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COLLAPSE OF DIBLOCK COPOLYMER IN POOR SOLVENT. MOLECULAR DYNAMICS STUDY

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Abstract The modification of unsaturated polyesters (UPE) by poly (ethylene glycol) (PEG) end groups [1] and the computer simulation of the collapse of a single molecule of a diblock copolymer AB consisting of PEG (A) and UPE (B) blocks [2] were reported recently by us. In the present paper the static and dynamic characteristics of the final collapsed structure were investigated by a molecular dynamics simulation. The structure and the local dynamic of collapsed homopolymers (AA and BB) were studied also. The initial conformations in all cases were taken near completely extended ones. The final structures of the diblocks are similar to the structure of a core (UPE) and shell (PEG) model. The differences in torsion angle distributions between diblock and homopolymer are maximal for the CCOC dihedral angles (both in UPE and PEG blocks). The orientational order of the COC vectors ('chords' along backbone of polymer chain) inside both blocks is larger in the diblock than in the homopolymer. Local orientational mobility of the COC vector and the translational mobility of the monomers is larger in the diblock than in the homopolymers for both blocks.

Introduction

The modification of unsaturated polyesters by poly(ethylene glycol) end groups was described in a recent work by Schulze et al.[1]. This was made in order to increase the toughness of the cured unsaturated polyester (UPE), and to lower the shrinkage during curing. The modification reaction was done by an end-group reaction of a carboxyl-terminated unsaturated polyester with poly(ethylene glycol) (PEG) mono methyl ethers of various molecular weights (range 350 to 2000 g/mol). Analysis revealed that diblock copolymers of the AB type were formed, and that the diblock copolymers had usually one poly(ethylene glycol) end group per polyester segment.

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An atomistic molecular dynamics simulation of a similar single AB diblockcopolymer molecule consisting of PEG (A) and UPE (B) blocks (as well as simulation of homopolymers AA and BB of the same molecular weight) was done by us in previous paper [2]. We used as the initial conformation for the diblock AB and for the homopolymers AA and BB the completely extended conformations in which all torsion angles are in the trans positions and studied the collapse of single copolymer (or homopolymer) molecule in vacuum. The similar approach have been used earlier in a MC simulation of the collapse-coil transition of single polymer chain by Szleifer et al. [3]. In another work, Kavasalis and Sundararajan simulated collapse of a single polyethylene (PE) chain in vacuum from all-trans initial conformation and applied the results for description of crystallisation of a single polyethylene (PE) chain from dilute solution [4]. Mattice with co-workers used the similar approach to study the collapse of single chain of poly(1,4-trans-butadiene) [5] and poly(vinyl chloride) of different lengths [6]. Choi et al. [7] used this method to study the 'miscibility' and structure of two polyethylene (PE) and polypropylene (PP) molecules placed near each other in vacuum. It was shown that the segregation of blocks into two separate PE and PP domains with small The main feature of the final collapsed structure obtained by us in [2] is that the UPE block stays in a compact state inside the PEG block. The more flexible PEG block surrounds the UPE core as a shell. We thus obtained a partial separation of the two blocks but contrary to the collapse of PE and PP entangled molecules [7] there is no segregation of UPE and PEG blocks into two separate dumb-bell like domains. The goal of the present work is to obtain more detailed information about the structure and dynamic of the final collapsed state of diblock copolymer studied by us in [2].

Model

We studied the single molecule of an UPE and PEG diblockcopolymer AB with the total molecular weight near 4000 g/mol. The PEG (A) and UPE (B) blocks of the copolymer are the same as in our previous paper [2]. Both blocks had molecular weigh near 2000 g/mol but due to different molecular weights of UPE and PEG monomers the numbers of monomers in A and B blocks were different. The PEG and UPE homopolymers of the same molecular weight (4000 g/mol) as AB copolymer were studied. (Homopolymer AA consisted of two blocks A (2000 g/mol each) and BB consisted of two blocks B (2000 g/mol each) were taken). In all cases we used as initial state the extended all-trans conformation. Simulations were fulfilled using the molecular modelling software packages InsightII and Discover from MSI [8]. The force field used was CVFF. In this forcefield the total potential energy is described by the summation of bonded and non-bonded energies. The bonded energy consists of bond, valence angle and torsion energies. The bond and bond angle distortion energies are described by quadratic functions with the equilibrium bond lengths and angles as the reference points, respectively. The torsion energy is described by a summation of cosine functions in the torsion angle defined by four consecutive atoms. Non-bonded energy includes Lennard-Jones and electrostatic energies. A Lennard-Jones 6-12 potential is used in the CVFF forcefield. We did not introduce cut off distance in these calculations. Coulombic electrostatic interaction were taken into account and partial charges were taken as they were in CVFF forcefield. The potential energy of the initial structure was minimized until the root-mean-square gradient became less than 10 kcal/mol. After the minimisation the chains in all cases remained close to all-trans conformation. Molecular dynamics simulations were performed in vacuum at the temperature 298K. For each system (AA, BB and AB) three different initial conditions (different initial velocities) were used and all results were averaged through these 3 trajectories. During the simulation the bond lengths were fixed via the RATTLE (extension of SHAKE) algorithm allowing the use of time steps from 1 to 3fs. Molecular dynamics trajectories were collected every 100 fs from a total duration of near 1000 ps. For monitoring of the structure and the shape of homo and diblock copolymers the pictures of chains were plotted every 100 ps. The total energy of the system was controlled during the simulation run. The attractive non-bond forces which extend over large distances are the driving forces for the collapse process. The situation is similar as the collapse of a polymer chain in a poor solvent. In our case the solvent is not taken into account directly but vacuum can be treated as continuos poor solvent for our systems.

Results and discussion

The MD procedure described above was applied for descriprion of diblock copolymer AB and homopolymers (UPE and PEG) collapse. The main feature of final collapsed structure is that UPE block stays in compact state inside PEG block. More flexible PEG block surrounds the UPE core as shell. In previous paper [2] it was obtained that the inter UPE block (B) is more compact in the diblock copolymer AB than in the BB homopolymer. At the same time the size of the outer PEG block (A) in diblock copolymer AB is greater than in the homopolymer AA.

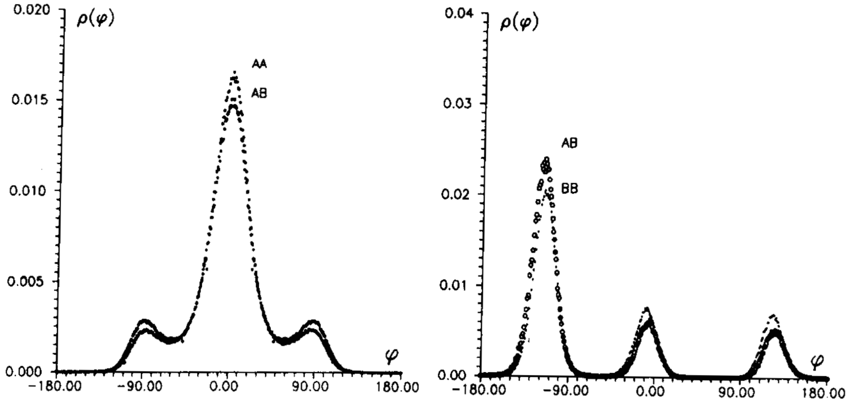


Fig.1 Distribution function of dihedral angles CCOC in diblock (solid) and in homopolymers (dashed lines): a) in PEG and b) in UPE blocks

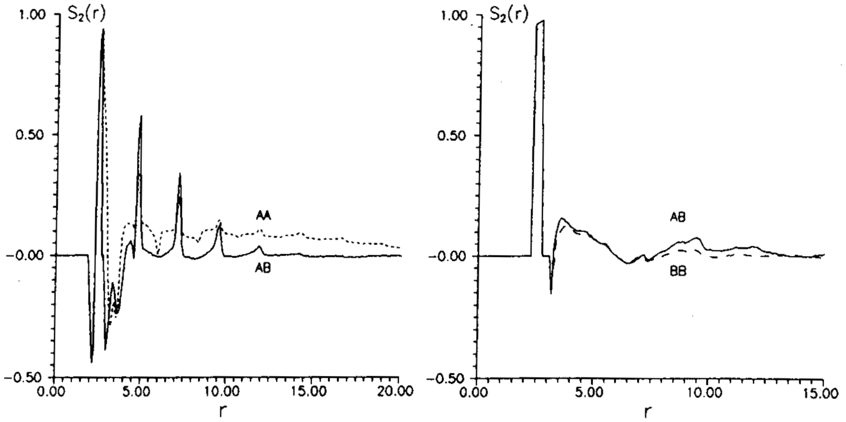
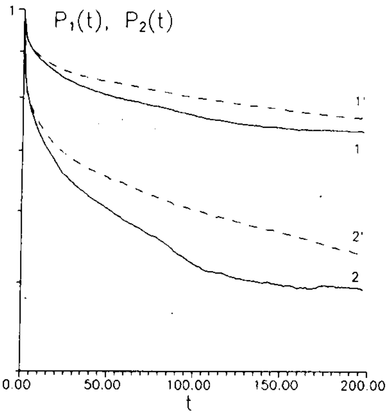


Fig.2 Orientational order $S_2(r)$ in diblock (solid) and homopolymer (dashed) at different distances r between chords: a) in PEG and b) in UPE blocks

To get more information about the internal structure of the AB diblock copolymer we calculated in the present paper also the conformational and orientational distribution functions. For distributions of dihedral angles the largest differences in diblock in comparison with homopolymer are for the CCOC dihedral angles both in PEG (Fig.1a) and UPE (Fig.1b) blocks. In both blocks the percent of trans isomers ($\varphi = 0$) decreases in the blockcopolymer in comparison with the homopolymers. The distributions of other dihedral angles did not change significantly from homopolymer to diblock.

For characterisation of the translational and orientational correlations between fragments of the main chain we calculated the pair correlation function and orientational order parameter (Fig.2) between chain 'chords' (CCO vectors along the local directions of polymer chain backbone) both in diblock AB and in homopolymers AA and BB. Comparison of radial distribution functions of PEG monomers in homopolymers and in AB blockcopolymer shows that the local translational order is more pronounced for diblock copolymers (both for A and B blocks). Orientation order $S_2(r)$ in PEG blocks (A) (Fig.2a) at small distances r is larger in the homopolymer AA than in the diblock AB. At larger distances the peaks $S_2(r)$ are more pronounced in the diblock than in the homopolymer where a constant correlation exists at all distances r . For UPE block the behavior of $S_2(r)$ functions in diblock and homopolymer is similar (Fig2b) but the order is slightly greater in the diblock. Beside the local structure we calculated also local orientational and translational mobility inside both blocks in diblock AB and in homopolymers AA and BB. Local orientational mobility was characterized by first and second order time correlation functions $P_1(t)$ and $P_2(t)$) of the same chords (CCO vectors) in diblock AB and in AA and BB (Fig.3). In diblock copolymer AB the orientational mobility of the CCO vector in the PEG block is greater than the mobility of the CCO vector in the UPE block. For the UPE block, the orientational mobility is also larger in the diblock than in the homopolymer. Local orientational mobility of the similar chords CCO of block A and block B in the diblock copolymer AB was also compared. In the PEG block (block A) the orientational mobility of chords is greater than in the UPE block. This is both due to a larger flexibility of block A compared to block B, and due to an absence of bulky side groups in the block A (PEG chain) in comparison with B block.

Local translational mobility of monomers (mean square displacements) also was calculated separately for both blocks in AB and in homopolymers (in AA and BB). It was obtained that in blockcopolymer it is higher than in homopolymers both for UPE and PEG monomers (Fig.4). In diblock AB the translational mobility of PEG block is essentially larger than mobility of UPE block. It correlate very well with flexibility of blocks and with structure of diblock AB obtained in [2]: UPE block is always inside total structure and due to this reason has smaller translational mobility.



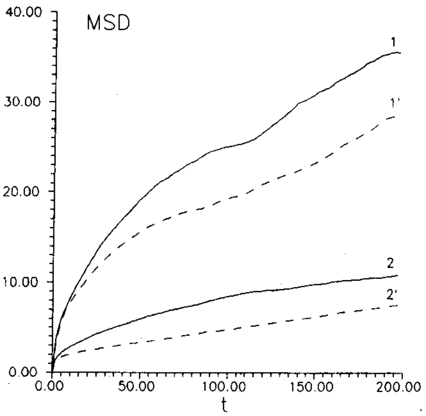


Fig.3 Time correlation function of first $P_1(t)$ (1,1') and second $P_2(t)$ (2,2') order for the chords CCO in diblock AB - (1,2) and in homopolymer AA - (1',2') at different distances between chain chords

Fig.4 Mean square displacements of monomers in blocks A (1) and block B (2) of diblock AB and of the same monomers in homopolymers:AA (1') and in BB (2')

Conclusions

The collapsed structure of the diblock copolymer containing UPE and PEG blocks were studied by atom-based molecular dynamics simulation. The static and dynamic properties of final core and shell structure were studied. It was obtained that the differences in torsion angle distributions between diblock and homopolymer are maximal for CCOC dihedral angles (both in UPE and PEG blocks) and number of trans isomers in both blocks is smaller in diblock. The orientational order inside both blocks is larger in diblock. Local orientational mobility of CCO 'chord' vectors is larger in the diblock than in the homopolymer for both blocks. Local translational mobility of monomers in the blockcopolymer is also higher than in the homopolymers (both for UPE and PEG monomers). In the diblock the translational mobility of the outer PEG block is essentially larger than the mobility of the UPE block which is inside the diblock. Thus all calculated characteristics of the final structures of UPE and PEG diblock copolymer AB are in accordance with a core and shell model for a collapsed UPE-PEG diblock copolymer as proposed in our previous work [2].

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