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RIS Metropolis Monte Carlo studies of poly(L-lactic), poly(L,D-lactic) and polyglycolic acids

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Abstract

Single chain properties (characteristic ratio and persistence length) have been calculated for poly(L-lactic), poly(L,D-lactic) and polyglycolic acids (PLLA, PLLA/PDLA and PGA, respectively) utilizing the RIS (rotational isomeric state) Metropolis Monte Carlo (RMMC) method. The polymer consistent force field (PCFF), that previously was modified by reoptimizing some of its torsion parameters to data of a few model molecules for the current polyesters, was used in the generation of chain conformations in Monte Carlo steps. The same single chain properties have also been calculated using the original PCFF to study the effects of the force field modifications on the results. Calculations were carried out with two different chain lengths (DP = 50 or 100) and cut-off limits for nonbonded interactions (Max_Bonds = 4 or 6, and also 9 for PLLA) due to the sensitivity of the RMMC method to these run parameters. The modified PCFF predicted the PLLA/PDLA chains to be the most flexible, the characteristic ratio being 6.5 for the copolymer with alternating L,D-diads, and 6.8 for the copolymer with random combination of L,D- and D,L-diads (using Max_Bonds = 4 and DP = 100), whereas the PLLA chains were found to be the least flexible (with a characteristic ratio of 7.7). On the other hand, using the original PCFF the order of flexibility was totally reversed, and the characteristic ratios became 8.0 and 8.5 for the PLLA/PDLA and 5.6 for the PLLA chains. For the selected chain lengths the characteristic ratios were found to depend significantly on the cut-off parameter for nonbonded interactions, but only slightly on chain length. The dependence of the characteristic ratios on the cut-off limit was also found to be different in the calculations with the modified and original PCFFs. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Rotational isomeric state; RIS Metropolis Monte Carlo studies; Aliphatic polyesters

1. Introduction

The RIS (rotational isomeric state) Metropolis Monte Carlo (RMMC) method, developed by Honeycutt [1], is an efficient method to calculate single chain properties, especially of polymers with flexible side groups and of copolymers. In the RMMC method the generation of chain conformations and calculation of properties is performed by using force fields. Therefore, in Refs. [2,3], the reliability of the polymer consistent force field (PCFF), developed for synthetic polymers by Hagler et al. [4–11], was studied regarding the generation of conformational statistics for the polyester chains under investigation. Due to severe disagreements with the torsional quantum mechanical MP2/6-31G(d) results, the PCFF was modified in Refs. [2,3] to reproduce the MP2 rotational behavior of the C(sp^2)–O(sp^3), C(sp^3)–O(sp^3) and C(sp^2)–C(sp^3) backbone bonds in some esters, representing model units for polyesters with isolated and strongly interacting carboxyl groups. Since the intrinsic torsion potentials are local in nature, they can be reoptimized separately from the other energy terms of the force field without causing additional errors to other computed properties.

This paper is a continuation of our studies on the single chain properties of polyesters. In Ref. [12], RMMC calculations were carried out for polyesters that have isolated carboxyl groups, i.e. for poly(methyl acrylate), poly(methyl metacrylate), poly(vinyl acetate) and for a set of main chain polymers. The effect of the choice of run parameters (i.e. the cut-off limit for nonbonded interactions and the chain length for calculation of properties in the Θ-state of polymer chains) on the results was investigated in that paper. In the present paper, polyesters with strongly interacting polar carboxyl groups are considered. Poly(L-lactic), poly(L,D-lactic) and polyglycolic acids (PLLA, PLLA/PDLA and PGA, respectively) were chosen for these studies on flexibility due to their importance as biodegradable polymers. Here, too, single chain properties are calculated for these polymer chains with the RMMC method using the

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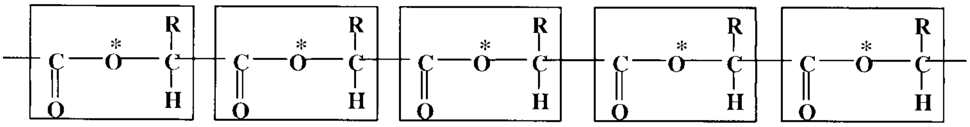

Fig. 1. Definition of the charge groups for PLLA (R=CH$_3$), PLLA/PDLA (syndiotactic with R=CH$_3$) and PGA (R=H). The predefined switching atoms, which are used to define the starting point for the count of the number of bonds in the Max_Bonds method, are marked with an asterisk. When the number of the bonds is below the cut-off limit, all the atoms in these particular charge groups and between these charge groups are taken into account in the nonbonded interactions.

modified PCFF [2,3]. The corresponding properties have also been calculated with the original PCFF to study the effects of the differences between the force fields.

There are experimental results available only for single chain properties of PLLA and PLLA/PDLA [13,14]. However, the experimental characteristic ratios of PLLA vary a lot. Tonelli and Flory [13] obtained the value 2.0 ± 0.2 (with virtual bonds of length 3.70 Å) from viscosity and light scattering measurements in bromobenzene at 85°C. On the other hand, according to Refs. [15–17], the characteristic ratio C_∞ can be calculated from the equation

$$C_\infty = \left[\frac{K_\Theta}{\Phi_0}\right]^{2/3} \frac{M_r}{n_v\langle l_v^2\rangle}, \qquad (1)$$

in which K_Θ is the Mark–Houwink constant at Θ conditions (in cm^3 mol$^{1/2}$ g$^{-3/2}$), Φ_0 the Flory constant (2.51×10^{23} cm^3 mol$^{1/2}$ g$^{-3/2}$), M_r the molecular weight of the repeat unit, n_v the number of real or virtual bonds per repeat unit, and l_v the average length (in cm) of a (real or virtual) bond in the repeat unit. Using extrapolation according to the Stockmayer and Fixman method [18], Schindler et al. [17] determined, from their viscosity measurements in chloroform and benzene, K_Θ to be 0.42 cm^3 mol$^{1/2}$ g$^{-3/2}$ for PLLA and 0.17 cm^3 mol$^{1/2}$ g$^{-3/2}$ for PLLA/PDLA (copolymer made by ring opening polymerization of racemic dilactide). By using $n_v = 3$ and $l_v = 1.41$ Å [19] (real bond length obtained from crystallographic data), the characteristic ratios calculated from Eq. (1) by Grijpma et al. [14] were 17.0 (PLLA) and 9.3 (PLLA/PDLA). Grijpma et al. also obtained the value 11.7 for PLLA in solution using the observed value of K_Θ and a virtual bond length of 2.95 Å [19] in Eq. (1). They also calculated C_∞ using the K_Θ values obtained with the group contributions method developed by van Krevelen [20,21], the n_v and l_v (real bonds) being the same as mentioned above, and obtained 11.6 for PLLA and 9.1 for PLLA/PDLA. Tacticity was taken into consideration so that $K_\Theta = 0.24$ for PLLA and $K_\Theta = 0.16$ for PLLA/PDLA (copolymer made by ring opening polymerization of L-lactide and D-lactide with 50% *meso* and 50% racemic diads).

Because the exact chain configuration of the experimental copolymer of L-lactide and D-lactide units [17] is not known, calculations in this paper were carried out for a copolymer of alternating L-lactide and D-lactide units (alternating PLLA/PDLA) and for a random copolymer of combinations of L,D- and D,L-diads (random PLLA/PDLA). The calculations were performed in the Θ-state which, however, is not so easily achieved in all experimental measurements. Therefore the effect of the cut-off for nonbonded interactions on the calculated characteristic ratios has been studied in more detail in PLLA.

2. Computational details

RMMC calculations were performed with the RIS module of the MSI INSIGHTII/DISCOVER software package [22] on an SGI Origin 2000 supercomputer at the Center for Scientific Computing (Espoo, Finland). The RMMC method is described in more detail in Refs. [1,12].

In addition to being very sensitive to the force field used, the RMMC results also depend on the choice of cut-off for nonbonded interactions and the length of the generated polymer chains. For reasons discussed in Ref. [12], the Max_Bonds criterion was also chosen in this paper to determine the cut-off instead of distance, since the nonbonded interactions can then be restricted to a short range along the chain also in flexible polymer chains (Θ-state) [23]. Also, to avoid unbalanced Coulomb interactions, the polymer chains are divided into neutral charge groups. The general division into neutral charge groups is explained in more detail in Ref. [12]. The natural choice of charge groups for PLLA, PLLA/PDLA and PGA is shown in Fig. 1.

According to Flory [15], short-range interactions are defined as interactions between atoms and groups which are near neighbors in sequence along the chain. The Θ-state of the polymer is defined by interactions up to the second order [15], i.e. by interactions that can be described in terms of the rotational state of two adjacent bonds along the chain [23]. In the studied polyesters, with the division into neutral charge groups, this is achieved when the nonbonded distance is 3 bonds since the interactions have to be extended to the charge group containing the nearest switching atom. Because the Min_Bonds value is 3 (due to the standard definition of nonbonded interactions as 1,4 and higher interactions), the smallest Max_Bonds value studied has been raised to 4. There is, however, no known way to a priori determine the ideal value of Max_Bonds for a particular polymer type, and calculations with different values of the parameter are needed. Usually values for the Max_Bonds parameter range from 4 to 6 for polymer chains

[1]. In the polyester chains studied in this paper with a cut-off value of 4, interactions between three adjacent charge groups are taken into account (see Fig. 1). A cut-off value of 6 extends the interactions to five charge groups. Therefore, the RMMC calculations done here were carried out with Max_Bonds values of both 4 and 6. However, for one chain length (100 repeat units) of PLLA, the effect of longer-range nonbonded interactions on the results were also studied, due to variations in the experimental results (interactions between seven adjacent charge groups were then taken into account, i.e. Max_Bonds = 9).

As regards the chain length, the RMMC calculations utilizing the modified PCFF were performed with two different lengths, corresponding to a degree of polymerization (DP) of 50 or 100 repeat units. The chain lengths were chosen so as to produce about the same number of rotatable backbone bonds as in the polymer chains studied in Ref. [12]. In PGA the actual number of rotatable backbone bonds was smaller (149 for DP = 50 and 299 for DP = 100) than in PLLA and PLLA/PDLA (199 for DP = 50 and 399 for DP = 100) since in PLLA and PLLA/PDLA the side methyl groups were also allowed to rotate. The RMMC calculations were also carried out with the original PCFF for PLLA, PLLA/PDLA and PGA using the 100 repeat-unit chains. The number of equilibration and production steps in the calculations were 3,000,000 and 6,000,000, respectively, which yields sufficient statistics for the computed properties (see Ref. [12]). The calculations were performed at a temperature of 298 K.

3. Results and discussion

In this paper, as usually for polymer chains containing rigid backbone units, the results are given in terms of virtual bonds (i.e. with the ‘bonds’ connecting the link atoms on opposite sides of the rigid units [15]), if not otherwise noted. In Tables 1–3, however, the characteristic ratios are presented for both real and virtual bonds. Characteristic ratios can be calculated from the equation

$$C_n = \frac{\langle r^2 \rangle}{n l_{\mathrm{v}}^2}, \tag{2}$$

in which $\langle r^2 \rangle$ is the mean square end-to-end distance and n is the number of bonds in the polymer chain. The calculated characteristic ratios determined with real bonds (C_n) are slightly more precise than those with virtual bonds (C_n^{virt}) since C_n is computed using the exact bond lengths of the polymer chain whereas, in the computation of C_n^{virt}, the virtual bond used is the average value of all the virtual bonds in the polymer chain. The differences in the accuracy of the calculated results, however, are not significant.

The characteristic ratios C_n and C_n^{virt} of PLLA, PLLA/PDLA and PGA calculated with the modified PCFF, and for the 100 repeat-unit chains also with the original PCFF, are compared with available experimental values [13,14] in Tables 1–3. The average length of the virtual bonds was determined from the generated chains used in the RMMC calculations, and it is 3.75 Å for all studied polyester chains using the modified PCFF, and 3.78, 3.75 and 3.73 Å for PLLA, PLLA/PDLA and PGA, respectively, using the original PCFF. The calculated ratios of the mean square end-to-end distance r to that of the radius of gyration s, $\langle r^2 \rangle / \langle s^2 \rangle$, and the persistence lengths a are also given in the tables.

In all studied polyesters, the calculated $\langle r^2 \rangle / \langle s^2 \rangle$ ratios are close to 6, which is the ratio for ideal gaussian chains [15]. The $\langle r^2 \rangle / \langle s^2 \rangle$ ratios are not very sensitive to the selected force field, nor to the chain length or the Max_Bonds value. Both the calculated characteristic ratios C_n^{virt} (or C_n), as well as the persistence lengths a, come out about the same when the chain length is 50 repeat units as when it is 100 repeat units. Thus, a chain length of about 50 repeat units is sufficient for computation of the single chain properties of PLLA, PLLA/PDLA and PGA. The persistence lengths are also much shorter than the contour lengths, indicating that the selected chain lengths are sufficient for reliable RMMC calculations. They also follow the same trend as the calculated characteristic ratios as a function of run parameters. In the following, the characteristic ratios are discussed in more detail for each polyester chain separately.

3.1. Poly(L-lactic) acid

The RMMC values for C_n^{virt} (or C_n) are calculated clearly larger by the modified PCFF than by the original PCFF, indicating that the PLLA chains are more flexible with the original PCFF (see Table 1).

The RMMC characteristic ratios, at least with the chain lengths used here, depend much more on the cut-off value than on the chain length. C_n^{virt} increases significantly as a function of Max_Bonds when the modified PCFF is used, while these values instead decrease when the original PCFF is used. A cut-off value of 9 already includes higher than second order nonbonded interactions according to the definition by Flory [15], and the value of C_n^{virt} is then clearly larger than that calculated with smaller cut-off values. The PLLA chains thus become less flexible when the nonbonded interactions between more distant carboxyl groups are taken into account in the RMMC calculations.

The calculated characteristic ratios differ from the experimental ones, which also deviate a lot from each other. One reason for this is that some of the experimental values for C_n^{virt} (11.7 and 7.2) [14] are calculated using Eq. (1) whose reliability depends on how accurately the constants Φ_0 and K_Θ, and the average bond lengths are determined. The virtual bond length of 2.95 Å [19], that was used in calculating the C_n^{virt} value of 11.7, is much smaller than our virtual bond lengths (3.75 and 3.78 Å with the modified and original PCFF, respectively) and also smaller than the corresponding value given by our ab initio MP2/6-31G(d) calculations (3.72 Å [3]). It is not clear why the characteristic ratio 2.0 ± 0.2 obtained by Tonelli and Flory [13], using a

Table 1
The characteristic ratios C_n (with real bonds (see text)) and C_n^{virt} (with virtual bonds of 3.75 Å), the ratios $\langle r^2\rangle/\langle s^2\rangle$ and the persistence lengths a of PLLA as a function of the cut-off value for nonbonded interactions (Max_Bonds), with 50 and 100 repeat units in the chain. PCFF (mod) and PCFF (orig) refer to the modified [2,3] and original MSI's PCFF [4–11], respectively. Notation of the polyester is given in Fig. 1

Max_Bonds	Property	DP = 50	DP = 100		Exp.
		PCFF (mod)	PCFF (mod)	PCFF (orig)	
4	C_n	6.08 ± 0.07	5.67 ± 0.09	4.21 ± 0.07	
	C_n^{virt}	8.29 ± 0.13	7.68 ± 0.16	5.62 ± 0.13	11.7[a], 2.0[b], 7.2[c]
	$\langle r^2\rangle/\langle s^2\rangle$	5.76	6.13	5.73	
	a	5.35 ± 0.05	4.83 ± 0.05	3.86 ± 0.04	
6	C_n	7.81 ± 0.08	7.37 ± 0.12	2.76 ± 0.05	
	C_n^{virt}	10.67 ± 0.17	10.01 ± 0.21	3.69 ± 0.05	11.7,[a] 2.0,[b] 7.2[c]
	$\langle r^2\rangle/\langle s^2\rangle$	6.26	6.16	5.78	
	a	6.82 ± 0.07	6.23 ± 0.07	2.78 ± 0.03	
9	C_n	–	12.09 ± 0.21	–	
	C_n^{virt}	–	16.42 ± 0.38	–	11.7,[a] 2.0,[b] 7.2[c]
	$\langle r^2\rangle/\langle s^2\rangle$	–	6.99	–	
	a	–	10.49 ± 0.09	–	

[a] Calculated by Grijpma et al. [14] using Eq. (1), a virtual bond length of 2.95 Å [19] and $K_\Theta = 0.42$ [17].
[b] Ref. [13] (from viscosity and light scattering measurements, the virtual bond length is 3.70 Å).
[c] Calculated using Eq. (1), a virtual bond length of 3.75 Å (obtained from the present RMMC results) and $K_\Theta = 0.42$ [17].

virtual bond length of 3.70 Å (which is close to our virtual bond length), deviates from the calculated ones. Experimental values depend on the condition of the material and, for example, the solvent may also have a significant effect on characteristic ratios. The characteristic ratio of 7.2, shown in Table 1, was obtained from Eq. (1) using the virtual bond length from the present RMMC calculations (3.75 Å) and the experimentally determined K_Θ value (0.42 [17]). Our RMMC results with Max_Bonds = 4 are closest to this experimental characteristic ratio, which according to the discussion above seems to be the most reliable experimental result. Thus, a Max_Bonds value of 4 would best describe the Θ-state of the PLLA chains. More accurate measurements in the Θ-state would be needed, though, for a proper determination of this relation.

Table 2
The characteristic ratios C_n (with real bonds) and C_n^{virt} (with virtual bonds of 3.75 Å), the ratios $\langle r^2\rangle/\langle s^2\rangle$ and the persistence lengths a of alternating and random PLLA/PDLAs as a function of the cut-off value for nonbonded interactions, with 50 and 100 repeat units in the chain. Abbreviations and notations as in Table 1

Max_Bonds	Property	DP = 50	DP = 100		Exp.
		PCFF (mod)	PCFF (mod)	PCFF (orig)	
Alternating PLLA/PDLA					
4	C_n	4.59 ± 0.05	4.79 ± 0.08	5.89 ± 0.10	
	C_n^{virt}	6.18 ± 0.10	6.49 ± 0.14	7.98 ± 0.18	4.0[a]
	$\langle r^2\rangle/\langle s^2\rangle$	5.909	5.95	6.296	
	a	4.08 ± 0.04	4.22 ± 0.04	5.11 ± 0.05	
6	C_n	4.66 ± 0.05	4.89 ± 0.08	6.80 ± 0.12	
	C_n^{virt}	6.27 ± 0.11	6.64 ± 0.14	9.22 ± 0.21	4.0[a]
	$\langle r^2\rangle/\langle s^2\rangle$	5.701	5.941	6.155	
	a	4.30 ± 0.04	4.28 ± 0.04	5.56 ± 0.06	
Random PLLA/PDLA					
4	C_n	5.08 ± 0.06	5.02 ± 0.08	6.26 ± 0.11	
	C_n^{virt}	6.71 ± 0.11	6.84 ± 0.15	8.53 ± 0.20	4.0[a]
	$\langle r^2\rangle/\langle s^2\rangle$	5.732	5.858	5.932	
	a	4.61 ± 0.05	4.46 ± 0.05	5.24 ± 0.06	
6	C_n	4.53 ± 0.07	5.12 ± 0.09	6.83 ± 0.12	
	C_n^{virt}	5.97 ± 0.13	6.97 ± 0.15	9.31 ± 0.22	4.0[a]
	$\langle r^2\rangle/\langle s^2\rangle$	5.803	5.979	6.316	
	a	4.09 ± 0.04	4.51 ± 0.05	5.75 ± 0.06	

[a] Calculated using Eq. (1), a virtual bond length of 3.75 Å (obtained from the present RMMC results) and $K_\Theta = 0.17$ [17].

Table 3
The characteristic ratios C_n (with real bonds) and C_n^{virt} (with virtual bonds of 3.75 Å), the ratios $\langle r^2\rangle/\langle s^2\rangle$ and the persistence lengths a of PGA as a function of the cut-off value for nonbonded interactions, with 50 and 100 repeat units in the chain. Abbreviations and notations as in Table 1

Max_Bonds	Property	DP = 50	DP = 100	
		PCFF (mod)	PCFF (mod)	PCFF (orig)
4	C_n	5.65 ± 0.05	5.54 ± 0.07	4.35 ± 0.06
	C_n^{virt}	7.65 ± 0.11	7.53 ± 0.13	5.98 ± 0.12
	$\langle r^2\rangle/\langle s^2\rangle$	6.05	6.04	5.91
	a	4.93 ± 0.05	4.80 ± 0.05	4.07 ± 0.04
6	C_n	4.63 ± 0.04	5.03 ± 0.06	3.99 ± 0.07
	C_n^{virt}	6.28 ± 0.09	6.84 ± 0.12	5.49 ± 0.11
	$\langle r^2\rangle/\langle s^2\rangle$	5.97	5.99	5.97
	a	4.16 ± 0.04	4.37 ± 0.05	3.61 ± 0.04

3.2. Poly(L,D-lactic) acid

The RMMC characteristic ratios (obtained with the modified PCFF) of the alternating and random PLLA/PDLAs are all close to each other, the results for the random PLLA/PDLA being somewhat larger, except for the chain having DP = 50 and Max_Bonds = 6 (see Table 2).

In contrast to the corresponding results for PLLA, the C_n^{virt} are practically independent of the chain length and the Max_Bonds value. As regards the corresponding results obtained using the original PCFF, the characteristic ratios are calculated to be somewhat larger than those given by the modified PCFF. The disagreements between the two force fields, however, are much less severe than they were for PLLA.

The characteristic ratios (C_n^{virt}) are clearly smaller for (alternating and random) PLLA/PDLA than for PLLA, indicating that the PLLA/PDLA chains are more flexible than the pure PLLA chains. This result is in agreement with the values obtained with the group contributions method in the work by Grijpma et al. [14], who found that the characteristic ratio of the PLLA/PDLA copolymer (containing 50% *meso* and 50% racemic diads) increased when the percentage of the LLA part became larger.

The experimental value of 4.0 for the characteristic ratio was obtained by using Eq. (1) with a virtual bond length of 3.75 Å from the present RMMC results and $K_\Theta = 0.17$ [17]. As for PLLA, the deviations between the available experimental data and the calculated RMMC results are rather large. However, the results given by the modified PCFF are again closer to the experimental value than the results obtained with the original PCFF. For the PLLA/PDLAs, Max_Bonds values of 4 and 6 both give results which are of equal quality relative to the experimental value. The smaller of these values is thus recommended as cut-off for nonbonded interactions because of the smaller computational effort involved.

3.3. Polyglycolic acid

Contrary to the corresponding PLLA and PLLA/PDLA results, the characteristic ratios of PGA decrease when the cut-off value increases (see Table 3). This is the case with both PCFFs. As was the case with PLLA, C_n^{virt} is calculated to be smaller by the original PCFF than by the modified PCFF, but the differences are not so large. For PGA, there is no experimental data available, and recommendations concerning suitable Max_Bonds values, thus, cannot be given.

According to the potential energy maps calculated for PLLA and PGA in Ref. [3], the PGA chains were more flexible than the PLLA chains. It was found that the $C(sp^3)–O(sp^3)$ rotation of the polylactic acid chains was less flexible than the corresponding rotation of PGA chains whereas the $C(sp^3)–C(sp^2)$ rotations were of practically equal flexibility. The $C(sp^2)–O(sp^3)$ rotation, which was studied in Ref. [2], is a rather rigid one, and was also found to be very similar in all the studied esters. These results are in agreement with the present study, since the characteristic ratios calculated for PLLA are much larger than those for PGA. The PLLA/PDLA chains in most cases seem to be even more flexible than the PGA chains. However, using the original PCFF, C_n^{virt} is larger for PGA than for PLLA, and for the PLLA/PDLAs they are larger than for PGA. Thus, in disagreement with the results given by the modified PCFF, the original PCFF predicts the PLLA chains to be the most flexible and the PLLA/PDLA chains to be the least flexible. In this case, the original and modified PCFFs are even in qualitative disagreement. However, the modified PCFF results agree with those of other studies (see e.g. Refs. [14,24]). The flexibilities of the polyester chains studied in this paper are affected by tacticity and steric effects. For example, in Ref. [12] the characteristic ratio of poly(methyl metacrylate) was found to be smallest between 60 and 70% of racemic dyads. Similarly, the PLLA/PDLA chains of 50% of racemic dyads have a smaller characteristic ratio than the pure PLLA chains. On the other hand, the PLLA chains, due to steric effects caused by the methyl groups, are expected to be less flexible than the PGA chains.

It is interesting to compare the characteristic ratios of polyesters containing strongly interacting carboxyl groups (studied in this paper) with those having isolated carboxyl groups (main chain polyesters with alkyl chains of various lengths between the carboxyl groups studied in Ref. [12]). The characteristic ratios (with real bonds) were 5.1–6.4 for the polyesters studied in Ref. [12]. Comparing these values with those of PLLA, (alternating and random) PLLA/PDLA and PGA (real bonds, Max_Bonds = 6 and DP = 50), the flexibility of the chains is found to be in the following order: PLLA/PDLA is the most flexible, PGA and the main chain polyesters with isolated carboxyl groups of Ref. [12] have about the same flexibility, whereas the PLLA chains are clearly less flexible. The flexibility of the polyester chains studied, thus, seems to be practically independent of the chemical environment of the carboxyl groups. Alkyl chains of various lengths between the carboxyl groups of the main chain polyesters have, however, a significant effect on other properties such as biodegradability [25].

4. Conclusions

The RMMC method has proved to be a reliable method for computation of the single chain properties of different types of polymers, including copolymers and polymers with flexible side groups. However, as already pointed out in Ref. [12], care has to be taken in the choice of run parameters. The results depend especially on the cut-off limit for nonbonded interactions and on the choice of charge groups to balance the Coulombic interactions. Since the RMMC method uses potential energy functions directly, the results are also very sensitive to the force field used. This was clearly seen in the present calculations where the results given by the original PCFF [22] were compared with those given by the modified PCFF containing reoptimized torsion potentials for the $C(sp^2)–O(sp^3)$, $C(sp^3)–O(sp^3)$ and $C(sp^2)–C(sp^3)$ backbone bonds (see Refs. [2,3]).

The characteristic ratios calculated using the original PCFF predicted the flexibility of the PLLA, PLLA/PDLA and PGA chains in totally reversed order compared to the results obtained with the modified PCFF. Also, the original and modified PCFFs disagree on the dependence of the characteristic ratios on the cut-off values. The RMMC calculations presented in this paper were carried out in the Θ-state whereas this is not so easily achieved in experimental measurements. This is one reason why the experimental results may vary a lot, as is the case for the polymer chains studied in this paper. According to Flory [15], if nonbonded interactions are extended to second order interactions, this is considered a Θ-state of a polymer chain. In PLLA, PLLA/PDLA and PGA this means a Max_Bonds value of 4. There is, however, no consistent way to determine an ideal Max_Bonds value for a particular polymer type. Therefore, calculations were also carried out with a Max_Bonds value of 6 since, due to division of the polymer chains into neutral charge groups, the nonbonded interactions are extended to include the groups containing the closest switching atoms. Further, in PLLA, due to large variations in the experimental values, a cut-off value of 9 was also used in the calculations to find out the dependence of the characteristic ratio on the cut-off value. The cut-off value of 9 is, nevertheless, too large to retain the state as a Θ-state. Thus, Max_Bonds values of 4 or 6 are recommended as cut-off distances for nonbonded interactions in the polyester chains studied in this paper. The same values were also suggested by Honeycutt [1] for this type of polymer chains. According to our studies in this paper and in Ref. [12], it seems that for polyesters with short side groups the value 4 would be sufficient whereas for polyesters with longer side groups the value should be raised to 6. A chain length of about 50 repeat units was found long enough for the kind of flexible chains studied here as the calculated characteristic ratios obtained with chain lengths of 50 and 100 repeat units were close to each other.

Comparison between experimental and calculated results was difficult to make due to the uncertainty in the experimental values. Using Eq. (1), it is difficult to obtain reliable results since the equation contains parameters that depend on the state of the polymer chains in the sample. More accurate measurements in the Θ-state would thus be needed. However, the characteristic ratios obtained using the modified PCFF are closer to these experimental values than the results given by the original PCFF.

In this paper, the flexibility of the biodegradable PLLA, PLLA/PDLA and PGA polymer chains was considered. Further studies on the amorphous phase properties of the corresponding materials are in progress [26], since the hydrolysis and biodegradability mainly take place in the amorphous phase of the polymer.

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