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Block and alternating copolymer chains of styrene–vinylmethylether and styrene–methylmethacrylate by molecular dynamics simulation

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Abstract

Chains of the copolymers formed by styrene (S) with two different comonomers, vinylmethylether (VME)and methylmethacrylate (MMA), are studied to see how these two comonomers influence the expansion of the coil and the segregation between blocks (the comonomers differ in that homopolymer PS forms miscible blends with PVME and is incompatible with PMMA). Two comonomer sequences are considered: di-block and alternating. Their chains are simulated by molecular dynamics, at two coil densities: the unperturbed random coil state (attained by use of a cut-off for the non-bonded interactions), and a more dense, collapsed coil state (with no cut-off). Properties analysed are: radius of gyration, scattering form factor, separation between block' centres of mass, and pair distribution function between blocks' monomer units. The alternating copolymers (and the corresponding homopolymers) are divided into two parts and treated as 'block' copolymers, for comparison. The di-block copolymer chains are no more expanded than the corresponding homopolymer chains, and no clear distinction between the VME-S and MMA-S pairs can be established. The analysis of 'copolymer' form factors show a slightly larger global segregation of the MMA-S blocks. On the other hand, the alternating copolymer chains of VME-S and MMA-S can be clearly differentiated. Compared to their corresponding homopolymer chains, the VME-S alternating chain is more contracted, and its two blocks are in closer proximity, while the MMA-S alternating chain is more expanded, and its two blocks are more segregated. Thus, a correlation between the compatibility of the homopolymer pair and the degree of segregation of the alternating copolymer chain has been found.

Keywords: Copolymer chain; Block and alternating; Molecular dynamics

1. Introduction

The attraction or repulsion between two chain fragments having different monomer compositions ($\cdots$AAA$\cdots$ and $\cdots$BBB$\cdots$) depends on the balance of interactions between the like (A–A, B–B) and unlike (A–B) monomer units constituting the chain fragments. This balance leads to attraction only in few cases, when there are specific interactions between complementary groups. For the rest (majority) of cases, this balance of interactions leads to repulsion between the chain fragments. In a block copolymer, the fragments with different monomer composition are bonded in a single chain and cannot separate freely. Thus, in a block copolymer the repulsion between unlike monomer units leads to a micro-phase segregation (below the order–disorder transition temperature). This bulk segregation is accompanied, at the single macromolecule level, by the stretching of the chains, in order to allow for the spatial separation of blocks with different compositions.

The single chain segregation in block copolymers has been calculated both theoretically and numerically [1–23]. Most of the work has been done considering the chains as composed of unspecified units, A and B, which interact through a generic Lennard–Jones type potential (ε/kT), where the effects of temperature and solvent are gauged through parameters ε_{AA}, ε_{BB}, ε_{AB}. However, there is some lack of studies about the influence of the detailed atomic structure of the units on the properties of the copolymer chains. Here, we apply simulation at the atomistic level for the comparative study of two different copolymers. Both have a common monomer, styrene (S), and the second monomer is vinylmethylether (VME) in one case, and methylmethacrylate (MMA) in the other case. These two copolymers are expected to present very different balances

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of interactions between their respective comonomer units. At least, their corresponding homopolymers have opposite behaviour with respect to miscibility: the pair polystyrene (PS)–polyvinylmethylether (PVME) forms compatible blends showing negative values of the interaction parameter, while the pair PS–polymethylmethacrylate (PMMA) is highly incompatible with positive values of the interaction parameter. As far as polymer miscibility is partially a consequence of the balance of cross-interactions between monomer units, one can expect a different type of interaction of the VME and MMA units with the S units, and, furthermore, a different degree of segregation in the chains of the VME-S and MMA-S copolymers. Obviously, the connection of bulk miscibility with balance of interactions between monomer units and chain segregation is only a simplified one, since other factors, such as volume changes, differences in expansivity, packing efficiency, chain stiffness, etc. are important in determining the bulk behaviour of blends (tacticity also has an influence on the miscibility of PVME and PS) [24–27].

The realistic simulation of bulk copolymers is a very demanding task. If the cross-interactions between different units of a copolymer chain would have a significant influence on chain segregation, then the simple simulation of a single chain would provide some information useful to interpret and predict block copolymer structures and even polymer compatibility. This is the test that we attempt here: to simulate single chains of the copolymers, using a realistic forcefield capable of describing the interactions between units at the detailed atomic level, and see what is the influence of different monomers on the overall shape of the chain and on the spatial distribution of monomers. The idea that the miscibility of polymer blends could be determined from the microstructure of block copolymer single chains in vacuum has been advanced already [28].

The interactions between different parts of a macromolecular chain can occur under different thermodynamic conditions. The conformation representative of the chain in bulk or in a theta solvent is the unperturbed state. The unperturbed state is well defined both from the theoretical and experimental points of view, so it gives a good reference for the simulation. However, the coil density is low in such a state and, consequently, the interacting units are far apart, so some of the differences in chain segregation that may arise because of the different balance of interactions may be washed out. For this reason we compare both copolymer chains also in a more dense situation with the chain collapsed. A more contracted conformation of a single chain is a better representation of the density prevailing in the bulk state [28]. It is clear that the local density in collapsed chains, and, consequently, the density of interactions between different types of units are closer to the bulk state. On the other hand, we have to consider that the chain conformation of homopolymers in bulk will be similar to (isolated) theta chains and much more expanded that collapsed chains. Therefore, the prediction of differences of mean square dimensions and distances within coils resulting from the present simulations for the collapsed chain cannot be representative of the bulk state in absolute values.

As mentioned above, the tendency of the blocks to avoid each other increases with concentration in the case of copolymers with incompatible blocks, leading to microphase separations and even more expanded configurations in bulk as compared to isolated chains. Near the order–disorder transition, experiments [29,30] and simulations [2,9,31,32] of course-grained models have given clear evidence of pretransitional stretching [33]; an even stronger stretching occurs in the mesophase ordered structures. Such an effect clearly cannot be attained within a single (isolated) coil. Consequently, our single chain calculations cannot surely help to understand the behaviour of incompatible copolymers in the bulk, which, as previously stated, is not the purpose of this work. (From the strict point of view of providing directly a correct representation of real systems, they can only correspond to single S-VME and S-MMA copolymers in vacuum or, eventually, in very bad solvent).

With regard to theoretical modelling, a collapsed conformation is the natural outcome of the simulation for a detailed representation of a long chain at room temperature in the vacuum, because long range attractions between units tend to contract the chain. In order to describe the unperturbed state it is common practice to restrict the spatial range of the non-bonded interactions by cutting their potential above a given separation between the interacting units. This is done in order to mimic the influence of intermolecular interactions (other molecules interposed between the units of the chain). The use of cut-offs for the long range interactions is standard in the rotational isomeric state (RIS) method [34] and in other chain theories or computational methods [35–37]. Our strategy is to study the conformational properties of the copolymer chains both with cut-offs (unperturbed state) and free of cut-offs (collapsed state).

The properties studied are radius of gyration, distance between centers of mass, chain copolymer form factor (as it will be conveniently defined below), and pair distribution function between atoms. These properties of the copolymers will be compared with those of the corresponding homopolymers, in order to detect any segregation that may arise due to the presence of different monomer units bonded in the same chain.

The distribution of comonomer units along the chain will be considered in two extreme cases: the di-block copolymer and the alternating copolymer. On the experimental side, there is abundant information regarding the synthesis, characterization and properties of block and alternating copolymers of VME and MMA with S, [38–43] and theoretically, the di-block VME-S and MMA-S copolymers have been studied by computing their interaction parameter and phase diagrams, [44] with a lattice model for the chains.

Here, we use the more realistic molecular dynamics (MD) simulation with detailed atomistic representation.

2. Methods

2.1. Chains

The monomers styrene (S), methylvinylether (VME), and MMA can give chains with different tactic forms. In practice, the most common case is when the polymers are 'atactic', but this term does not mean the same microstructure in all the polymers studied here; thus, atactic polystyrene (PS) and atactic polymethylmethacrylate (PMMA) have more racemic diads than meso diads, while in polyvinylmethylether (PVME) the reverse is true. In order to limit the number of variables of our study, all the chains are built with the same overall tacticity: half meso (*m*), half racemic (*r*). Still, one has to determine the distribution. In order to be truly atactic, the distribution of *m* and *r* should be random, but random, with a finite number of units, means that not all chains would have the same microstructure, and hence, comparison between copolymers could be influenced by differences in their diad distributions. Again for the sake of simplifying the number of variables affecting the problem, all the chains are built with the same distribution. Being half *m* and half *r*, the easiest way is to assume an alternate distribution: $\cdots mrmr \cdots$ (heterotactic, as in Ref. [36]).

Homopolymer chain fragments containing 20 monomer units are built with this microstructure (the first and last diads in the 19 diad sequence being both *m*). These homopolymer fragments of 20 units are used as blocks to build the di-block copolymer chains, which result, thus, with a total of 40 monomer units. The blocks are joined by means of an additional methylene group, $-CH_2-$, acting as central piece to which two different fragments of 20 units are bonded (in such a way as to give a *r* configuration for the new diad generated embracing this central $-CH_2-$). By this bonding we get the 40 units chains of the di-block VME-S and MMA-S copolymers. Homopolymer chains of the same length as these di-block chains (40 units) are obtained when the two fragments bonded to the central $-CH_2-$ are equal. Homopolymer chains of the same length as the blocks (20 units) are obtained simply by capping the 20 units fragments with a CH_3. The alternating copolymer chains are built with the same length (40 units) and the same tactic microstructure as the block copolymer chains

2.2. Unperturbed state

In classical RIS calculations, the usual values for the cut-off distance, in polymers like PS, lie around 4–5 Å, [34] but more recent molecular dynamics (MD) simulation has used 6 Å [35]. In MD, the optimum cut-off that gives good results for the average dimensions can depend on other parameters of the simulation, like the dielectric constant of the medium or the temperature. However, in our MD simulations the dimensions are much less sensitive to dielectric constant or temperature than they are to cut-off distance. Hence, we have tried to optimise with care the value chosen for the cut-off distance. Temperature has a notable influence on the effectiveness of sampling, lower temperatures requiring longer trajectories. The temperature should then be as high as possible in order to get good sampling. However, the system PVME–PS has a LCST at around 385–390 K (the range depending on tacticity), so that its miscibility disappears above this temperature. Then, as a compromise, the value 375 K was chosen for the simulation. The dielectric constant was distance dependent with upper value equal to three.

We try to approximate with our calculations the real dimensions known for the homopolymers constituting the blocks. The experimental characteristic ratios for these polymers are in the range $C_\infty = 6-10$. This we can get with cut-off distances in the range 5.5–6.0 Å. We choose the intermediate value 5.75 Å as fixed cut-off for all simulations (homopolymers and copolymers).

To generate the molecular dynamics trajectories we use commercial software: Discover3, with the forcefield Compass (both from Accelrys). The working temperature is reached by stepwise gradual heating from a minimized structure. Then an equilibration period follows, and finally, the data collection trajectory is run under the Nosé thermostat. Data are recorded every ps, and more than 5000 frames are taken for any polymer chain (trajectory >5 ns).

2.3. Collapsed state

The collapsed state is attained by freeing the cut-off restriction. This is done in two ways: one gradual and controlled (step method), the other sudden and abrupt (abrupt method). In the step method the initial condition is the unperturbed state, from which the chain collapse is achieved gradually by step-wise liberating the cut-off in a controlled way. This way, we expect a smaller kinetic dependence on the properties of the final chain conformations. In the abrupt method the initial condition is the chain in its full extension, and the contract ion starts by sudden suppression of the cut-off, which lets the chain collapse freely. The final temperature is somewhat lower in this abrupt method.

The initial state in the step method is the final state of the unperturbed state trajectory. From this, the cut-off distance is increased step-wise until, in the last step, no cut-off is imposed. Since the trajectory of the unperturbed state can end in any conformation, even in a very contracted one, in order to favour the more expanded ones as starting states for the contract ion, the first step is run at a shorter cut-off distance of 4.5 Å. Then, in the following steps, this distance is increased in the series (Å): 6.0, 6.5, 7.0, 7.5, 8.0, 9.0, no cut-off. Contract ion of the chain occurs in the steps up to 8.0 Å; after that, it remains more or less stationary (this is similar to previous MD simulations of polyvinylchloride (PVC) [45], where the collapse of the chain in vacuum was attained with a cut-off distance of 8 Å). In each step at a fixed cut-off, the trajectory is run for 1 ns, at 375 K (Nosé thermostat), recording 1001 frames (one every ps).

In the abrupt method the chain is initially forced to an end-to-end distance of 100 Å by a constraint. The structure is first minimized with this constraint. Then, the constraint is freed and the MD trajectory is run for 1 ns with no cut-off, at the temperature of 300 K (Nosé thermostat). The end-to-end distance contracts abruptly in the first third of the trajectory and then fluctuates around a stationary value (similarly, in the MD simulation of PVC [45], after approximately the first 100 ps of the trajectory the chain had collapsed and fluctuated around an equilibrium collapsed state).

The data recorded during the last third of the trajectory are used for the calculations (334 frames, one every ps).

3. Results and discussion

The copolymer chains can be expanded, contracted, and distorted with respect to the corresponding homopolymer chains. Such effects will be analyzed in terms of the chain dimensions and the scattering form factor, $S(x)$. Distortion and segregation between blocks of the chain will be analyzed in terms of the separation between centres of masses of the two blocks and through the pair distribution function for monomer units in different blocks, $g(r)$. For this purpose, each chain is formally divided in two halves or 'blocks', A and B, where A is the chain fragment consisting of monomers 1–20, and B is the chain fragment consisting of monomers 21–40. When the chain is a true di-block copolymer, these two halves or blocks are of different monomer composition, but when the chain is a homopolymer or an alternating copolymer these two blocks are of identical composition.

3.1. Dimensions

The dimensions to be discussed are the radius of gyration of the whole chain, S, the distance between the centres of mass of the two blocks of the chain, G, and the end-to-end distance of each block K, R_K. Before discussing the information obtained about expansion and segregation from these magnitudes, let us, first, use them to check the validity of the MD trajectories.

A basic requisite is that the chain blocks be realistically modelled. We have checked that the simulations in the unperturbed state reproduce well the average chain dimensions known from experiment. Thus, for the PS homopolymer of chain length equal to one block, the mean squared radius of gyration obtained for the 20 monomer chain is 120 Å^2, in excellent agreement with the experimental value (123 Å^2), determined by SAXS for atactic PS on oligomeric samples (interpolated for this chain length) [46,47]. For the PMMA and PVME homopolymers, the mean squared radii of gyration obtained for the 20 monomer chains are lower: 105 and 87 Å^2, respectively, in good accordance also with the relative values of the characteristic ratios of these two polymers with respect to those of PS: $C_\infty = 10$ (PS); [48] $C_\infty = 9$ (PMMA) [49,50]; (the experimental value obtained from SAXS data for oligomers of atactic PMMA [51] is slightly higher); $C_\infty = 6$–8 (PVME) [52,53]. Thus, the molecular dynamics trajectories in the unperturbed state give realistic dimensions for all three types of chains here studied. The analysis of internal distances (between units in different locations of the chain) gives also very uniform distributions that do not vary significantly along the contour of the chain.

Regarding reproducibility of results, we can check the results from different MD runs on the same system. The properties analysed are the mean squared values for the radius of gyration of the whole chain, $\langle S^2\rangle$, and for the distance between the centres of mass of the two blocks of the chain, $\langle G^2\rangle$. The reproducibility between two runs on the same system is excellent in the unperturbed state. Differences in the root mean squared values are up to 2% for $\langle S^2\rangle^{1/2}$ and up to 3% for $\langle G^2\rangle^{1/2}$. The situation is not so good in the collapsed state. Regarding property, the deviations between runs are smaller for the radius of gyration than for the distance between blocks. Regarding method, the deviations are smaller in the step method than in the abrupt method. We shall discuss only results for the radius of gyration with the step method, where deviations in $\langle S^2\rangle^{1/2}$ are only up to 10%.

The expansion suffered by the dimensions of the copolymer chains, with respect to the free homopolymers of equal length, can be expressed in terms of the ratios σ_S and σ_G, defined as:

$$\sigma_\mathrm{S} = \frac{\langle S^2\rangle_\mathrm{AB}}{\frac{1}{2}(\langle S^2\rangle_\mathrm{AA} + \langle S^2\rangle_\mathrm{BB})} \tag{1}$$

$$\sigma_\mathrm{G} = \frac{\langle G^2\rangle_\mathrm{AB}}{\frac{1}{2}(\langle G^2\rangle_\mathrm{AA} + \langle G^2\rangle_\mathrm{BB})} \tag{2}$$

Here, subindex AB denotes the copolymer, and subindices AA, BB the corresponding homopolymers of equal chain length. The expansion suffered by each individual block, K, in the copolymer chain can be expressed by the ratio $\gamma_{R(\mathrm{K})}$, defined in terms of the end-to-end distance of the block, R_K :

$$\gamma_{R(\mathrm{K})} = \langle R_\mathrm{K}^2\rangle / \langle R_\mathrm{K-H}^2\rangle \qquad \mathrm{K} = \mathrm{A,B} \tag{3}$$

Here, $\langle R_\mathrm{K}^2\rangle$ is the mean squared end-to-end distance of block K in the copolymer, and $\langle R_\mathrm{K-H}^2\rangle$ is the mean squared end-to-end distance of the free homopolymer K that has the same chain length as the block in the copolymer.

The results for σ_S and σ_G are given in Table 1. We can compare the copolymers in terms of composition (VME-S

Table 1
Expansion ratios for the copolymer chains, with respect to the corresponding homopolymer chains (of equal length as the copolymer)

Chain		σ_S unperturbed	σ_S collapsed[a]	σ_G unperturbed
di-block	VME-S	0.97	0.99	1.00
	MMA-S	0.96	1.02	0.94
alternating	VME-S	0.88	0.91	0.83
	MMA-S	1.09	1.07	1.01

σ_S = expansion of radius of gyration, as defined in Eq. (1); σ_G = expansion of distance between blocks' centres of mass, as defined in Eq. (2).

[a] Step method.

vs MMA-S) and in terms of sequence (di-block vs alternating). The di-block copolymers have radii of gyration practically equal to their homopolymers (σ_S very close to 1), in both the unperturbed and collapsed states. Also, σ_S is practically the same in both the VME and MMA di-block copolymers. When looking at the alternating copolymers, the situation changes. The radius of gyration ratio, σ_S, is different in the alternating VME and MMA copolymers. Compared to the di-block copolymer, or to the respective homopolymers, the alternating chain is more contracted in the VME copolymer (σ_S below 1) and more expanded in the MMA copolymer (σ_S above 1). The difference in σ_S values between both alternating copolymers: 0.21 in the unperturbed state and 0.16 in the collapsed state, is beyond the error estimated from duplicate MD runs (see above). So, the effects of contract ion in the VME-S chain and of expansion in the MMA-S are to be considered real (at least, in the framework of the interactions considered by the forcefield). The distinction between the VME and MMA alternating copolymers comes again when considering the distance separating the centres of mass of the two halves of the chain (blocks A and B in the formal definition). Thus, the ratio σ_G is larger for MMA-S than for VME-S, the difference in values being 0.18. However, this difference in σ_G is contributed only by the VME-S copolymer, which shows a noticeable approach of its two blocks (σ_G well below 1), while the blocks of the MMA-S copolymer have similar separation as the homopolymers (σ_G practically equal to 1). The difference in σ_G values between the two di-block copolymers is in the opposite sense, but the difference, 0.06, is less significant compared to the error.

Let us consider now the expansion of each individual block in the di-block copolymers, through the ratios $\gamma_{R(\mathrm{K})}$. The values for the styrene block are $\gamma_{R(\mathrm{S})} = 1.18$ with VME and $\gamma_{R(\mathrm{S})} = 1.20$ with MMA. The values for the VME and MMA blocks in their respective copolymers are $\gamma_{R(\mathrm{VME})} = 1.11$ and $\gamma_{R(\mathrm{MMA})} = 0.81$ (all in the unperturbed state). We can see that the S block is expanded ($\gamma_{R(\mathrm{S})} > 1$) very similarly in both copolymers, the influence of its companion block, be it VME or MMA, is not great on the dimensions of the S block. The value for the VME block is also larger than 1. Thus, in the VME-S copolymer, both blocks are expanded (something which is in line with the experimental finding from neutron scattering of PVME + PS blends that there is some stiffening of these chains when they are in mutual presence) [25]. But, in the MMA-S copolymer, the MMA block is contracted ($\gamma_{R(\mathrm{MMA})} < 1$) with respect to the homopolymer, as if it were hiding out of the contact with S. Probably, this contract ion of the MMA block also contributes to the σ_G lower than 1 in this copolymer (Table 1).

3.2. Scattering form factor

Another useful way to explore the segregation of blocks within a copolymer chain is provided by computing its copolymer form factor, defined as:

$$S_{\mathrm{copo}}(q) = M_{\mathrm{T}}^{-2} \sum_{i}^{N} \sum_{j}^{N} f_i f_j \exp(-i\mathbf{q}\cdot\mathbf{R}_{ij}) \tag{4}$$

where $\mathbf{q}$ is the scattering vector, $\mathbf{R}_{ij}$ is the vector connecting atoms i and j, and the scattering (or contrast) factors are defined as:

$$f_{\mathrm{k}} = \pm(M_{\mathrm{T}}/2M_{\mathrm{bl}})M_{\mathrm{k}} \tag{5}$$

where sign + (or −) is chosen for all the atoms in block A (or B), M_{T} is the total mass of scattering active atoms (all except those in the central joining group) and M_{bl} is the total mass of the block to which atom k belongs. This set of factors ensures that $S_{\mathrm{copo}}(q = 0) = 0$, which can be experimentally achieved in a dilute solution of copolymer chains by setting the refractive index of the solvent to be intermediate between those of the different types of monomers in the two blocks. Alternatively, if all the contrast factors are set as M_{k} we recover a normalized form factor for the homopolymer $S_{\mathrm{homo}}(q = 0) = 1$. However, we can also compute $S_{\mathrm{copo}}(q)$ defining the same blocks, irrespective of their real chemical structures, for homopolymer chain and for alternating copolymers (and consistently with the definitions employed in our study of dimensions), in order to monitor the degree of segregation between the two parts around the central unit, and use these curves as references.

We have obtained $S_{\mathrm{copo}}(q)$ for all the molecular dynamics trajectories obtained with the different chains (homopolymer or copolymers). The results are presented as $S_{\mathrm{copo}}(x)$, with $x = q^2\langle S^2\rangle$, in Figs. 1–4, for the unperturbed state trajectories. We also present in these Figs. 1–4 the theoretical result for an ideal Gaussian chain, assuming that $S_{\mathrm{homo}}(q)$ is described by the Debye function:

$$S_{\mathrm{copo}}(x) = (8/x^2)[\mathrm{e}^{-x/2} - e^{-x}/4 + (x/4) - (3/4)] \tag{6}$$

This function has a maximum about $x = 4$ and corresponds to the value of x, where a distance similar to the size of a block is monitored. The maximum increases in intensity when the two blocks tend to segregate in a global fashion and it actually diverges for the collective scattering function

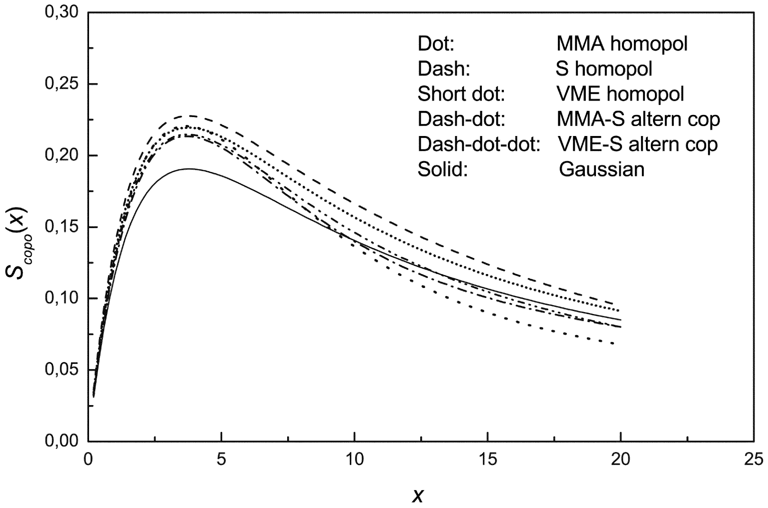

Fig. 1. Copolymer form factors for the two alternating copolymers VME-S and MMA-S. $S(x)$, calculated from the molecular dynamics trajectories, using Eqs. (4) and (5). $x = q^2\langle S^2\rangle$ (q, scattering wavevector; $\langle S^2\rangle$, mean squared radius of gyration). Curves corresponding to the three homopolymers and the Gaussian chain (Eq. (6)) are also shown for comparison. In the cases of all these chains, with uniform composition along their contour, we have artificially defined a block as a side (one half) of the corresponding chain, see the text.

of many-chains systems when the segregation of blocks leads to form ordered mesophases. At large x, however, smaller values of the function indicate a more pronounced presence of units belonging to the opposite block in the short distance range. All the curves for homopolymers and copolymers obtained in the present study have a value in the peak higher than the Gaussian chain. This indicates that the balance of interactions present in the model, though adequate to mimic the theta behaviour of global average distances as the mean radius of gyration, does not give a very accurate reproduction of the ideal chain form factor at all distance ranges, though the ideal curve still can be employed as an indicative reference.

In Fig. 1, the functions for different homopolymers, and also for the alternating copolymers are presented. It can be observed that the functions for different homopolymers have distinct values both at the peak and in the long q range. PS blocks seem to suffer a slightly higher global segregation in their homopolymer chains than the rest, while, according to the large q values, the presence of units belonging to the opposite block is more remarkable at short distances in PMMA. It can be observed that, as expected, the interpenetration between the two blocks in an alternating copolymer is similar to that in homopolymer chains. (It should be again remarked that the copolymer form factors for alternating copolymers monitor differences of positions relative to the 'defined blocks', not between the different repeat units.) The peak results show, in fact, a slightly smaller global segregation tendency. In Fig. 2, we show the functions corresponding to the homopolymers PMMA and PS, now compared with the common block copolymer. The block copolymer shows a greater global segregation, according to the peak results. It is satisfactory to detect this effect, since the tendency to segregation is not expected

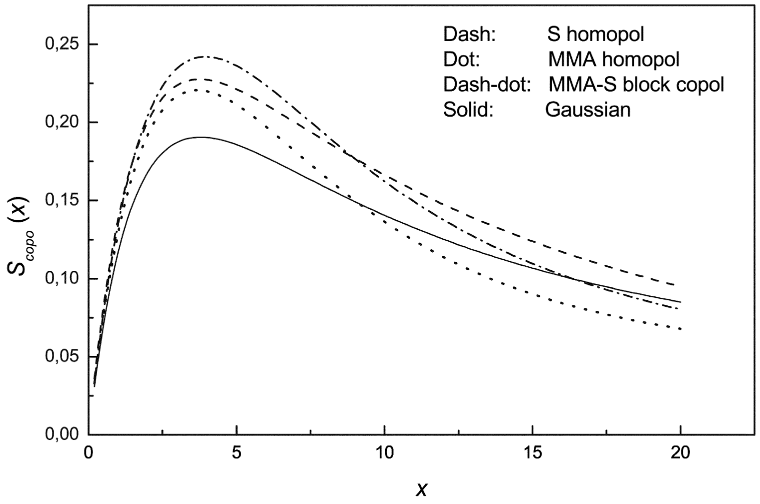

Fig. 2. Copolymer form factors for the di-block copolymer MMA-S and the corresponding homopolymers PMMA, PS. Symbols and definitions as in Fig. 1.

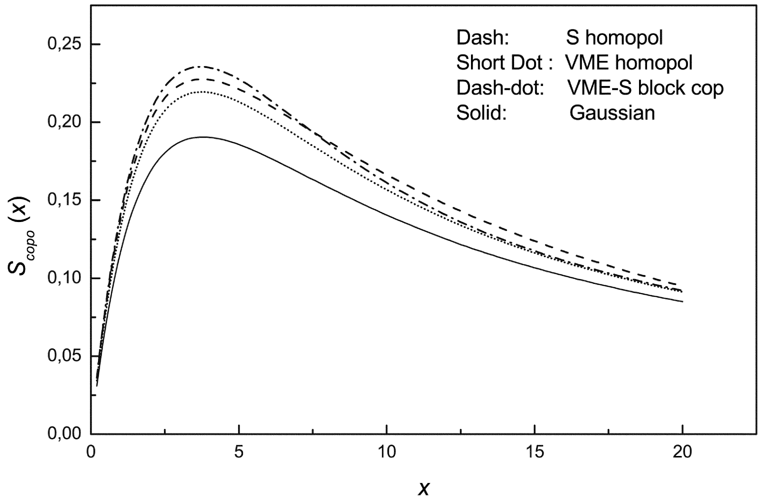

Fig. 3. Copolymer form factors for the di-block copolymer VME-S and the corresponding homopolymers PVME, PS. Symbols and definitions as in Fig. 1.

to be large for the present chain length range. In fact, the experimental incompatibility between PMMA and PS can disappear for oligomers of very short length [54]. At short distances, the copolymer function is intermediate between the two remarkably different homopolymer values. In Fig. 3, we show the curves for PS, PVME and their common block copolymer. At the peak, the three curves are noticeably similar, especially when compared with the MMA-S case. This feature may be an indication of greater compatibility between blocks in the VME-S copolymer. At short distances, the PS homopolymer exhibits a slightly smaller number of contacts with units of the opposite block than the other chains, though the differences between curves are small. Finally, in Fig. 4, we compare the curves corresponding to the different (alternating or di-block) copolymers. From the peak values, it is again verified that the MMA-S copolymers shows the largest global segregation, while the two blocks of the alternating di-block copolymers exhibit a more moderate tendency to separate. At short distances, the VME di-block copolymer presents less contact with units of the other block.

The small differences with respect to the Gaussian behaviour shown by the form factors curves are surely due to the fact that a single chain in the theta chains has not a large number of strong heterointeractions. Consequently, we have tried to obtain a clearer distinction between the cases by obtaining the form factor curves corresponding to the collapsed state for the different polymers. Obviously, the Gaussian chain is not a good reference for these simulation data. Moreover, the results, in particular the location and value of the peaks, are very sensitive to kinetic factors and, consequently, they strongly depend on particular features of the simulation trajectory. Due to these effect, we have not been able to perform a systematic comparison between different cases.

3.3. Pair distribution function

Detailed information about the spatial distribution of the blocks in the chain can be obtained from the pair distribution function, $g(r)$, between atoms in blocks A and

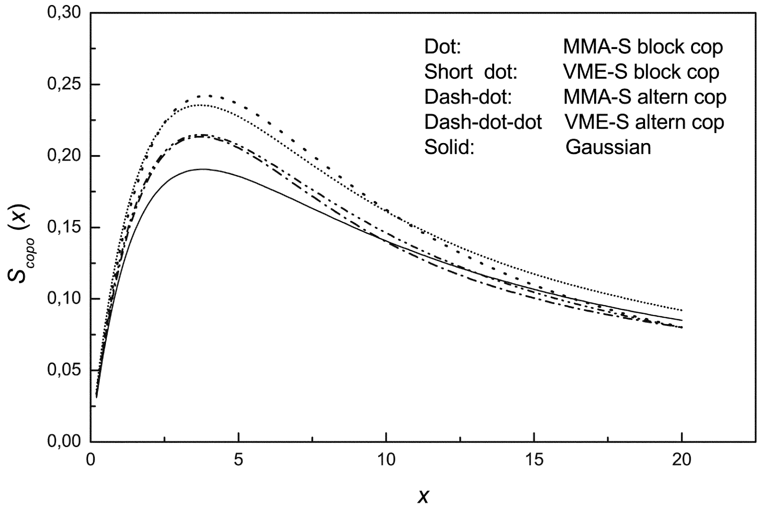

Fig. 4. Copolymer form factors of the different di-block and alternating chains considered in this study. Symbols and definitions as in Fig. 1.

B. $g(r)$ is defined such that $4\pi r^2 g(r)\mathrm{d}r$ measures the probability of finding atoms of block B at a distance between r and $r + \mathrm{d}r$ from atoms of block A, as a function of the separation distance, r. The function $4\pi r^2 g(r)$ is thus a normalized radial distribution. It passes through maxima that give the most probable values of the separation between atoms of block A and atoms of block B. The position, height and width of these maxima provide a measure of the segregation in space of the two blocks.

Each conformation of the chain gives a different form for the pair distribution function. We compute the mean distribution by averaging over all the frames in a MD trajectory. For the calculation of $g(r)$ we exclude the two monomer units connected to the mid point of the chain. The mutual separation of these two central units is forced by their direct bonding and provides no information on the conformational distribution. Thus, in the calculation of $g(r)$ we consider only 19 monomers in each block, excluding the atoms that are not separated by at least six backbone bonds.

The results of $4\pi r^2 g(r)$ are shown in Figs. 5 and 7 for the unperturbed state, and in Figs. 6 and 8 for the collapsed state. The distribution passes through a single smooth maximum, at distances in the range 11–24 Å. Other sharper maxima, at shorter distances, would have appeared if we had considered all the monomer units of the chain. By filtering out the central units which bracket the mid point between blocks, we get only a smooth maximum. This maximum is the relevant one for the analysis of the distribution of block units dictated by chain conformation. The position of this smooth maximum occurs at much shorter distances in the collapsed state than in the unperturbed state (around 13 and 23 Å, respectively), as expected.

We have tested the reliability of the distributions obtained by comparing the results of different MD runs on the same system. In the case of the unperturbed state, a second run produces almost coincident results that are practically superimposed when plotted with the resolution of Figs. 5 and 7. In the case of the collapsed state, we have used two methods which are compared in Figures 9 and 10. As we can see in Fig. 9 for the copolymer with VME, both methods give the same distribution in this case. However, in the case of the copolymer with MMA shown in Fig. 10, the shape of the distribution is much broader and with a shoulder, when the abrupt method is used. However, it is comforting that even in this worst case the position of the maximum is very similar in both methods. At any rate, the step method is more reproducible and, for this reason, the results of the collapsed state which are shown in Figs. 6 and 8 are those obtained with the step method.

Let us compare now the block and alternating copolymers with the corresponding homopolymers. First, the results for the VME-S pair. In the unperturbed state (Fig. 5), the block copolymer is very similar to the average homopolymer. The difference is that the block copolymer distribution is slightly shifted towards longer separations between blocks A and B than the average homopolymer, but the height and width of the curve are very similar. The alternating copolymer, on the other hand, has a distribution significantly shifted towards shorter separations between blocks, and its maximum (at a shorter distance) is higher. In summary, the A and B halves of the chain are only slightly segregated in the block copolymer with respect to the average homopolymer, but they are significantly closer to each other in the alternating copolymer. In the collapsed state (Fig. 6), some features are common to this behaviour of the unperturbed state, but some are different. The alternating copolymer has still a higher maximum at a shorter distance, but its difference with the average homopolymer is now small, and the block copolymer is now the one significantly

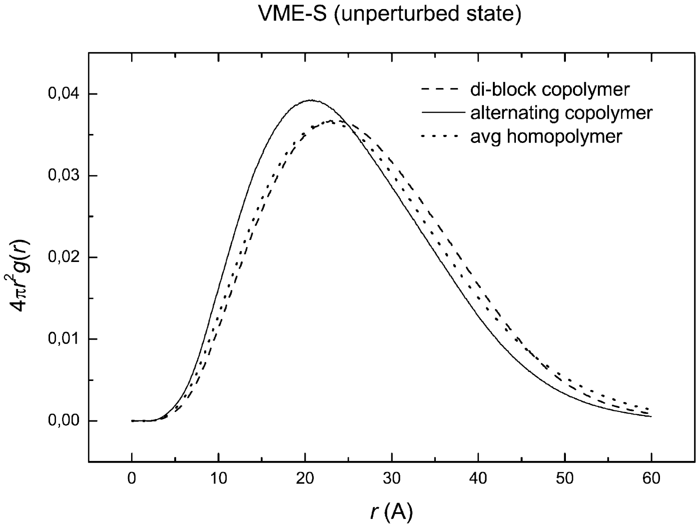

Fig. 5. Radial pair distribution function between blocks A and B of the chain. Comparison between di-block and alternating copolymers with the average of the corresponding homopolymers. The function $4\pi r^2 g(r)\mathrm{d}r$ measures the probability of finding atoms of block B at a distance between r and $r + \mathrm{d}r$ from atoms of block A, as a function of the separation distance, r. Each block comprises one half of the chain (excepting two middle monomer units).

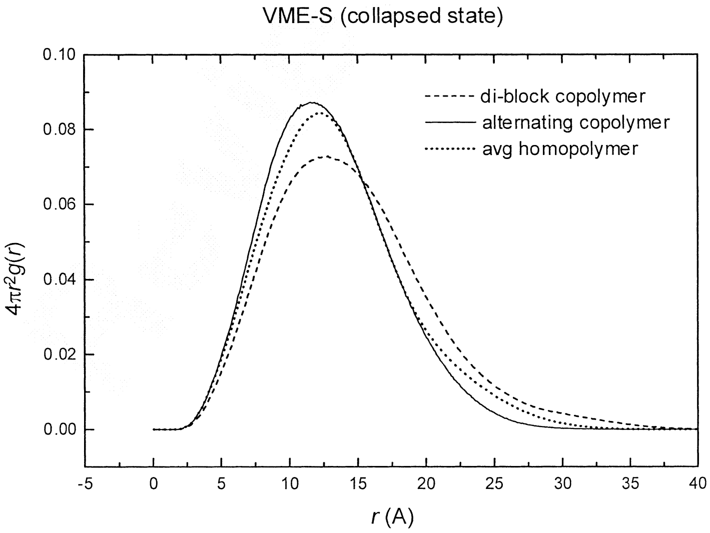

Fig. 6. Radial pair distribution function between blocks A and B of the chain. Comparison between di-block and alternating copolymers with the average of the corresponding homopolymers. The function $4\pi r^2 g(r)\mathrm{d}r$ measures the probability of finding atoms of block B at a distance between r and $r + \mathrm{d}r$ from atoms of block A, as a function of the separation distance, r. Each block comprises one half of the chain (excepting two middle monomer units). (Step method).

different, with a broader distribution covering longer separations. Thus, at both coil densities (unperturbed and collapsed), the alternating sequence of unlike monomers gives the closer proximity between blocks (halves of the chain), while the blocky sequence of monomers gives the larger separation (segregation).

Let us consider now the MMA-S pair. In the unperturbed state (Fig. 7), the block copolymer has its maximum at a separation very close to that of the average homopolymer, but its height is larger. The alternating copolymer, on the other hand, has its maximum at longer separation, and it is of lower height (contrary to what we have seen before in the alternating VME-S pair). However, the differences between curves are very small in this case. In the collapsed state of the MMA-S pair (Fig. 8), it is more clearly observed that the alternating copolymer has a maximum at longer distance and of lower height than the block copolymer. Hence, at both coil densities, the alternating sequence of unlike monomers gives the larger separation between blocks, compared to that of the blocky sequence.

Gathering the information from both pairs, VME-S and MMA-S, we can say that the block copolymer structure does not give a clear difference that allows to distinguish between the compatible pair, VME-S, and the incompatible pair, MMA-S. However, the alternating copolymer structure gives such a systematic difference. Compared with the average of the two copolymers, the alternating copolymer

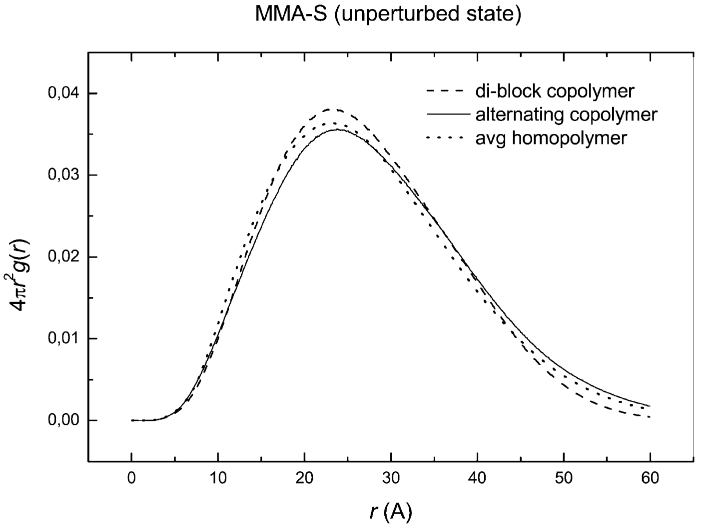

Fig. 7. Radial pair distribution function between blocks A and B of the chain. Comparison between di-block and alternating copolymers with the average of the corresponding homopolymers. The function $4\pi r^2 g(r)\mathrm{d}r$ measures the probability of finding atoms of block B at a distance between r and $r + \mathrm{d}r$ from atoms of block A, as a function of the separation distance, r. Each block comprises one half of the chain (excepting two middle monomer units).

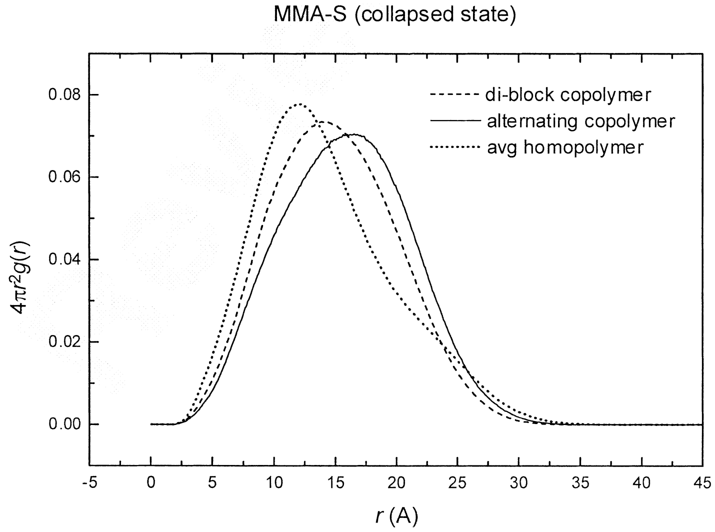

Fig. 8. Radial pair distribution function between blocks A and B of the chain. Comparison between di-block and alternating copolymers with the average of the corresponding homopolymers. The function $4\pi r^2 g(r)\mathrm{d}r$ measures the probability of finding atoms of block B at a distance between r and $r + \mathrm{d}r$ from atoms of block A, as a function of the separation distance, r. Each block comprises one half of the chain (excepting two middle monomer units). (Step method).

has a closer proximity of blocks when the copolymer is composed of the compatible pair VME-S, and gives a wider separation of blocks when it is composed of the incompatible pair MMA-S. How do we understand this sensitivity that occurs only in the alternating structure? If it is due to the balance of interactions between units, probably the units being at shorter distances have the higher influence. In most conformations, the majority of unlike units are further apart than the distance where the interactions are important, if the structure is blocky, while they inevitably are closer in the alternating structure.

At any rate, the distinction between the compatible and incompatible pairs has been possible with single chain simulation, mainly by comparison of the alternating copolymer with the corresponding homopolymers.

4. Conclusions

Regarding the modelling of the chains, the unperturbed random coil state of single chains is well described and gives reproducible results. Thanks to the adjustment of the cut-off distance for the non-bonded interactions, the dimensions of the chains are in agreement with experimental results for oligomers. By letting this cut-off distance increase gradually, it has been possible to reach a more dense, collapsed state of the chain, with monomer density closer to that in bulk. By this step-wise controlled method the collapsed state is still statistically valid and gives some reproducible results. When the same collapsed state is reached by free contract ion from the stretched chain, the final conformation is not a good statistical representation of the chain.

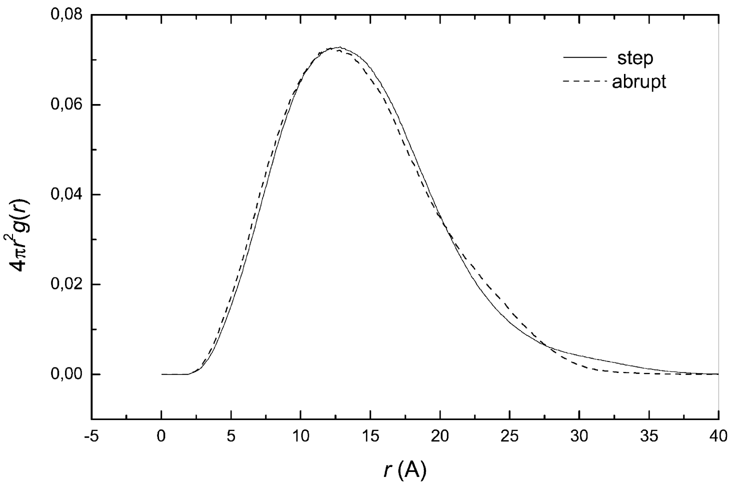

Fig. 9. Radial pair distribution function between blocks A and B of the chain. The function $4\pi r^2 g(r)\mathrm{d}r$ measures the probability of finding atoms of block B at a distance between r and $r + \mathrm{d}r$ from atoms of block A, as a function of the separation distance, r. Each block comprises one half of the chain (excepting two middle monomer units). Comparison between the step and abrupt methods of the collapsed state, for the di-block VME-S copolymer chain.

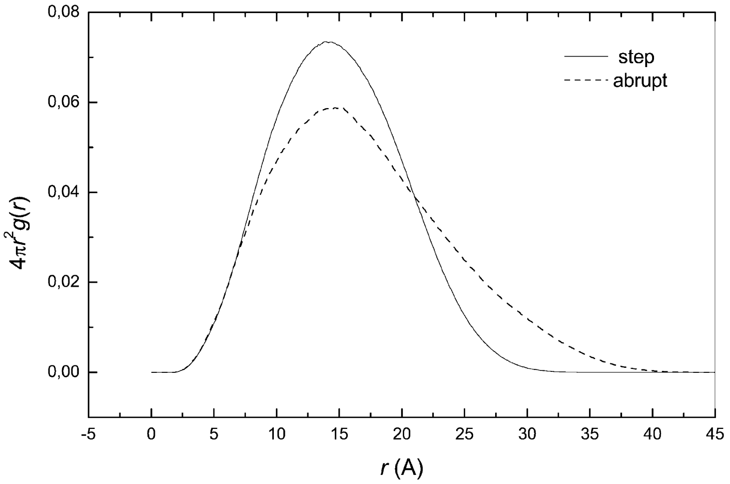

Fig. 10. Radial pair distribution function between blocks A and B of the chain. The function $4\pi r^2 g(r)\mathrm{d}r$ measures the probability of finding atoms of block B at a distance between r and $r + \mathrm{d}r$ from atoms of block A, as a function of the separation distance, r. Each block comprises one half of the chain (excepting two middle monomer units). Comparison between the step and abrupt methods of the collapsed state, for the di-block MMA-S copolymer chain.

Regarding the expansion of the chain, due to cross-interactions between unlike monomers, it is found that both the VME and the MMA di-block copolymers are now more expanded, with respect to the average of the corresponding homopolymers. There is a small difference in such expansion and segregation between the VME and MMA di-block copolymers that cannot be correlated with the widely different compatibility that VME and MMA homopolymers show with polystyrene in bulk.

The alternating copolymers offer a different picture. The MMA-S copolymer is expanded and the VME-S copolymer is contracted, with respect to the average of the corresponding homopolymers. The comonomer that gives incompatibility in the homopolymers, gives also wider separation between chain halves, and the comonomer that gives miscibility in the homopolymers, gives also closer approach between chain halves.

Comparison between the copolymer form factors of the block copolymers in the theta state only yields a faint indication of incompatibility between the blocks. Nevertheless, it is able to distinguish that a VME block in a di-block copolymer with S has a weaker global segregation tendency than a MMA block. This is interesting, since the other features related with the di-block copolymers studied in this work cannot be easily associated to block segregation. However, the differences are not large. As expected, segregation of the two sides (or artificially defined blocks) in an alternating copolymer is similar to the case of homopolymers. A similar comparison study of copolymer form factors in the collapsed state is not possible, due to the great influence of kinetic factors on the location of the blocks.

Finally, the study of the pair distribution functions indicate that the blocks of alternating MMA-S copolymers in the collapsed state are clearly more separated than those of alternating VME-S. This is the most remarkable difference to be associated with the compatibility between homopolymers of distinct compositions.

We can conclude that the study of different conformational properties of single chain di-block and (more remarkably) of alternating copolymers shows some features that correlate with the compatibility behaviour of homopolymers in the bulk. Nevertheless, and according to the arguments sketched along this article, our approach has intrinsic limitations and, therefore, can only give moderately successful conclusions. Because of these shortcomings, it would be of interest to further investigate if the connection found for the present case between single chain conformation and bulk miscibility holds in other copolymer systems.

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