DOI: 10.14529/jsfi180319

Reverse Mapping Algorithm for Multi-scale Numerical Simulation of Polylactic Acid

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An algorithm is proposed to convert the coarse-grained A-graft-B model of polylactic acid into the atomistic representation. In the A-graft-B model the atoms of the backbone are mapped onto A beads, which form the linear backbone of the coarse-grained macromolecule, the methyl groups are mapped onto B side pendants. The algorithm restores atomic positions based on positions of coarse-grained beads with the help of pre-defined chain fragments, called templates. The dimensions of the templates are adjusted by affine transformation to ensure coincidence of the backbone in coarse-grained and atomistic representation. The transition between coarse-grained and atomistic models conserves information about the fine structure of polymer chains. The restored configurations are suitable for further molecular-dynamic simulations. Both atomistic and coarse-grained representations require standard GROMACS software. The algorithm can be used for reverse mapping of other A-graft-B polymer models.

Keywords: molecular dynamics, multiscale simulation, reverse mapping, poly(lactic acid).

Introduction

Polylactic acid (PLA) is a biocompatible, biodegradable polymer which can be cheaply produced in industrial quantities from renewable resources [7]. To bring it on equal footing with the currently used petroleum-based plastics, its mechanical and barrier properties need to be tuned [2]. In pure PLA and in mixtures with its oligomers (OLA) these depend on stereosequence and molecular weight of the chains. Identical structure of the monomer units in short and long PLA chains complicates the experimental analysis of the materials and makes computer simulations an indispensable tool for their guided development. The simulations of deformation, diffusion, and crystallization require large timescales and determine the applicability of the multi-scale approach [4, 6]. The latter includes coarse-grained simulations using specially tailored models and requires efficient algorithms for switching between the coarse-grained and atomistic representations. In the previous paper [3] we proposed an A-graft-B coarse-grained model of PLA, with each monomer unit represented by an A-B dumbbell. The assignment of separate side pendant for the methyl group allowed explicit treatment of the PLA stereosequence. The macroscopic and microscopic properties of the systems calculated using the coarse-grained model closely resemble those calculated using atomistic simulations for both polymer and oligomer melt in a wide range of temperatures [3].

1. A-graft-B Model

The mapping scheme of the coarse-grained model [3] is shown in Fig. 1. It determines the mutual correspondence of atom groups and coarse-grained beads. The atoms of the backbone, including the attached hydrogens and ester groups, are mapped onto A beads, which form the linear backbone of the coarse-grained macromolecule. Each methyl group is mapped onto a B bead, which is connected to the A bead as side pendant. To make the A beads closer to the

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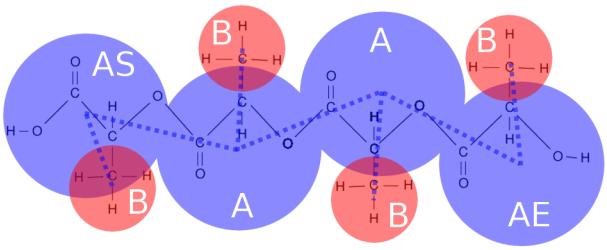

Figure 1. Mapping scheme of A-graft-B model of PLA

corresponding B beads, the backbone is chunked into A beads across the ester groups. The extra atoms at the ends of the chains are incorporated into the terminal A beads. The latter are assigned special types AS (start) and AE (end). The force-field of the coarse-grained model was derived to fit the parameters of atomistic simulations of OLA melt [5]. The simulations using the coarse-grained model were performed using an unmodified version of GROMACS [1] on "Lomonosov-2" supercomputer [8]. It was shown [3] that the coarse-grained model provides a 17-fold speedup compared with atomistic calculations.

2. Reverse Mapping

2.1. Structure Restoration

The atomistic structure was restored based on positions of coarse-grained beads with the help of monomer-scale structure fragments (templates). The templates included atomic coordinates and the positions of A and B coarse-grained beads calculated as centers of masses of the corresponding atoms according to the forward mapping procedure [3].

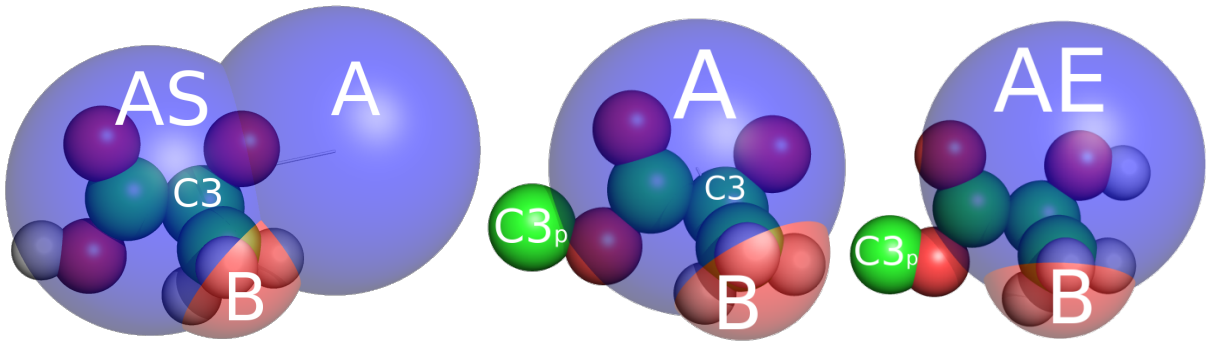

Figure 2. Template for start unit (left), middle unit (center), and end unit (right)

The templates for the start, middle, and end monomer units are shown in Fig. 2. The starting template also included the position of the next (second) coarse-grained A bead required for alignment of the atomistic structure. The reverse mapping was carried out for one chain at a time. For each of the chains, the restoration of the atomistic structure was performed sequentially and began with the start unit. The AS bead of the starting template (Fig. 2, left) was superimposed on AS bead of the coarse-grained configuration and served as a fixed anchor. The template was then rotated around AS bead so that the AS-A axis of the template was aligned with the corresponding axis of the coarse-grained configuration. The dimensions of the template were adjusted by affine transformation along the AS-A axis to ensure coincidence of A beads. After that, the template was rotated around the AS-A axis to orient the AS-B bond of the template in accordance to the AS-B bond of the coarse-grained configuration. As a result

of the procedure, the positions of the atoms of the first monomer unit of PLA were established. The templates for middle and end monomer units additionally contained the carbon atom of the previous monomer unit (denoted as C3p). As the first step of monomer restoration, the C3p atom of the template was superposed directly onto the C3 (shown in green) atom of the previous, already restored monomer. The procedures described above for the start unit (fitting, affine transformation, and AS-B orientation) were repeated for all monomer units with C3p/C3 atom serving as an anchor. The procedure ensured positioning of coarse-grained A beads of the templates precisely at positions of A beads of the coarse-grained system and correct orientation of methyl groups. The algorithm was applied in turn for each of the macromolecules.

2.2. Eqilibration

The restored atomistic structures underwent steep descent energy minimization using GROMACS with a step size of 10^{-5} to reduce the maximum force to 200 kJ/mol/nm. After that, the system was equilibrated in several steps first at constant volume and then at the constant pressure of 1 bar. The timestep of the molecular dynamics simulation was gradually increased from 10^{-6} ps to 10^{-3} ps. The total equilibration time of the system was around 100 ns.

2.3. Verification

To check the validity of the reverse mapping algorithm, we compared the macroscopic and microscopic parameters of the system containing 113 OLA molecules during atomistic and coarse-grained simulations. By the end of the equilibration the properties of the system, such as melt density, the energies of excluded volume and electrostatic interactions, as well as that of bonds, angles and dihedrals were within the margin of error of the corresponding values in the original atomistic simulation run. The gyration radius of the OLA chains, which was slightly different in the coarse-grained model, was restored to the original value observed in atomistic simulations (see Tab. 1).

Table 1. Properties of OLA melt in original atomistic, CG, and restored atomistic simulations

Parameter	Original AA	CG	Restored AA
Melt density	968.6 ± 1.0	968.2 ± 0.5	967.8 ± 1.2
Gyration radius	0.889 ± 0.004	0.899 ± 0.001	0.887 ± 0.004

Conclusions

We completed the stack of algorithms for multiscale simulation of PLA by presenting a reverse mapping procedure for translation of coarse-grained A-graft-B model of PLA into atomistic representation. Both atomistic and coarse-grained representations require standard GROMACS software, and the simulations can be carried out in parallel on supercomputers. The equilibration time of the restored atomistic samples is 0.1 μs which is several orders of magnitude lower than the characteristic times of the processes which can be simulated in coarse-grained representation. The restored atomistic configurations are suitable for further molecular-dynamic simulations and detailed analysis.

Acknowledgments

The research is carried out using the equipment of the shared research facilities of HPC computing resources at Lomonosov Moscow State University supported by the project RFMEFI62117X0011 [8].

The research was supported by Russian Foundation for Basic Research, project No. 17-03-00742.

References

1. Abraham, M.J., Murtola, T., Schulz, R., Páll, S., Smith, J.C., Hess, B., Lindahl, E.: Gromacs: High performance molecular simulations through multi-level parallelism from laptops to supercomputers. SoftwareX 1-2, 19–25 (2015), DOI: 10.1016/j.softx.2015.06.001

2. Burgos, N., Tolaguera, D., Fiori, S., Jimenez, A.: Synthesis and characterization of lactic acid oligomers: Evaluation of performance as poly(lactic acid) plasticizers. Journal of Polymers and the Environment 22(2), 227–235 (2014), DOI: 10.1007/s10924-013-0628-5

3. Glagolev, M., Glova, A., Mezhenskaia, D., Falkovich, S., Larin, S., Vasilevskaya, V., Lyulin, S.: Coarse-grained a-graft-b model of poly(lactic acid) for molecular dynamics simulations. Journal of Polymer Science Part B: Polymer Physics 56(7), 604–612 (2018), DOI: 10.1002/polb.24567

4. Glagolev, M.K., Lazutin, A.A., Vasilevskaya, V.V., Khokhlov, A.R.: Influence of cross-linking rate on the structure of hypercrosslinked networks: Multiscale computer simulation. Polymer 86, 168–175 (2016), DOI: 10.1016/j.polymer.2016.01.040

5. Glova, A.D., Falkovich, S.G., Larin, S.V., Mezhenskaia, D.A., Lukasheva, N.V., Nazarychev, V.M., Tolmachev, D.A., Mercurieva, A.A., Kenny, J.M., Lyulin, S.V.: Poly(lactic acid)-based nanocomposites filled with cellulose nanocrystals with modified surface: All-atom molecular dynamics simulations. Polymer International 65(8), 892–898 (2016), DOI: 10.1002/pi.5102

6. Lazutin, A.A., Glagolev, M.K., Vasilevskaya, V.V., Khokhlov, A.R.: Hypercrosslinked polystyrene networks: An atomistic molecular dynamics simulation combined with a mapping/reverse mapping procedure. Journal of Chemical Physics 140(13) (2014), DOI: 10.1063/1.4869695

7. Maria Laura Di Lorenzo, R.A. (ed.): Synthesis, Structure and Properties of Poly(lactic acid). Advances in Polymer Science, Springer (2018), DOI: 10.1007/978-3-319-64230-7

8. Sadovnichy, V., Tikhonravov, A., Voevodin, V., Opanasenko, V.: "Lomonosov": Supercomputing at Moscow State University. In: Contemporary High Performance Computing: From Petascale toward Exascale. pp. 283–307. Chapman & Hall/CRC Computational Science, CRC Press, Boca Raton, United States (2013)