

Monte Carlo Study of Triblock Self-Assembly by Cooperative Motion Algorithm

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Abstract: We perform a comprehensive Monte Carlo study of the ABA triblock self-assembly by the Cooperative Motion Algorithm. Our attention is focused on three series of triblocks which are grown from parent AB diblocks of varying asymmetry. Unlike the previous studies in which the total length of the chain varies upon growing the terminal A-block, here we keep the fixed chain length for a given series. Moreover, we determine the order-disorder transition temperature as the τ parameter (being the ratio of the grown A-block to the length of the parent diblock) increases. In this case we find that the order-disorder transition temperature monotonically decreases for two asymmetric series which is different from the non-monotonic depression of T_{ODT} reported previously. We also construct a phase diagram which shows a variety of nanostructures as τ is increased.

Key words: Monte Carlo, triblock copolymers, Cooperative Motion Algorithm

I. INTRODUCTION

Block copolymer self-assembly still poses an interesting research topic [1]. Block copolymers self-assemble via the order-disorder transition which can be characterized by a well-defined temperature, referred to as the order-disorder transition temperatures, T_{ODT} , which marks the onset of the long-range order and formation of well-defined nanophases.

In this paper we intend to study the A_1 -B- A_2 triblock copolymer melt using the lattice Monte Carlo simulations. In [2] we investigated the ODT attributes of molecularly asymmetric monodisperse triblock copolymer melts by systematically varying molecular composition and asymmetry, starting with the given parent diblock and adding the second

A-block with systematically increasing length. Comparison of our simulation results with experimental data [3] yielded favorable agreement. We have successfully shown that (i) the reduced ODT temperatures acquired from MC simulations obey trends that are qualitatively similar to those observed experimentally, and (ii) the ODT temperature for molecularly asymmetric triblock copolymers with a short terminal block is, in fact, depressed. Here we follow the same procedure; however, varying molecular composition and asymmetry is limited by maintaining the constant chain length. We will demonstrate that in this case the competition between the chain length and its composition leads to more complex variations of the order-disorder temperature compared with the previous fixed-length parent diblock case.

II. METHOD

The Cooperative Motion Algorithm (CMA) [4–8], based on a face-centered cubic (fcc) lattice, is used to simulate the di-/triblock melts. The CMA allows the simulation of a dense copolymer melt on an fcc lattice with the standard periodic boundary conditions. The lattice is completely occupied by monomers, and the monomers in each chain are connected by the bonds of constant length which are not allowed to be broken or stretched. The chains satisfy the excluded volume condition. A dense system of block copolymer chains is moved by cooperative rearrangements. These moves are strictly cooperative, as in the dense system all lattice sites are occupied, and a segment of one chain can only move if other segments move simultaneously. In Fig. 1 the representative CMA moves are presented.

We apply standard MC simulations with the Metropolis algorithm [9] as well as the parallel tempering (PT) method [10–12]. In the PT case, M replicas of systems are simulated in parallel, each in different temperature T_i 's with i ranging from 1 to M . After 5000 MC steps we try to exchange replicas with neighboring T_i 's in a random order with probability,

$$p(T_i \leftrightarrow T_{i+1}) = \min\{1, \exp[-(\beta_i - \beta_{i+1})(U_{i+1} - U_i)]\}, \quad (1)$$

where $\beta_i = 1/kT_i$ and U_i is the potential energy of the replica at T_i . This method offers efficient equilibration at low temperatures. We repeat the experiment at least three times starting with different initial configurations in which the polymer chains assume statistical conformations and random orientations and are uniformly distributed within the simulation box. A single MC step is defined as an attempt to move a given segment. Usually, the first half of the run is used to equilibrate the system, and the second one is used to collect the data. The results are averaged over all simulation runs. We use the following set of interaction energies which are limited to the nearest neighbors,

$$\epsilon_{AB} = \epsilon, \quad (2)$$

$$\epsilon_{AA} = 0, \quad (3)$$

$$\epsilon_{BB} = 0, \quad (4)$$

where ϵ is an energy unit and we define the reduced energy per lattice site and the reduced temperature as

$$\frac{E^*}{n_a} = \frac{E/\epsilon}{n_a}, \quad (5)$$

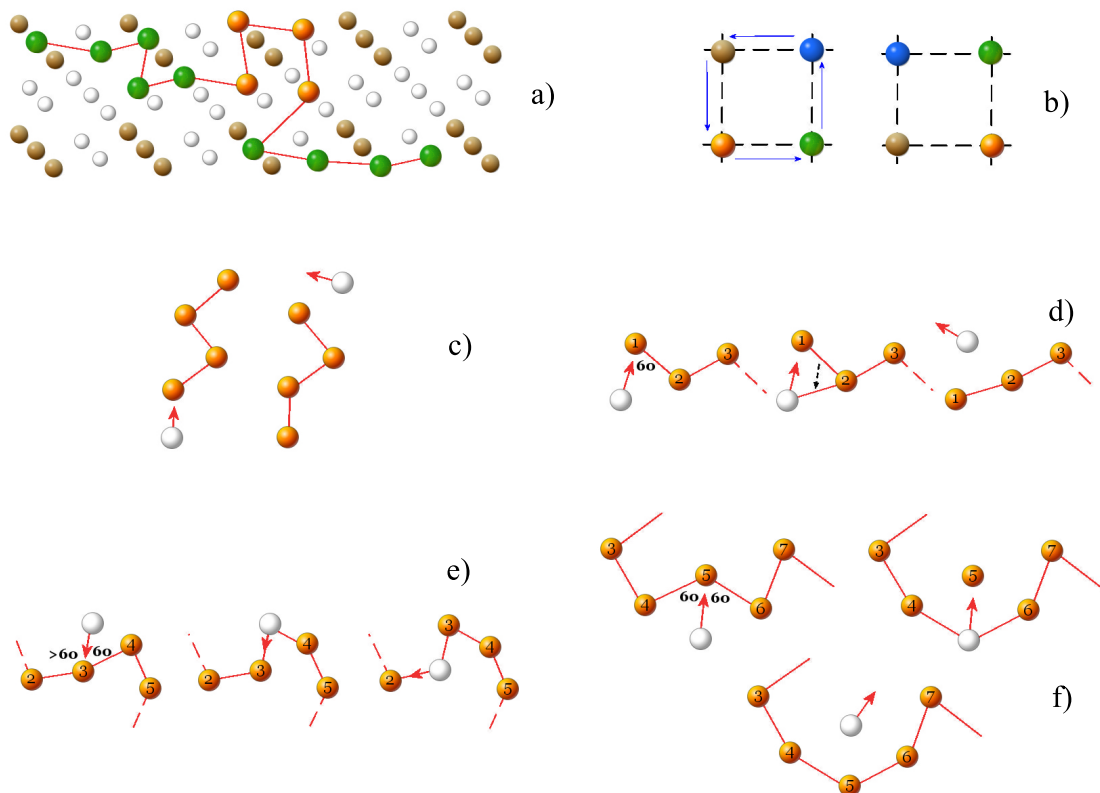


Fig. 1. Cooperative Motion Algorithm: (a) a representative triblock copolymer conformation on the FCC lattice, (b) the general idea of the cooperative motion; (c) reptation motion, (d) rotation of the terminal bond, (e) cooperative displacement of part of the chain, (f) kink-type rotation

$$T^* = \frac{kT}{\epsilon}. \quad (6)$$

On the basis of considerations presented in Ref. [13], we can relate T^* used in this paper to the Flory χ parameter employed in the self-consistent field theory [14] by the following approximate equation:

$$\chi = \frac{7.5}{T^*}. \quad (7)$$

The above equation can also be used in order to relate theoretical T^* 's to experimental χ 's. Although we do not provide any direct link to experimental data in this paper, it is well established that the method which we use gives at least a qualitative agreement with the experimental data as, for example, the order-disorder temperature depression for highly asymmetric polystyrene-polyisoprene-polystyrene triblocks [2] and surprising phase diagrams for nearly symmetric poly(styrenesulfonate)-polymethylbutylene (PSSPMB) [14] also for asymmetric PSS-PMB [15].

The CMA simulations were carried out for the set of monodisperse A_1 -B- A_2 triblock copolymer melts with chain length, $N = 52$. This set was specified in a τ - β parameter space defined as follows. The ratio of length of A-blocks with respect to the parent diblock one (A_2) is denoted by τ which is expressed by the following equation:

$$\tau = \frac{N_{A_2}}{N_{A_1} + N_{A_2}}. \quad (8)$$

Moreover, the parent diblock asymmetry parameter is described by β which is expressed below:

$$\beta = N_B/N_{A_2}, \quad (9)$$

where B- A_2 is the parent diblock.

III. RESULTS AND DISCUSSION

The list of all simulated systems is summarized in Tabs. 1–3 by β parameter. For each system, we performed three independent simulations using the parallel tempering (PT) method in the temperature range from above the order-disorder transition (ODT) to the temperatures deep in the strong segregation limit (SSL).

First, in Fig. 2 we present the dependence of $T_{ODT,r}$ on τ for three cases considered in this study, with β 's as (a) $\beta = 1$, (b) $\beta = 2$, and (c) $\beta = 3$. The reference $T_{ODT,r}$ is defined by:

$$T_{ODT,r}(\tau) = \frac{T_{ODT}(\tau)}{T_{ODT}(\tau = 1)}, \quad (10)$$

where $T_{ODT}(\tau = 1)$ is the order-disorder temperature of a given parent diblock. We can see that the non-monotonic order-disorder depression is noticeable only in the case of

significant parent diblock asymmetry $\beta = 3$, as shown previously [3].

Next, we rescale the reference order-disorder temperature, $T_{ODT,r}$, taking into account the length of the parent diblock (B- A_2), and thus the impact of actual diblock length on the order-disorder temperature. We have therefore introduced a new parameter given by:

$$T_{ODT,rs}(\tau) = \frac{T_{ODT}(\tau)}{T_{ODT}(\tau = 1) \frac{N_B(\tau) + N_{A_2}(\tau)}{N_B(\tau=1) + N_{A_2}(\tau=1)}}. \quad (11)$$

In Fig. 3 we show $T_{ODT,rs}$ as a function of τ for three values of parent diblock asymmetry parameter: (a) $\beta = 1$, (b) $\beta = 2$, and (c) $\beta = 3$. In this case, we can clearly see

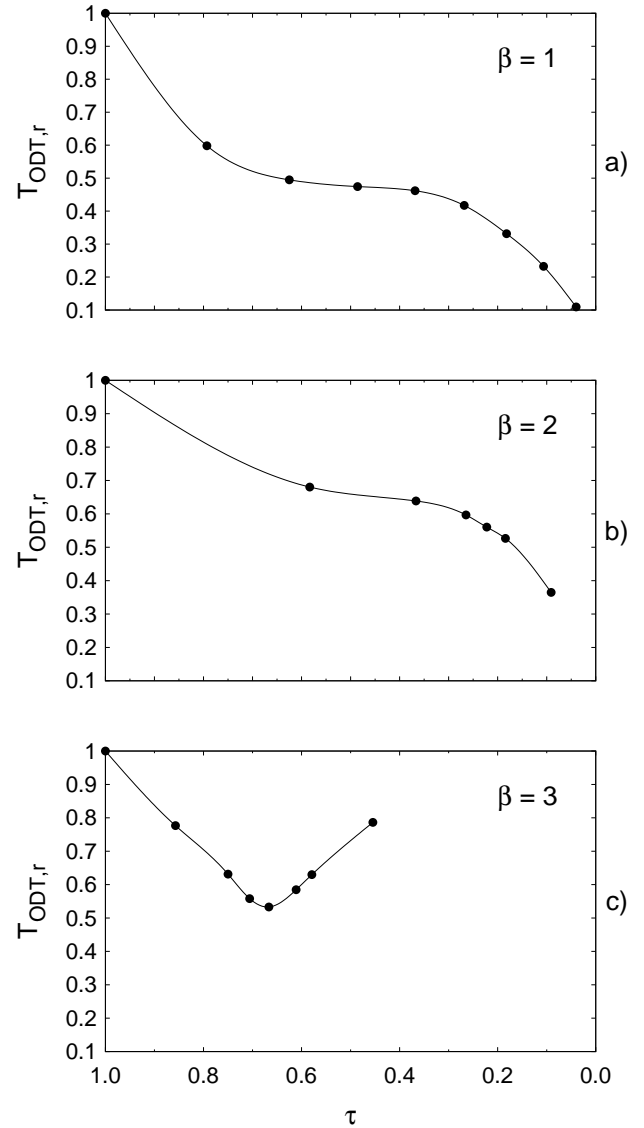


Fig. 2. Dependence of $T_{ODT,r}$ (T_{ODT} normalized to the value of the parent diblock of length N , $\tau = 1$) on τ for three values of parent diblock asymmetry parameter: (a) $\beta = 1$, (b) $\beta = 2$, and (c) $\beta = 3$ considered in this study

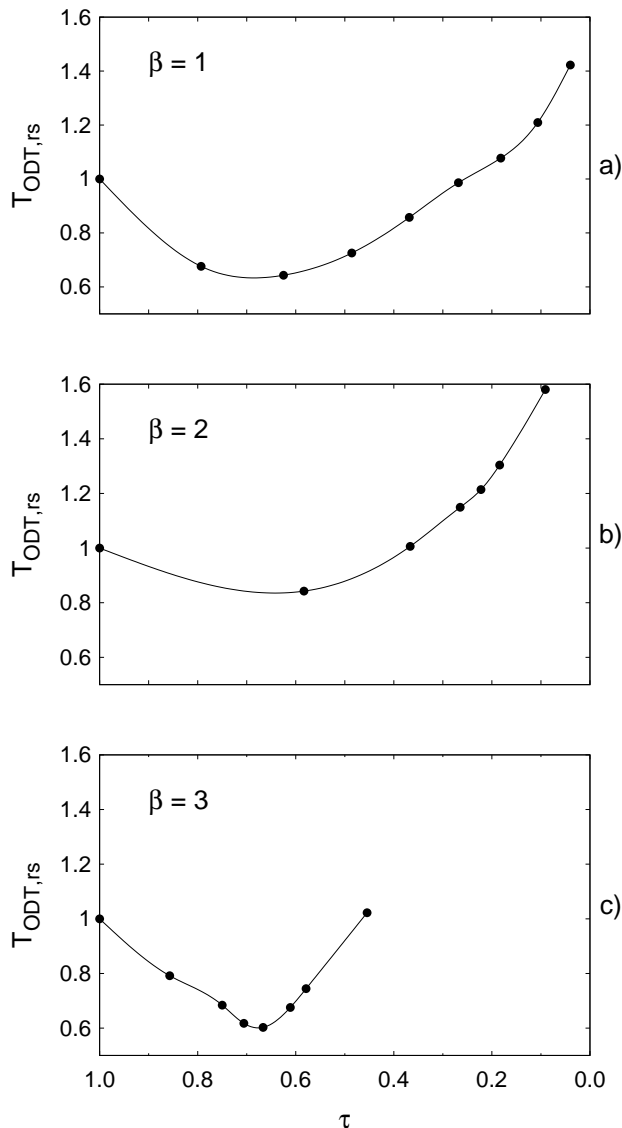


Fig. 3. $T_{ODT,rs}$ (T_{ODT} normalized to the value of the parent diblock for a given τ) as a function of τ for three values of parent diblock asymmetry parameter: (a) $\beta = 1$, (b) $\beta = 2$, and (c) $\beta = 3$

that the non-monotonic depression exists for all considered β cases.

In Fig. 4 an outline of phase diagrams for simulated copolymer melts listed in Tabs. 1–3 is shown. We observe a variety of nanostructures i.e. lamellar (L), gyroid (G), hexagonally packed cylinders (HPC), perforated lamellar (PL), rods (R), Y-channels (Y), continuous (1C), and micellar (M). In a few cases we observe the presence of two morphologies simultaneously, e.g. R/Y. Fig. 5 is a compilation of snapshots of several selected morphologies: (a) lamellar, L, 10-28-14, $T^* = 5.13$; (b) perforated lamellar, PL, 7-34-11, $T^* = 6.92$; (c) hexagonally packed cylinders, HPC, 4-36-12, $T^* = 6.14$; (d) gyroid, G, 18-17-17, $T^* = 5.13$; (e) rods and y-channels, R/Y, 40-8-4, $T^* = 3.5$; (f) micelles, M, 48-2-2, $T^* = 1.45$.

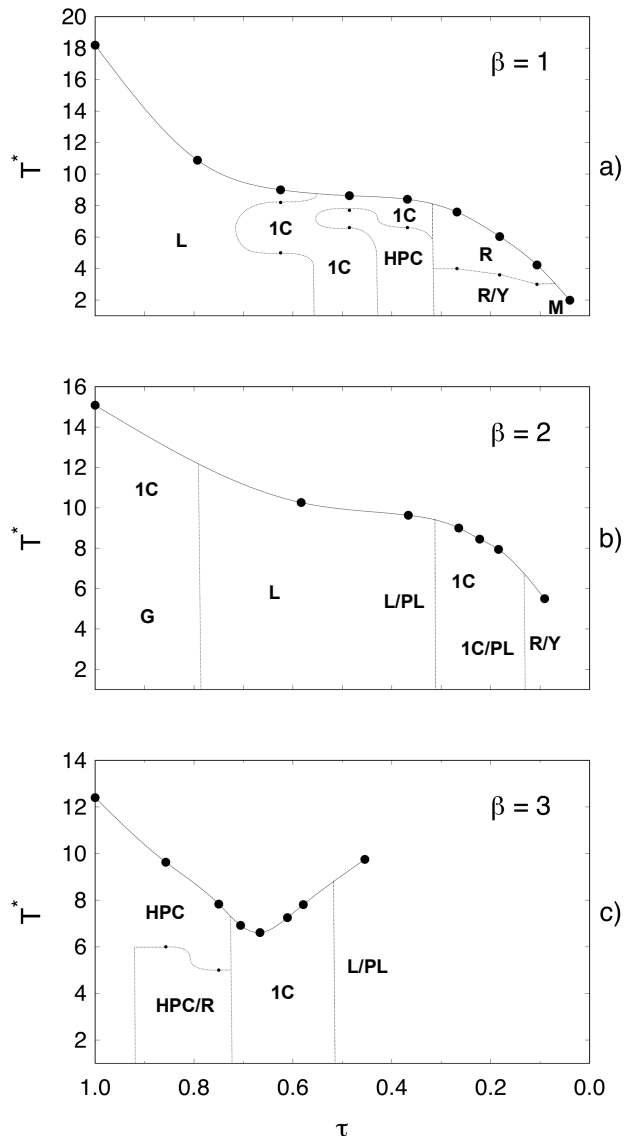


Fig. 4. An outline of phase diagrams for simulated copolymer melts listed in Tabs. 1–3

IV. CONCLUSIONS

We performed a comprehensive Monte Carlo study of ABA triblocks. Our attention was focused on three series of ABA triblocks which were grown from parent AB diblocks of varying asymmetry. Unlike the previous studies in which the total length of the chain varies, here we kept the fixed chain length for a given series. Moreover, we determined the order-disorder transition temperature as the τ parameter (being the ratio of the grown A-block to the length of the parent diblock) increases. In this case we find that the order-disorder transition temperature monotonically decreases for two asymmetric series which is different from the non-monotonic depression of T_{ODT} reported previously. We also constructed a phase diagram which shows a series of nanostructures as τ is increased.

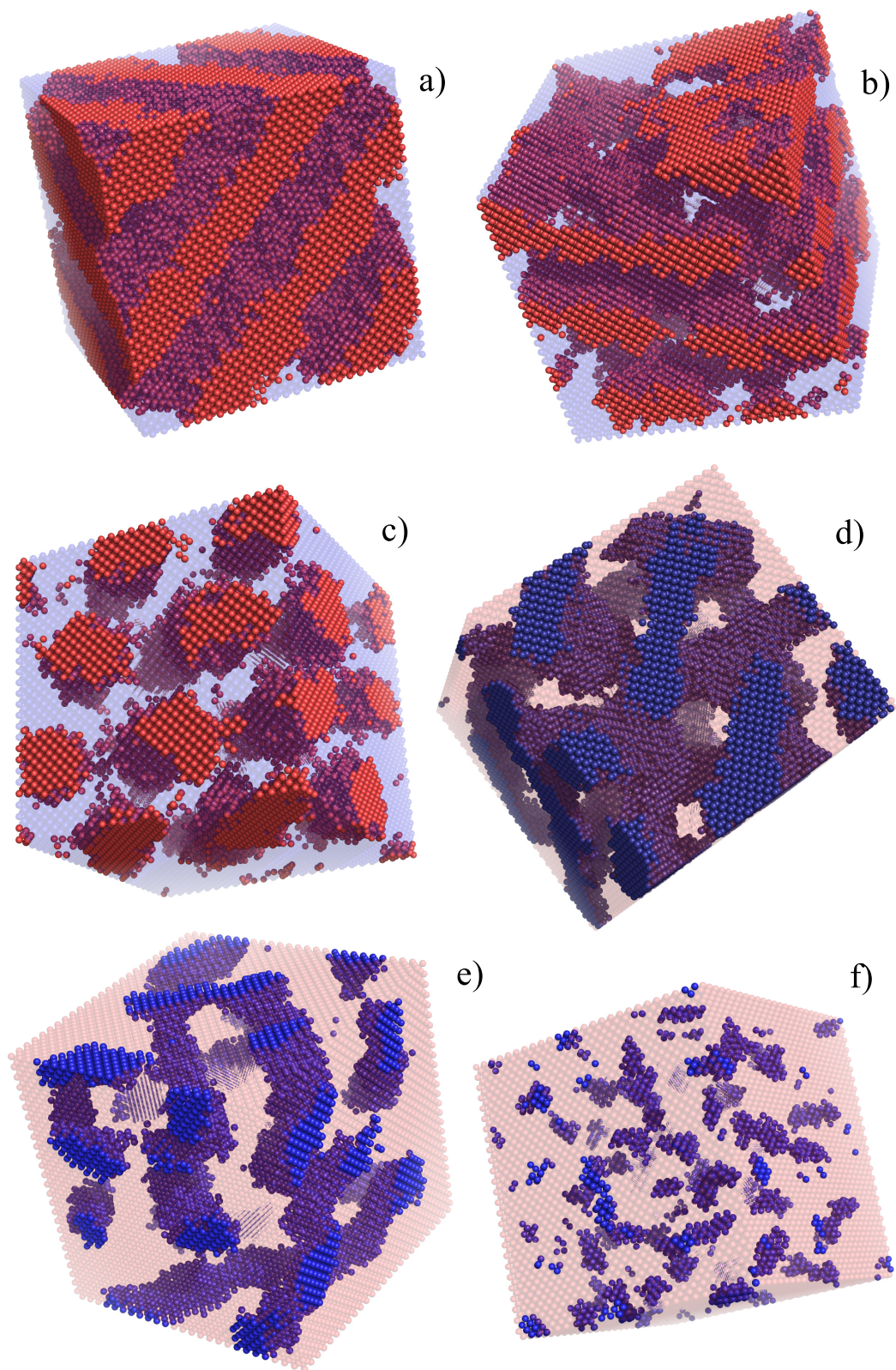


Fig. 5. Snapshots of selected representative nanostructures: (a) lamellar, L, 10-28-14, $T^* = 5.13$; (b) perforated lamellar, PL, 7-34-11, $T^* = 6.92$; (c) hexagonally packed cylinders, HPC, 4-36-12, $T^* = 6.14$; (d) gyroid, G, 18-17-17, $T^* = 5.13$; (e) rods and Y-channels, R/Y, 40-8-4, $T^* = 3.5$; (f) micelles, M, 48-2-2, $T^* = 1.45$

Tab. 1. List of selected parameters of simulated copolymer melts for parent diblock asymmetry parameter, $\beta = 1$

τ	chain microarchitecture	f_A
1.00	0-26-26	0.50
0.79	6-23-23	0.56
0.63	12-20-20	0.62
0.49	18-17-17	0.67
0.37	24-14-14	0.73
0.27	30-11-11	0.79
0.18	36-8-8	0.85
0.11	42-5-5	0.92
0.04	48-2-2	0.96

Tab. 2. Selected parameters of simulated copolymer melts for parent diblock asymmetry parameter, $\beta = 2$

τ	chain microarchitecture	f_A
1.00	0-35-17	0.32
0.58	10-28-14	0.50
0.37	19-22-11	0.58
0.27	25-18-9	0.65
0.22	28-16-8	0.69
0.18	31-14-7	0.73
0.09	40-8-4	0.85

Tab. 3. List of parameters of simulated copolymer melts for parent diblock asymmetry parameter, $\beta = 3$

τ	chain microarchitecture	f_A
1.00	0-39-13	0.25
0.86	2-39-12	0.27
0.75	4-36-12	0.31
0.71	5-35-12	0.33
0.67	6-34-12	0.35
0.61	7-34-11	0.35
0.58	8-33-11	0.37
0.46	12-30-10	0.42

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