Monte Carlo (RMMC) method, conformations of polymer chains are generated with the well-known Monte Carlo technique [6]. In a RMMC simulation chain conformations are not restricted only to discrete energy states, but are generated using potential energy functions (force fields) directly. (In a

classical model interactions between atoms in molecular systems are described by potential energy functions, which contain several parameterized terms, see e.g. Refs. [7–9].) The generated conformations of the polymer chains are then used to calculate average values for single chain properties like characteristic ratio, radius of gyration and persistence length, i.e. properties derivable also with the conventional RIS method.

The most notable difference between the conventional RIS and RMMC methods is that the assumption of discrete rotational states, made in the RIS model [1,3], is not utilized in the RMMC method. Instead, continuous dihedral angles are allowed in the Monte Carlo steps. Use of continuous dihedrals also enables treatment of ill-defined bond rotational states, e.g. when there are energy plateaus or shallow potential energy minima with low energy barriers. In such cases the statistical weight matrix elements $u_{ij}u_{ij} = A_{ij} \exp(-\epsilon_{ij}/kT)$ where A_{ij} is the pre-exponential factor, ϵ_{ij} is the energy of the bond rotational state, k is the Boltzmann factor and T is the temperature) as well as the dihedral angles of the discrete energy states are difficult to determine unambiguously. The C_γN–N_γC bond rotation provides an extreme example of these kinds of bond rotations, since it has a low-energy plateau of about 1 kcal/mol around the orthogonal conformation (at the MP2/6-31G(d) level of

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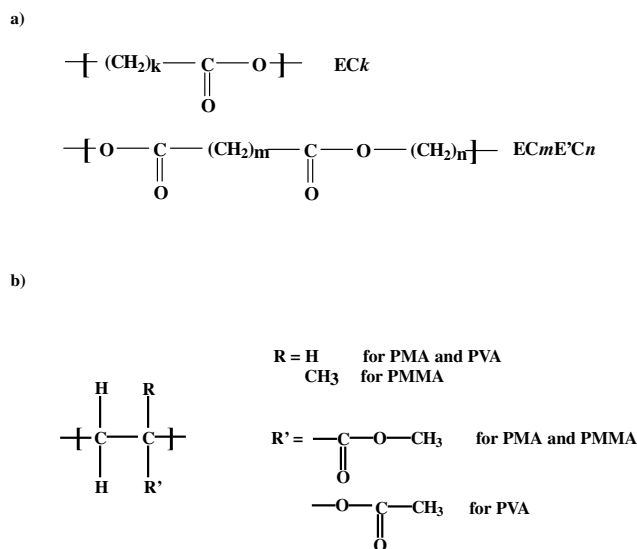


Fig. 1. (a) The main chain (EC*k* and EC*mE'n*) and (b) side group polyesters studied in this work.

theory) [10]. The RMMC method is able to treat such cases without any difficulties.

In the conventional RIS method, the theoretically derived statistical weight matrices can be scaled to reproduce known experimental results. In the RMMC method, where potential energy functions are used directly to calculate chain properties, similar scaling is not so straightforward, and the reliability of the potential energy functions used becomes crucial. In the RMMC procedure the torsion and nonbonded potentials, including the electrostatic potential, are the only potential energy terms that are used to compute the conformational energies of polymer chains. The other terms, i.e. those that depend on changes in valence coordinates (bond and valence angle deformations), only indirectly affect the calculated properties of the polymer chains through the (initially) optimized geometry.

The RMMC method, strictly speaking, is not a true RIS method, since the bonds are not restricted to discrete rotational states, but vary continuously. However, the same type of properties are calculated with the RIS and RMMC methods, and many of the assumptions made are similar. Since RMMC is considerably more time consuming than the conventional RIS method, the latter is preferred in calculations on linear homopolymers with well defined bond rotational states, when statistical weight matrices are available.

Developments in quantum chemical, and especially in the computationally less expensive density functional (DFT) methods [11] have made the utilization of quantum chemistry more applicable also for test and development of potential energy functions. Several groups have investigated the performance of different DFT methods for prediction of molecular properties in various types of molecular systems, see e.g. [10,12–13]. In a recent study by Blomqvist et al. [14], the C(sp²)–O(sp³) and C(sp²)–C(sp³) backbone

rotations, next to the carbonyl C=O group, were investigated in a few esters serving as model molecules for the polymer chains studied in this paper. In that study quantum chemical ab initio (MP2) and DFT (B-LYP and B3-LYP) methods as well as the PCFF force field, developed for synthetic polymers [15–22] were used. Due to the severe disagreements found between the PCFF force field and the quantum chemical results, the PCFF torsion potentials for the particular bond rotations were re-optimized. It should be emphasized that the re-optimized torsion parameters are not directly transferable into other force fields due to correlation with other parameters, in particular with those for nonbonded and electrostatic interactions. Therefore, they should be used only in the PCFF force field. The PCFF force field, thus modified, has now been used in this study in the RMMC generation of chain conformations of polyesters with isolated carboxyl groups (i.e. poly(methyl acrylate) PMA, poly(methyl methacrylate) PMMA, poly(vinyl acetate) PVA and a set of main chain polymers (see Fig.1)).

2. Computational details

The RMMC calculations were performed using the RIS module of the MSI software [23] on an SGI Origin 2000 supercomputer at the Center for Scientific Computing (Espoo, Finland).

In the RMMC method, conformational states of the chains are generated using the Metropolis Monte Carlo method [6]. The RMMC procedure can be described briefly as follows: First, the structure of a polymer chain is optimized using the whole force field in order to obtain reasonable values for bond lengths and valence angles. Second, a rotatable backbone bond is selected randomly. Third, a random torsion angle ϕ for the bond between -180 and 180° is selected. Fourth, the bond is rotated to the new torsion angle and the energy of the system is computed using a reduced force field consisting of torsion and nonbonded terms, including those for Coulombic electrostatic interactions. Fifth, a random number r between 0 and 1 is generated, and if $\exp[-(E_{\text{new}} - E_{\text{old}})/kT] > r$, the new torsion angle is accepted (E_{new} and E_{old} refer to the energies of the new and old conformational states, k is the Boltzmann factor and T is the temperature). Otherwise the previous value of the torsion angle is restored. Sixth, the properties of interest are computed, and the running averages of the properties are updated. This is not done until after equilibration of the system, and is performed after every n th step, where n is large enough to ensure that the chain structures are not correlated. Items 2–6 are repeated until the desired number of Monte Carlo steps is reached (usually $> 2 \times 10^6$).

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 (Max_Bonds), or use of a distance dependent cut-off. In both cases, it is preferable

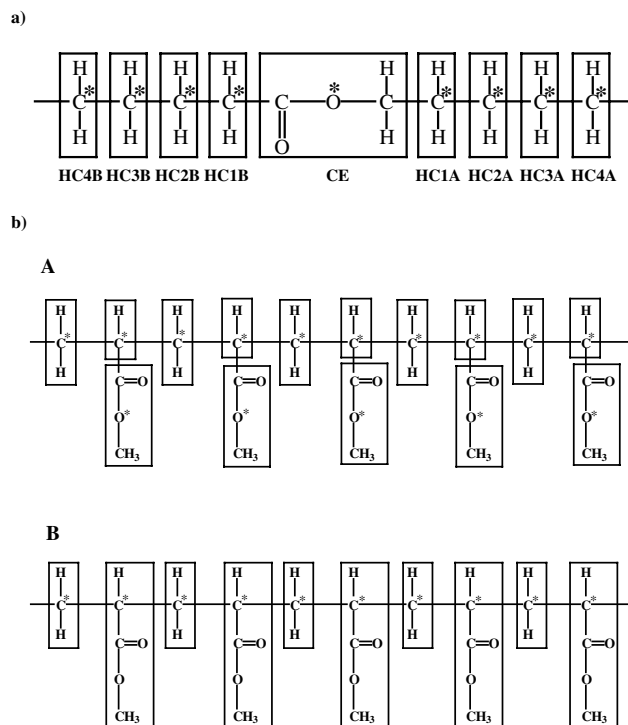


Fig. 2. (a) Definition of charge groups for main chain polyesters. (b) Two plausible choices of charge groups for side group polyesters (PMA). The switching atoms are marked with an asterisk.

to divide the polymer chain into electrically neutral charge groups, each of which containing an atom assigned as a switching atom. The function of the switching atom is to define the starting point when counting the number of bonds, or for measuring the distance between interacting atoms. When the distance between the pre-assigned switching atoms in two charge groups is below the cut-off limit, interactions between all the atoms in these charge groups (and of a shorter range) are taken into account, to avoid fluctuations in the Coulomb energy due to otherwise unbalanced charges. For the main chain polyesters an obvious choice of charge groups is shown in Fig. 2a. For side group polyesters there are two plausible choices of charge groups shown in Fig. 2b.

The first choice (partition A in Fig. 2b) is analogous to that of main chain polyesters. When using a distance dependent cut-off this is a proper choice: If the charge groups were larger as in partition B interactions, which are less significant (i.e. longer range interactions) could inadvertently be included in the calculations. When the Max_Bonds cut-off method, however, is used, difficulties arise in finding a properly balanced cut-off limit for different charge groups simultaneously: If in partition A of Fig. 2b the number of bonds was counted from the ester oxygen of one of the side groups, and the interactions between two neighboring side groups were taken into account, the interactions along the backbone would no longer be restricted to a short range as they should be in the Θ -state of polymer chains. Therefore, for side group polyesters, partition B in Fig. 2b, with larger charge

groups, is chosen in this work. With this choice, a backbone atom in the chain can be selected always as a switching atom for a charge group, which enables a balanced cut-off limit for all charge groups.

In Ref. [5] Honeycutt discusses about the choice of the Max_Bonds value, and concludes that typical values range from 4 to 6 depending on the polymer chain architecture. A value of 4 neglects interactions beyond the “pentane effect” [1,3], i.e. beyond the second order interactions, which is defined as the Θ -state of a polymer chain. 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. In the polymer chains studied in this paper the second order interactions correspond the Max_Bonds value of 4, but division of the chains into neutral charge groups increases the cut-off value to 6, since the interactions have to be extended to the closest switching atoms.

When comparing results (e.g. C_n , where n = number of bonds in the main chain) of RMMC calculations with those of conventional RIS calculations, or with those measured in the Θ -state, the Max_Bonds cut-off method is preferable since the nonbonded interactions can then be restricted to a short range along the chain also in flexible chains. For example, if in Fig. 2a Max_Bonds = 4 (i.e. interactions between CE and HC3A and between CE and HC3B as well as of shorter range are taken into account), in the alkyl chain only the first and second order interactions

Table 1

Characteristic ratios C_n and ratios $\langle r^2 \rangle / \langle s^2 \rangle$ of main chain polyesters as a function of a chain length with Max_Bonds = 4. Notation of the polyesters is given in Fig. 1a. Experimental results are from Ref. [24]

Polyester	Rotatable bonds				
	100		200		C_∞ (exp)
	C_n	$\langle r^2 \rangle / \langle s^2 \rangle$	C_n	$\langle r^2 \rangle / \langle s^2 \rangle$	
EC6	5.89 \pm 0.06	6.13	6.03 \pm 0.07	6.12	
EC10	6.35 \pm 0.06	6.25	6.51 \pm 0.07	6.15	5.1
EC2E/C6	5.50 \pm 0.06	6.18	5.67 \pm 0.07	6.08	5.25
EC8E/C6	5.90 \pm 0.06	6.34	5.78 \pm 0.07	6.15	5.8
EC8E/C16	6.42 \pm 0.06	6.28	6.60 \pm 0.07	6.18	6.5

[1,3] are taken into account. However, in interactions between charge group CE and the alkyl chain this means that the first, second and third order interactions are taken into account due to the larger size of charge group CE. In the RMMC method, the choice of charge groups and switching atoms has a significant effect on the results. If in Fig. 2a the carbonyl carbon had been chosen as switching atom for CE, interactions between CE and HC4B, and between CE and HC2A would have been included with Max_Bonds = 4, but not interactions between CE and HC3A and beyond.

3. Results and discussion

3.1. Main chain polyesters

RMMC calculations utilizing the modified PCFF force field [14] were performed for a set of main chain polyesters ($k = 6$ and 10, $(m, n) = (2, 6)$, $(8, 6)$ and $(8, 16)$, see Fig. 1a) for which there are experimental values available for the characteristic ratios C_∞ [24].

These polyesters can be regarded as block copolymers comprised of carboxyl groups and alkyl chains of various lengths. Since the RMMC results depend on the chain length, the calculations were performed using two different lengths, the degree of polymerization being about 100 or 200. In the case of 100 repeat units the number of equilibration and production steps were 800 000 and 3 000 000, respectively. For the longer chains the respective numbers of steps were 1 500 000 and 5 000 000. In order to test the reproducibility

of the simulation results (i.e. to test that the amount of steps is sufficient), the characteristic ratios were calculated for one of the main chain polyesters (EC6, with the chain length of 100 repeat units and with Max_Bonds = 4) with different random number seeds. Six calculations were carried out, out of which one of the results was out of the statistical error (the difference from the average value being 0.11, while the statistical error is 0.06). As cut-off for nonbonded interactions, the Max_Bonds method was used with three different cut-off values: 4, 5 and 6. Charge groups and switching atoms as defined in Fig. 2a were used in all these calculations. The temperature was set to 298 K. Typical CPU times for one of the main chain polyesters (EC6, see Fig. 1) with 100 repeat units were about 30 min on the supercomputer used for our calculations.

The RMMC calculated characteristic ratios C_n as functions of the chain length and cut-off values for nonbonded interactions are compared with the experimental results [24] in Tables 1 and 2. Since there is no tacticity related to the main chain polyesters, the computationally fast Quantitative Structure Property Relationship (QSPR) method can also be applied to determine the characteristic ratios. This method is based on topological indices and was developed by Bicerano [25]. The characteristic ratios calculated with the QSPR method are compared with the RMMC and experimental results in Table 2. Also the calculated ratios of the mean square end-to-end distance r to the radius of gyration s , $\langle r^2 \rangle / \langle s^2 \rangle$, are given in Tables 1 and 2. For ideal Gaussian chains this ratio is equal to 6 [1].

A chain length of 100 repeat units was found sufficient for this type of flexible chains, the calculated characteristic ratios being in good agreement with the experimental results. The lengthening of the chain into 200 repeat units did not significantly affect the results (see Table 1). On the other hand, the cut-off value has a prominent effect on the results (see Table 2). For the main chain polyesters studied, a Max_Bonds value of 4 corresponds most closely to the Θ -state of the chains and the results obtained with this value should be compared with the experimental data. The RMMC calculated characteristic ratios are, indeed, in good agreement with the experimental values, and also with those calculated using the QSPR method. The only exception is polyester EC10, whose experimental value differs from the calculated ones, which again are close to

Table 2

Characteristic ratios C_n and ratios $\langle r^2 \rangle / \langle s^2 \rangle$ of main chain polyesters as a function of a cut-off value for nonbonded interactions with 100 rotatable bonds in the chain. Notation of the polyesters is given in Fig. 1a. Experimental results are from Ref. [24]

Polyester	4		5		6		C_∞ (QSPR)	C_∞ (exp.)
	C_n	$\langle r^2 \rangle / \langle s^2 \rangle$	C_n	$\langle r^2 \rangle / \langle s^2 \rangle$	C_n	$\langle r^2 \rangle / \langle s^2 \rangle$		
EC6	5.89 \pm 0.06	6.13	8.70 \pm 0.09	6.40	8.53 \pm 0.09	6.40	6.01	5.9
EC10	6.35 \pm 0.06	6.25	8.66 \pm 0.09	6.44	8.27 \pm 0.08	6.47	6.54	5.1
EC2E/C6	5.50 \pm 0.06	6.18	9.54 \pm 0.11	6.55	9.97 \pm 0.12	6.48	5.49	5.25
EC8E/C6	5.90 \pm 0.06	6.34	8.77 \pm 0.09	6.51	8.31 \pm 0.08	6.44	6.18	5.8
EC8E/C16	6.42 \pm 0.06	6.28	9.01 \pm 0.09	6.57	8.26 \pm 0.08	6.47	6.70	6.5

Table 3
Persistence lengths of the main chain polyesters in Å. For notation of polyesters see Fig. 1a

Polyester	Rotatable bonds				
	100			200	
	4	5	6	4	5
EC6	5.36 \pm 0.06	7.58 \pm 0.08	7.48 \pm 0.08	5.34 \pm 0.06	8.06 \pm 0.09
EC10	5.77 \pm 0.06	7.71 \pm 0.08	7.36 \pm 0.08	5.81 \pm 0.06	7.67 \pm 0.08
EC2E/C6	4.91 \pm 0.05	8.08 \pm 0.09	8.54 \pm 0.09	5.01 \pm 0.05	8.71 \pm 0.10
EC8E/C6	5.28 \pm 0.06	7.87 \pm 0.08	7.34 \pm 0.08	5.17 \pm 0.05	7.63 \pm 0.08
EC8E/C16	5.90 \pm 0.06	8.10 \pm 0.08	7.50 \pm 0.08	5.93 \pm 0.06	7.62 \pm 0.08

Table 4
Characteristic ratios C_n and ratios $\langle r^2 \rangle / \langle s^2 \rangle$ for side group polyesters as a function of a chain length with Max_Bonds = 5. Experimental values are from Refs. [24,26–33]

Polyester	100		200		$C_\infty(\text{exp})$
	C_n	$\langle r^2 \rangle / \langle s^2 \rangle$	C_n	$\langle r^2 \rangle / \langle s^2 \rangle$	
PMA-at	11.93 \pm 0.19	6.77	9.39 \pm 0.23	6.25	8.4–9.4
PMMA-it	8.77 \pm 0.21	6.70	11.67 \pm 0.37	6.95	9.4–10.8
PMMA-at	8.66 \pm 0.20	5.94	8.64 \pm 0.28	5.72	6.05–9.0
PMMA-st	10.22 \pm 0.22	7.17	10.07 \pm 0.32	6.06	7.3–9.8
PVA-at	10.73 \pm 0.17	6.73	9.51 \pm 0.22	6.26	9.0–11.3

each other. The fact that the experimental and calculated results are otherwise very compatible indicates that the experimentally determined characteristic ratio for EC10 may be inaccurate.

The calculated $\langle r^2 \rangle / \langle s^2 \rangle$ ratios are all somewhat larger than 6. With the cut-off value of 4, the ratios always lie closer to 6 than with the larger cut-off values (see Table 2). As regards chain lengths, the longer chains are closer to ideal Gaussian chains, but the differences are mostly small (see Table 1).

The calculated persistence lengths as a function of chain length and the maximum number of bonds between interacting atoms are given in Table 3. The cut-off value of 4 gives results practically independent of the chain length. With cut-off values of 5 and 6, the persistence lengths are clearly larger, and the values depend slightly more on the chain length. The values are, however, much smaller than the contour lengths of the chains (i.e. sums of the bond

lengths in the chains), which is an indication of chain flexibility, and that the chain lengths chosen for the calculations are sufficient.

3.2. Side group polyesters

RMMC calculations utilizing the modified PCFF force field [14] were also performed for atactic poly(methyl acrylate) (PMA-at) and poly(vinyl acetate) (PVA-at) as well as for poly(methyl methacrylate) (PMMA) with varying tacticity of the chain since there is experimental and RIS data available for these polyesters [1,3,4,26–33] (for polyesters see Fig. 1b). In the atactic chains the probability of meso dyads was chosen to be 0.5. The chain lengths used were 100 or 200 repeat units. The actual number of rotatable bonds was larger than for the main chain polyesters since also the side groups were allowed to rotate. Due to the larger number of rotatable bonds, the number of equilibration and

Table 5
Characteristic ratios C_n and ratios $\langle r^2 \rangle / \langle s^2 \rangle$ for side group polyesters as a function of a chain length with Max_Bonds = 4. Experimental values are from Refs. [24,26–33]

Polyester	100		200		$C_\infty(\text{exp})$
	C_n	$\langle r^2 \rangle / \langle s^2 \rangle$	C_n	$\langle r^2 \rangle / \langle s^2 \rangle$	
PMA-at	7.59 \pm 0.13	6.02	7.78 \pm 0.19	6.08	8.4–9.4
PMMA-it	3.65 \pm 0.09	6.49	5.65 \pm 0.18	6.62	9.4–10.8
PMMA-at	5.96 \pm 0.14	5.35	5.11 \pm 0.16	5.48	6.05–9.0
PMMA-st	10.12 \pm 0.22	6.92	10.15 \pm 0.27	4.92	7.3–9.8
PVA-at	6.15 \pm 0.10	6.13	6.19 \pm 0.14	6.19	9.0–11.3

Table 6

Characteristic ratios C_n for the PMMA chains of varying tacticity (in % of racemic dyads). Max_Bonds = 5 and the number of rotatable backbone bonds is 200. Experimental values are from Refs. [24,26–33]

Tacticity	C_n	$C_\infty(\text{exp})$
0 (PMMA-it)	11.67 \wedge 0.37	9.4–10.8
17	–	9.3
20	11.39 \wedge 0.21	–
40	10.10 \wedge 0.21	–
50 (PMMA-at)	8.64 \wedge 0.28	6.05–9.0
60	7.08 \wedge 0.14	–
65	–	7.5
ca. 75–80	–	7.3–7.5
		8.4
		9.3–9.8
80	8.54 \wedge 0.14	–
89	–	9.2
100 (PMMA-st)	10.07 \wedge 0.32	7.3–9.8

production steps was increased for the longer chains to 3 000 000 and 6 000 000, respectively. For the shorter chains the respective numbers of steps were 2 000 000 and 5 000 000. Cut-off values of 4 and 5 were used in these calculations. The charge groups and switching atoms were those of partition B, shown in Fig. 2b. The calculations were performed at a temperature of 303 K.

The calculated characteristic ratios are compared with experimental results in Tables 4–6, and the persistence lengths are given in Table 7.

In side group polyesters, the cut-off value has an even more pronounced effect on the results than in the main chain polyesters, since interactions between the bulky polar side groups play an important role in conformational statistics. With a cut-off value of 5 (Table 4), the calculated characteristic ratios are in good agreement with the experimental values. When Max_Bonds is equal to 4 (Table 5), the interactions between different side and main chain groups are not properly taken into account, and the chains occasionally collapse. This is most prominently seen in PMMA-it. The calculated $\langle r^2 \rangle / \langle s^2 \rangle$ ratios, which also are presented in Tables 4 and 5, deviate more from the ideal value of Gaussian chains than in the main chain polyesters. A cut-off value of 5 gives somewhat larger ratios than a cut-off value of 4.

Table 7

Persistence lengths of the side group polyesters in Å

Polyester	Rotatable bonds			
	100		200	
	4	5	4	5
PMA-at	11.06 \wedge 0.09	7.02 \wedge 0.06	6.80 \wedge 0.08	8.12 \wedge 0.09
PMMA-it	3.69 \wedge 0.03	6.37 \wedge 0.07	5.19 \wedge 0.05	10.22 \wedge 0.11
PMMA-at	5.83 \wedge 0.05	7.80 \wedge 0.07	4.84 \wedge 0.05	7.72 \wedge 0.08
PMMA-st	9.32 \wedge 0.08	8.61 \wedge 0.09	10.54 \wedge 0.08	9.82 \wedge 0.09
PVA-at	5.59 \wedge 0.05	9.86 \wedge 0.08	5.59 \wedge 0.06	8.32 \wedge 0.09

For PMMA there is experimental and RIS data available also for characteristic ratios with different tacticities of the chain [1,3,4,24,26–30,32,33]. The characteristic ratios as a function of chain tacticity are calculated with a cut-off value of 5 and 200 repeat units. These results are presented in Table 6 and Fig. 3.

The characteristic ratio is largest (11.7) for isotactic PMMA and has its minimum (about 7.0) between 60–70% of racemic dyads. This behaviour is in agreement with the experimental results, though there are large variations in the experimental values depending on the solvent, methods used for experiments, and models used for determination of the characteristic ratios from the experimental results.

The calculated persistence lengths (Table 7) are again much smaller than the contour lengths of the chains, which shows that the chosen chain lengths are appropriate for these calculations.

4. Conclusions

As compared with the conventional RIS method, the RMMC method requires more computing time, but is valuable for calculation of single chain properties of polymer chains for which statistical weight matrices are not available. Flexible side groups are conveniently handled with RMMC by defining appropriate atoms in the side groups as chain atoms, which allows rotations of the side groups in the Monte Carlo steps. Some care has to be taken, however, in the choice of run parameters. The results are especially sensitive to the cut-off limit for nonbonded interactions and to the proper choice of charge groups. The effect of the chain length on the results also has to be considered.

Since the RMMC method uses potential energy functions directly, the results are sensitive to the reliability of the force field used. The torsion and nonbonded potentials, including the electrostatic interactions, are of particular importance, since these potential energy terms directly affect the conformational states of chains and properties related to them. The valence part of the force field has an indirect effect on the results since it affects the local geometry (bond lengths and valence angles), which

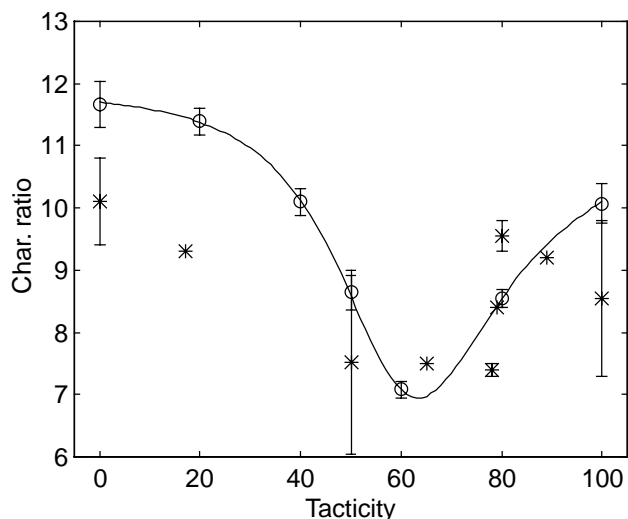


Fig. 3. The characteristic ratio C_n of PMMA as a function of chain tacticity (in % of racemic dyads). The calculated C_n and the experimental results (see Table 6) are expressed by O and *, respectively. In the calculated results Max_Bonds = 5 and the number of repeat units = 200.

influences the calculated chain properties through the initially optimized geometry of polymer chains. The actual parametrization of the force field (or statistical weight matrices in the conventional RIS method) used for calculations should be based on quantum chemical ab initio or density functional results of suitable model molecules. For RMMC this is of particular importance, since statistical weight matrices, whose elements could be optimized to reproduce chain properties of known polymers, are not used.

Bond lengths and valence angles are held rigid in RMMC calculations and the conformational dependence of these coordinates, thus, is of interest. Therefore, in a recent study by Blomqvist et al. [14], this dependence was investigated by ab initio and DFT methods. It was found that in the model esters for the polymer chains studied in the present paper the conformational dependence of the bond lengths was small, whereas changes in the valence angles were more significant. In the $C(sp^2)-O(sp^3)$ rotation next to the carbonyl group, the neighboring $C(sp^3)-C(sp^2)-O(sp^3)$ and $C(sp^2)-O(sp^3)-C(sp^3)$ valence angles opened about $6-7^\circ$ at the high-energy (8.75 kcal/mol at the MP2/6-31G(d) level of theory) *cis* minimum compared with these angles at the global *trans* minimum. The effect of conformational changes of valence angles on the RMMC results is, however, small due to the high energy and thus the low population of the *cis* state. In the $C(sp^2)-C(sp^3)$ rotation next to the carbonyl group the changes in valence angles were smaller, but not insignificant. Errors in the RMMC results caused by such small conformational changes in valence coordinates can, however, be reduced by randomizing the chain conformation prior to the energy minimization of the chain, which is then used for the actual RMMC calculation.

The conformational dependence of partial charges is also a matter of concern, since it affects the energy related to the

Coulomb potential. For aliphatic esters studied in the recent paper [14], the conformational dependence of the most significant atomic charges, as obtained from the quantum chemically calculated electrostatic potential, was in general small. The largest relative changes in the charges occurred mostly in nonpolar groups like methyl groups, especially during the $C(sp^2)-O(sp^3)$ rotation. A large part of this effect on conformational statistics is accumulated in the torsion parameters of the force field, particularly when the Max_Bonds cut-off method is used. The Max_Bonds method restricts the nonbonded interactions into a short range also when the longer range Coulomb interactions are more significant. If distance dependent cut-off is used, such cancellation of errors does not necessarily take place.

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