# Polymer chain generation for coarse-grained models using radical-like polymerization

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A versatile method is proposed to generate configurations of coarse-grained models for polymer melts. This method, largely inspired by chemical "radical polymerization," is divided in three stages: (i) *nucleation* of radicals (reacting molecules caching monomers), (ii) *growth* of chains within a solvent of monomers and (iii) *termination*: annihilation of radicals and removal of residual monomers. The main interest of this method is that relaxation is performed while chains are generated. Pure mono and polydisperse polymer melts are generated and compared to the configurations generated by the *push off* method from Auhl *et al.* [J. Chem. Phys. **119**, 12718 (2003)]. A detailed study of the static properties (radius of gyration, mean square internal distance, entanglement length) confirms that the *radical-like* polymerization technique is suitable to generate equilibrated melts. Moreover, the method is flexible and can be adapted to generate nanostructured polymers, namely, diblock and triblock copolymers. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2936839]

# **I. INTRODUCTION**

Molecular simulation is becoming an increasingly popular tool for the investigation of mechanical and thermomechanical properties of polymer materials. It can be applied to investigate the properties of homopolymer systems as well as to generate nanostructured copolymers or polymer based nanocomposites, and to gain a microscopic understanding of the properties of these technologically important materials.

The main issue is to understand relations between polymer nanostructure and mechanical properties. In order to bridge the gap between micro- and macroscales, coarsegrained molecular dynamics, where each "bead" represents several monomers, is becoming a standard tool. They allow for an investigation of qualitative and quantitative issues not directly accessible to experiments, while remaining affordable in terms of computational costs.

Investigating structure-property relations in polymeric systems requires the preparation of equilibrated melts with long and entangled chains. Above the glass transition, equilibrium can, in principle, be achieved using long molecular dynamics (MD) or Monte Carlo (MC) simulations. However, computational time severely increases in two cases: (i) when long chains are involved (chain length drastically increases reptation times) and (ii) when nanostructured phases are involved (the genesis of the nanostructure by demixtion or crystallization requires huge computational times).

For long polymer chains, hybrid methods combining MD and MC, in particular, the so-called "double bridging"

algorithm,<sup>1</sup> have been used to generate well equilibrated melts. These algorithms, apart from their technical complexity, are not particularly well suited for extension to more complex architectures.

The objective of our contribution is to propose a method for polymer chain generation. This method is an extension of the pioneer work of Gao.<sup>2</sup> It is (i) based on a realistic approach close to radical polymerization;<sup>3,4</sup> (ii) is particularly adapted to generate nonlinear architectures (branched polymers, star polymers, copolymers,...) and/or polydisperse chains, and (iii) provides equilibrated melts. The main idea of *radical-like polymerization* is that chains are partially relaxed simultaneously while polymerization is achieved.

This method, called "radical-like polymerization" will be tested on different system types (mono- and polydisperse homopolymers). It will be also compared to more the classical *push off* methods,<sup>5,6</sup> which are based on a two steps process: (i) random Gaussian chain generation and (ii) equilibration. Systems resulting from step (i) are usually quite far from equilibrium as chain interactions are not taken into account, thus requiring long equilibration times [step (ii)].

The manuscript is organized as follows. Section II describes the method. In Sec. III, we apply the method to several types of homopolymer melts, and show how it can be tuned to obtained well equilibrated melts at a reasonable computational cost. Finally, we point out in Sec. IV that the radical-like polymerization method is suitable for simulating block copolymers.

### II. DESCRIPTION OF SYSTEMS AND METHODOLOGY

Our simulations are carried out for a well established coarse-grained model<sup>6</sup> in which the polymer is treated as a chain of  $N=\sum_{\alpha}N_{\alpha}$  beads (where  $\alpha$  denotes the species for

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block copolymers). Monomers of mass m=1 are connected by a spring to form a linear chain. The beads interact with a classical Lennard-Jones (LJ) interaction

$$U_{\rm LJ}^{\alpha\beta}(r) = \begin{cases} 4\epsilon_{\alpha\beta} [(\sigma_{\alpha\beta}/r)^{12} - (\sigma_{\alpha\beta}/r)^6] & r \le r_c \\ 0, & r \ge r_c, \end{cases}$$
(1)

where  $r_c=2.5\sigma_{\alpha\beta}$  is the cutoff distance,  $\alpha$  and  $\beta$  represent the chemical species (e.g., monomers before polymerization  $\equiv$  solvent *s*, polymer *A*, polymer *B*,...). In addition to Eq. (1), adjacent monomers along the chains are coupled through the well known anharmonic finite extensible nonlinear elastic (FENE) potential

$$U_{\text{FENE}}(r)^{\alpha} = \begin{cases} -0.5k^{\alpha}R_{0}^{\alpha 2}\ln(1-(r/R_{0}^{\alpha})^{2}) & r \leq R_{0} \\ \infty, & r > R_{0}. \end{cases}$$
(2)

In the following, we will be only interested in semiflexible chains for which no angular potential is imposed.

The parameters are identical to those given in Ref. 6, namely,  $k^{\alpha}=30\epsilon_{\alpha\alpha}/\sigma_{\alpha\alpha}^2$  and  $R_0^{\alpha}=1.5\sigma_{\alpha\alpha}$ , chosen so that unphysical bond crossings and chain breaking are avoided. All quantities will be expressed in terms of length  $\sigma_{AA}=\sigma$ , energy  $\epsilon_{AA}=\epsilon$ , and time  $\tau_{LJ}=\sqrt{m\sigma^2/\epsilon}$ .

Newton's equations of motion are integrated with velocity-Verlet method and a time step  $\delta t$ =0.006. Periodic simulation cells containing *M* chains of size *N* were used under a Nosé–Hoover barostat, i.e., in the *NPT* ensemble. The pressure is fixed to *P*=0.5 $\epsilon/\sigma^3$  (cubic simulation box). In the particular case of lamellar block copolymer, an isobaric Nosé–Hoover barostat is used, leading to  $P_x = P_y = P_z = P = 0.5\epsilon/\sigma^3$ , leading to a tetragonal simulation box.

### A. Radical-like polymerization

# 1. Algorithm

The radical-like polymerization method is inspired by the radical polymerization reaction, which is composed of three stages:

- *starting*, wherein a radical (active molecule that interacts with monomers) is created by an active molecule  $A(A \rightarrow P^*)$  and interacts with a first monomer  $P^* + M \rightarrow PM^*$ ;
- *propagation*, wherein the radical captures a new monomer and moves to the chain end  $PM^*+M \rightarrow PMM^*$ ; and
- termination, in which four main mechanisms can usually be identified in polymerization reactors: (i) two radicals can annihilate leading to two separated polymer chains  $(PM \cdots M^* + PM \cdots M^* \rightarrow PM \cdots M + PM \cdots M)$  (disproportination); (ii) two radicals can annihilate leading to one polymer chain  $(PM \cdots M^* + PM \cdots M^* \rightarrow PM \cdots Mm \cdots MP)$  (coupling); (iii) a radical can be transferred to another monomer leading to a new growing chain (transfer) or annihilated by some defect. Radicals can also remain active and chain growth is stopped only when all monomers have been consumed, as in (living polymerization).

TABLE I. Relevant parameters used in the *radical-like polymerization al*gorithm.

| Parameters Signification |   |  |  |  |  |
|--------------------------|---|--|--|--|--|
| N <sub>monom</sub>       | Total number of beads in the simulation box               |  |  |  |  |
| Μ                        | Total number of chains                                    |  |  |  |  |
| $N_i$                    | Final length for a chain <i>i</i>                         |  |  |  |  |
| Ν                        | Desired chain length for monodisperse systems             |  |  |  |  |
| р                        | Nucleation probability                                    |  |  |  |  |
| Ngrowth                  | Number of growth steps                                    |  |  |  |  |
| n <sub>bG</sub>          | Amount of MD steps between each growth step               |  |  |  |  |
| n <sub>eq</sub>          | Number of MD steps during equilibration stage             |  |  |  |  |
| n <sub>tot</sub>         | Total number of MD steps                                  |  |  |  |  |
|                          | $n_{\rm tot} = N_{\rm growth} \times n_{bG} + n_{\rm eq}$ |  |  |  |  |

The radical-like polymerization process takes place in a solvent which is represented in our simulations as a (LJ) liquid of  $N_{\text{monom}}$ =50 000–600 000 monomers. This liquid has been prepared from an initial fcc crystal that has been melted and equilibrated at  $k_BT$ =2 and P=0.5, during 10000 time steps, which is more than enough to get an equilibrated LJ liquid (equilibrium has been checked investigating the monomer pair correlation function). The resulting density of the monomer melt is  $\rho = N_{\text{monom}}\sigma^3/v = 1$ , where v is the volume of the simulation box.

Note that the aim of our method is not to model the polymerization process in detail<sup>7,8</sup> but rather to take inspiration from it. As a reminder, in Table I, we give a summary of relevant parameters fully describing the radical-like polymerization algorithm.

The radical-like algorithm is then divided in five stages.

- (1) In the nucleation stage, each monomer has a probability p to be randomly functionalized as a radical. This probability p controls the number of chains  $M = p \times N_{\text{monom}}$  that will eventually be created.
- (2) In the growth stage, radical (index *i*) randomly chooses one of its first neighbors still in the monomer state (if any available) to create a new covalent bond (FENE potential) and increase the local chain length  $N_i$  of chain *i*. The amount of growth steps  $N_{\text{growth}}$ , defined initially, controls the maximum chain length  $N_i|_{\text{max}} = N_{\text{growth}}$ . This procedure, as mentioned previously, mimics the polydispersity associated with living polymerization. This stage of the process is schematically depicted on Fig. 1.
- (3) Relaxation is an essential ingredient of the method. Between two successive growth steps, a radical is allowed to explore its neighborhood during  $n_{bG}$  MD steps. This is equivalent to let a chain evolve in the solvent and explore a part of its conformational phase space *in situ* while polymerization is taking place, hence permitting a partial relaxation.
- (4) In the termination stage, for polydisperse systems, the generation procedure is stopped after a fixed number of growth steps N<sub>growth</sub>. To produce a monodisperse system, the process is stopped only when each chain has reached a desired size N, whatever the number of the growth steps. Naturally, the time elapsed before termi-



FIG. 1. (Color online) The growth step during the radical-like polymerization algorithm. A radical (white) is randomly assigned one of its first monomers neighbors (blue ones, numbered from 1 to 4) to create a new covalent bond and increase the local chain length  $N_i$ .

nation will depend on the ratio  $(N \times M)/N_{\text{monom}}$  which we took near 80%.

(5) Finally, in the equilibration stage, the residual monomers (or solvent) are removed and the system is equilibrated at constant pressure to reach the desired density during  $n_{eq}$  MD steps.

Three types of systems were generated using the radicallike polymerization process:

- Unretaxed: pure polydisperse melt. The polymerization procedure involve a finite value  $N_{\text{growth}}$  of growth steps but without coupling the system to a heat bath  $(k_BT = 0)$  by imposing  $n_{bG} \equiv 0$ , thus preventing any relaxation between growth steps.
- *Polydisperse*: pure polydisperse melt. The number  $N_{\text{growth}}$  of growth steps is also fixed to a finite value, but for this kind of polymerization, the system is coupled to a heat bath by fixing a finite number  $n_{bG}$  of relaxation steps between each growth step, and setting MD parameters using a Nosé–Hoover barostat with  $k_BT=2$  and P=0.5. For this kind of procedure, the polymerization process is stopped once the number of growth steps is reached.
- *Monodisperse*: pure monodisperse melt. For this kind of process, the number of growth steps is *a priori* infinite. Practically, growth stage occur until all chains reach the desired size *N*. The system is coupled to a heat bath (Nosé–Hoover thermostat and barostat with  $k_BT=2$  and P=0.5) during the relaxation stage:  $n_{bG}$  MD steps are performed after each growth step.

In the next section, these three types of generation processes will be tested and compared. The monodisperse generation procedure will also be compared to more classical push-off techniques.<sup>5,6</sup>

Within the push-off framework, chains are generated randomly in the simulation box without considering excluded volume.<sup>1</sup> Thus, Lennard-Jones interactions for nonbonded monomers cannot be introduced immediately because chains spatially overlap. To bypass this difficulty, modified LJ potentials (slow push off) or intermediate soft repulsive potentials (fast push off or FPO) are then introduced and eventually replaced by the LJ potential. Due to its relative simplicity, this method has been widely used in literature to generate monodisperse systems.

We refer to Auhl *et al.*<sup>5</sup> for details and discussions about FPO techniques. In our implementation, the systems generated with FPO (M=200 chains with chain length of N=200) are equilibrated during 10<sup>7</sup> MDS for systems under Nosé–Hoover thermostat ( $k_BT=2.0$ ) and barostat (P=0.5). It has to be noticed that this quite easy procedure is known to create significant distortions in the chain statistics on length scales comparable to the tube diameter,<sup>5,9,10</sup> thus requiring relatively long equilibration times. Consequently, chain length is generally limited to N < 400.

### 2. Parameters

The values of parameters used in our generation processes and subsequent simulation for the three types of protocols are summarized in Table II. For polydisperse systems, the min and max values of the chain length distribution are also quoted in the same table and will be discussed below.

For monodisperse systems, we also studied the influence of the number of relaxation steps  $n_{bG}$  between the growth steps on the final static properties of the polymer melt. This parameter can be considered as a control parameter for the exploration of configurational phase space during growth, at a given temperature and pressure.

### 3. Structural characterization

Three types structural parameters have been investigated to control the state of equilibration of polymer melts.

• The mean radius of gyration  $\langle r_g \rangle$  defined by

TABLE II. Parameters used to simulate the different *radical-like polymerization* processes discussed in text, during the generation stage.

|              | $N_{\rm growth}$    | $n_{bG}$ | М   | Ν         | N <sub>monom</sub> |
|--------------|---------------------|----------|-----|-----------|--------------------|
| Unrelaxed    | 350                 | 0        | 184 | [50: 344] | 50 000             |
| Polydisperse | $6.7 \times 10^{4}$ | 10       | 215 | [56; 390] | 50 000             |
| Monodisperse | 10 <sup>5</sup>     | 10       | 215 | 200       | 50 000             |
|              | 105                 | 300      | 215 | 200       | 50 000             |
| Monodisperse | 10 <sup>5</sup>     | 10       | 497 | 1000      | 600 000            |
|              | $10^{5}$            | 100      | 497 | 1000      | 600 000            |
|              | 10 <sup>5</sup>     | 300      | 195 | 1000      | 260 000            |

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FIG. 2. (Color online) Mean chain length size  $\langle N \rangle$  evolution during polymerization stage vs the number of growth step, and for the two polydisperse and unrelaxed simulated monodisperse systems. Also plotted is the standard deviation  $\sigma_N$  represented by vertical bars centered on symbols. Inset: size distribution P(N) for the same systems at the end of the generation procedure.

$$\langle r_g \rangle^2 = \sum_{i=1}^{M} \frac{\sum_{j=1}^{N} (r_j^i - \langle r^i \rangle)^2 / N^i}{M},$$
 (3)

where  $r_j^i$  is the position of the *j*th atom of the *i*th chain,  $\langle r^i \rangle$  is the center of mass of chain *i*, and  $N^i$  is the size of chain *i*.

The mean square internal distance (MSID) ⟨r<sup>2</sup>⟩(n) is the average squared distance between monomers j and j +n of the same chain. It is defined by

$$\langle r^2 \rangle(n) = \sum_{i=1}^M \frac{\sum_{j=1}^{N^i - n} (r_j^i - r_{j+n}^i)^2 / (N^i - n)}{M}.$$
 (4)

Note that the MSID  $\langle r^2 \rangle(n)$  is a function of *n* and  $\langle b^2 \rangle^{1/2} = \sqrt{\langle r^2 \rangle(1)}$  is the mean bond length.

• The primitive path analysis (PPA) is a powerful tool to investigate the distance between chains entanglements. It is a key parameter that controls the mechanical or rheological properties of the polymer melt. Section III C will be devoted to the PPA.

### **III. RESULTS FOR A HOMOPOLYMER MELT**

In this section, we present a detailed study of polymerization on chains of 200 monomers: from the dynamics of the polymerization to the final properties of the melt (radius of gyration, MSID, PPA). In addition, MSID parameter for chains of 1000 monomers is presented.

### A. Dynamics of the polymerization

A preliminary study is devoted to the growth dynamics of polydisperse system, namely, polydisperse and unrelaxed methods. In Fig. 2, the mean chain length  $\langle N \rangle$  is plotted as a function of the number of growth steps preformed during polymerization. It is worth noting that polydispersity has spontaneously appeared as a result of the growth process. We observe that both methods display the same evolution: a rapid increase, followed by a saturation due to the lack of available monomers. However, the unrelaxed procedure is stopped before the polydisperse one because thermal mobility allows a more efficient exploration of configurational space by the active radicals.

The standard deviation  $\sigma_N = \sqrt{\langle N^2 \rangle - \langle N \rangle^2}$  is also indicated for both systems with vertical bars centered on the respective symbols.

The final size distributions at the end of the generation procedure P(N) are plotted for both systems in the inset of Fig. 2. As expected, the peak is shifted toward the larger sizes and is slightly narrower for the polydisperse system.

In our simulations, the polydispersity index  $I_p = M_w/M_n$ <sup>11</sup> is accessible through the ratio  $I_p = \langle N^2 \rangle / \langle N \rangle^2$ . The final polydispersity index is a little lower for the polydisperse system (around 1.057) than for the unrelaxed system (around 1.103). Again, this is probably due to thermal mobility which allows smaller chains to find new monomers to continue the growth.

Our generation procedure, which is very close to living polymerization (see Sec. II A), leads to polydispersity indeces that are reasonably close to the experimental ones resulting from living polymerization (typically of the order of 1.3), which gives us confidence in the physical background of the radical radical-like polymerization algorithm. Moreover, it would be very easy to slightly modify our method to simulate other kind of polymerization processes which would lead to higher polydispersity by (i) allowing nucleating of new radicals all along the polymerization process and (ii) introducing a reaction probability between two radicals (e.g., coupling, transfer, or disproportination). Experimental values of polydispersity index can reach a value of 10 or more for classical polymers where coupling, transfer, or disproportination are indeed involved (see Sec. II A).

In order to quantify the evolution of the structural properties of chains during production runs for the polydisperse, unrelaxed, and monodisperse methods, we also investigated the evolution of the mean radius of gyration  $\langle r_g(t) \rangle$  normalized by the mean bond distance  $\langle b^2(t) \rangle^{1/2}$  during the growth (Fig. 3) and equilibration (Fig. 4) stages. Such evolutions are investigated for the three systems ( $n_{bC}$ =10 for polydisperse and monodisperse during the generation stage see Table II).

In Fig. 3, we observe that the generation proceeds in two distinct stages: (i) a pure growth stage characterized by a  $t^{1/2}$  growth kinetics and (ii) a saturation stage where gyration radii reach a plateau value. The power law simply means that during stage (i), each growth step is successful and leads, to an increase in the chain length  $N:N \propto N_{\text{growth}}$ . As  $r_g \propto N^{1/2}$ , we obviously get  $r_g \propto N_{\text{growth}}^{1/2}$ .

In Fig. 4, the time evolution of the mean radius of gyration for the unrelaxed, polydisperse, monodisperse, and also FPO are compared during the equilibration stage. The radius of gyration is plotted versus the number of MD steps necessary to reach a total number  $n_{tot}=N_{growth} \times n_{bG} + n_{eq}=10^7$  MD steps. The final values of gyration radii depend on mean chain length N: the unrelaxed method, which gives the smallest final mean chain length (N=172), leads to the smallest mean radius of gyration. Then, come the monodisperse and



FIG. 3. (Color online) Generation stage: evolution of the mean radius of gyration  $\langle r_g(t) \rangle$  normalized by the average bond length  $\langle b^2(t) \rangle^{1/2}$  and averaged over all chains. Generation exhibits two distinct stages: (i) a pure growth stage characterized by a  $t^{1/2}$  growth kinetics; (ii) a saturation stage where gyration radii reach a plateau value. A value of  $n_{bG}$ =10 has been used for polydisperse and monodisperse methods (see Table II).

the FPO methods, which converge logically to the same radius of gyration. Finally, the polydisperse method, which gives the largest final mean chain length (N=226), leads to the largest mean radius of gyration.

In order to investigate the evolution of the chain size (in terms of the radius of gyration) as a function of chain length during the growth and equilibration stages for all polymerization methods, we plotted  $\langle r_g(t) \rangle / \langle b^2(t) \rangle^{1/2}$  versus  $\langle N \rangle$  on Fig. 5. In this figure, equilibration process (at constant *N*) is represented by vertical arrows. We also plotted in this figure data from Kremer and Grest<sup>6</sup> resulting from long time equilibration, which predict a  $N^{1/2}$  dependence.<sup>12</sup>

After the removal of the remaining monomers and  $10^7$  MD equilibration steps, all generation methods (unrelaxed, polydisperse, and monodisperse with N=200) are in very good agreement with Kremer's results as far as the radius of gyration is concerned.

However, for unrelaxed, polydisperse, or monodisperse methods (with  $n_{bG}=10$ ), it seems that relatively long equili-



FIG. 4. (Color online) Equilibration stage (e.g., after polymerization): evolution of the mean gyration radius as a function of the number of MD steps necessary to reach a total number  $n_{tot}=N_{growth} \times n_{bG}+n_{eq}=10^7$  MD steps. Fast push off (FPO) and monodisperse methods converge to the same value.



FIG. 5. (Color online) Growth and equilibration stages: evolution of the mean radius of gyration as a function of the mean chain size during growth (curves) and equilibration (vertical arrows) stages. Data from Kremer and Grest (Ref. 6) and Gao (Ref. 2) are also represented. They predict a  $N(t)^{1/2}$  dependence. After the removal of the remaining monomers and  $\approx 10^7$  MD equilibration steps, all generation techniques are in very good agreement with Kremer and Gao's results.

bration times (up to  $10^7$  MD steps) are necessary to reach Kremer's target function. Therefore, in what follows, the effect of the number of MD steps between each growth step  $(n_{bG})$  will be investigated.

In Fig. 6, the mean normalized radius of gyration is plotted versus the simulation time for the generation of M = 215 chains of length N=200 at  $k_BT=2$  and P=0.5. Two different values of  $n_{bG}$  are investigated:  $n_{bG}=10$  and  $n_{bG}=300$ . It can be observed that a larger value of  $n_{bG}$  slows down the growth kinetics, but leads to better equilibrated systems once growth is completed. For  $n_{bG}=300$ , no equilibration is required to reach the radius of gyration obtained with the FPO method.

This shows that the chains generated here reach their equilibrium structure more rapidly for the protocol that



FIG. 6. (Color online) Evolution of the mean radius of gyration as a function of time (in MD steps) during growth and equilibration stages: generation of M=215 chains of length N=200 at  $k_BT=2$  and P=0.5. Two different values of  $n_{bG}$  (the number of MD steps between each growth step) are compared. A larger value of  $n_{bG}$  slows down the growth kinetics, but leads to better equilibrated systems once growth is completed. For  $n_{bG}=300$ , no equilibration stage is required to reach the mean radius of gyration obtained with the FPO method.



FIG. 7. (Color online) Mean square internal distance (MSID) of generated melts measured after long MD runs ( $10^7$  MD steps). The target function of Auhl *et al.* (Ref. 5) is compared to the following systems: unrelaxed, polydisperse, monodisperse (N=200) and FPO. Error bars are calculated using standard error function on statistical samples. All methods lead to well equilibrated melts.

spends more time during the growth stage, "(To win a race, the swiftness of a dart availeth not without a timely start.)"<sup>13</sup> thus pointing out the main interest of this algorithm: i.e., equilibration is occurring during generation, provided that an appropriate compromise for the number of MD steps between growth steps is chosen.

# B. Comparison of chains structure for monodisperse and FPO methods

The structure of a polymer melt can be characterized by a wide variety of static or dynamic interchain and intrachain correlation functions<sup>5,6,14–17</sup> which are more or less sensitive to the artifacts introduced by the preparation procedure and which equilibrate on different time scales. One may note that for fully flexible chains simulated in our model (only FENE+LJ interactions), the local monomer packing relaxes quickly, while deviations of chain conformations on large scale require large times to equilibrate.

To validate our generation methods according to more "classical" techniques, we will be investigate a measure of internal chain conformation, namely, the MSID  $\langle r^2 \rangle(n)$ . This function, defined in Eq. (4) above, gives the average squared distance between two monomers belonging to the same chain and is separated by a subchain of *n* monomers.

The MSID parameter is shown in Fig. 7 for the following systems: unrelaxed, polydisperse, monodisperse (with  $n_{bG}=10$  and N=200), and also Fast Push Off (FPO). After the total number of MD steps  $n_{tot}=N_{growth} \times n_{bG}+n_{relax}=10^7$  MD steps, they all converge to the same configuration since they fit nicely with the "target function" defined by Auhl *et al.*<sup>5</sup> as the signature of well equilibrated melts.

Error bars in Fig. 7 are estimated using the standard error function that includes the number of subset events taken into account to compute the MSID. As *n* reaches chain length  $N \ (n \rightarrow N)$ , less and less pairs of monomers are included in the statistics, leading to large error bars for large *n*.



FIG. 8. (Color online) MSID of monodisperse melts [(a): N=200, (b): N=1000]. The effect of the number of MD steps between each growth step is studied. A larger value of  $n_{bG}$  leads to better equilibrated systems: MSID fits nicely with FPO and the target function of Auhl *et al.* (Ref. 5).

Hence, error bars for large n have not been represented. We thus consider that the values obtained for large n are not statistically significant.

It has been shown on Fig. 6 that the number of relaxation steps  $n_{bG}$  between successive growth steps had a significant effect on the final structure of the melt. Therefore, the MSID of monodisperse melts has been investigated for various  $n_{bG}$  ranging from 10 to 300.

In Fig. 8(a), MSID resulting from monodisperse generation (with N=200,  $n_{bG}$ =10, and  $n_{bG}$ =300) are compared to MSID resulting from FPO generation and the target function of Auhl *et al.*<sup>5</sup> An equilibration stage of  $n_{tot} = n_{bG} \times N_{growth}$  $+n_{relax} = 10^6$  MD steps after generation has been performed. Despite this relatively low equilibration time, it can be observed that the monodisperse generation method with 300 MD steps between each growth step leads to well equilibrated systems, even possibly better than FPO method. This corroborates previous results from Fig. 6, and points out, once again, the main interest of this radical-like generation method: relaxation takes place while generation is performed. In addition, the efficiency of the relaxation stage between growth steps is proved for chain of N=1000 on Fig. 8(b). Indeed, for  $n_{bG}$ =300 and  $n_{tot}$ =10<sup>7</sup> MD steps, chains of 1000 monomers are well equilibrated.

# C. Primitive path analysis

Entanglements between chains are an important topological feature that controls many dynamical properties of polymer melts. A practical tool for characterizing entanglements is the PPA which will be the object of this section.

Proposed by Everaers *et al.*<sup>18</sup> with the aim of constructing a real space representation of de Gennes' tube model, the PPA technique is an interesting tool for obtaining informations about the density of entanglements which has not been accessible through other theoretical or direct experimental measurements.

Recently, Hoy and Robbins<sup>10</sup> applied this technique to quantify the effect of the generation procedure, namely, the FPO system and the double-bridging<sup>5</sup> equilibration technique. Following their idea, we apply this to our different radical-like generation methods, first focusing on the comparison between monodisperse and FPO method.

The principle of PPA is as follows.

- We start with any given configuration, during the growth or in the final state, after, or before the equilibration stage.
- (ii) The two chain ends are kept fixed, while the intrachain pair interaction (covalent bonds) are shifted to get their minimum energy at a zero distance while increasing the bond tension in Eq. (2) to k=100;
- (iii) To prevent chain crossing,<sup>19</sup> weak bonds lengths have been monitored and limited to  $1.2\sigma$ .
- (iv) The system is then equilibrated using a conjugate gradient algorithm in order to minimize its potential energy and reach a local minimum.
- (v) The contour length of the primitive path  $L_{pp}$  is then the total length of the chain (the sum of all straight primitive path segments length).

If no entanglement exists between chains,  $L_{pp}$  should be equal to their end-to-end distance  $r_{ee}$ . The presence of entanglements leads to  $L_{pp} > r_{ee}$  with a typical Kuhn length  $a_{pp} = \langle r_{ee}^2 \rangle / L_{pp}$  and an average bond length  $\langle b_{pp} \rangle = L_{pp} / N$ . The number of monomers in straight primitive path segments is then given by

$$N_{\rm pp}(N) = \frac{a_{\rm pp}}{\langle b_{\rm pp} \rangle} = \frac{N \langle R_{\rm ee}^2 \rangle}{L_{\rm pp}^2}.$$
 (5)

For short chains without any entanglements, the primitive path length equals end-to-end distance, leading to  $N_{\rm pp}$ = N. When chain lengths are comparable to the entanglement length,  $N_{\rm pp} < N_e$ ,  $N_e$  being the real entanglement value. For sufficiently long chains, i.e.,  $N > 2N_e$ , several entanglements per chains exist, and  $N_{\rm pp}(N) = N_e$ .

The PPA has been performed at different simulation times (during generation and equilibration stages) and the results are shown in Figs. 9 and 10.

Figure 9 displays the number of monomers in straight primitive path segments  $N_{pp}=N_e$  for FPO and monodisperse  $(n_{bG}=10 \text{ and } n_{bC}=300)$  generation methods. The vertical dashed line separates the generation and growth regimes. The horizontal line is the entanglement length  $N_e$  from Sukumaran *et al.*,<sup>19</sup> which is in good agreement with our data.



FIG. 9. (Color online) Evolution of the number  $N_e(t)$  of monomers in straight primitive path segments along simulation times for monodisperse systems, namely, monodisperse and FPO. PPA has been performed during both the generation stage and the equilibration stage separated by the vertical dashed line. Units of time are in  $\tau$  units, i.e.,  $n_{\text{tot}} \times \delta t$ . The horizontal line gives value for  $N_e$  from Sukumaran *et al.* (Ref. 19).

This asymptotic value is even reached during the generation stage for the monodisperse technique with  $n_{bG}$ =300.

The PPA has also been implemented for polydisperse and unrelaxed systems. Figure 10 shows the ratio  $N_e(t)/\langle N(t) \rangle$  for polydisperse systems (unrelaxed and polydisperse) against the simulation time. During the generation stage, the time scale is given in  $N_{\text{growth}}$  steps units, whereas given in  $n_{\text{eq}}$  MD steps during the equilibration stage.

For unrelaxed system, generation/equilibration transition is represented by a dashed vertical line, while a dot-dashed line is used for polydisperse system.

The same indicative value for the entanglement length  $N_e/N$  from Sukumaran *et al.*<sup>16</sup> for chain length of size N = 200 is also shown, and must be considered as a mean value for both polydisperse systems. Indeed, the mean chain length at the end of the generation phase for unrelaxed system is  $\langle N \rangle_{\text{unrelaxed}}(t \rightarrow \infty) = 172$ , while for the polydisperse  $\langle N \rangle_{\text{hot}}(t \rightarrow \infty) = 226$  (see Table II).



FIG. 10. (Color online) Ratio  $N_e(t)/\langle N(t)\rangle$  for polydisperse systems unrelaxed and polydisperse against simulation time. Dashed (middashed) vertical line separates generation to equilibration stages for the unrelaxed (polydisperse) method. Also shown is the same ratio from Sukumaran *et al.* (Ref. 19) for chains length N=200 as an indicative value.



FIG. 11. (Color online) Lamellar spacing of diblock copolymer after 10<sup>7</sup> MD steps at P=0.5 and kT=1. Scaling law  $d_l \propto N^{2/3} \tilde{\epsilon}^{1/6}$  expected in the strong segregation limit ( $\tilde{\epsilon}N/(k_BT) \ge 20$ ) (Refs. 27–32) is clearly observed.

For the unrelaxed method, the investigated ratio is almost constant along the whole equilibration stage, during which entanglements do not vary much.

For the polydisperse system, this ratio displays a more complex behavior. First, a power law decrease, as noted by dotted ( $\propto t^{-1/2}$ ) and dotted-dashed line ( $\propto t^{-1}$ ), is observed, until  $N_{\text{growth}} \sim 700$ , corresponding to a ratio  $N_e(t)/\langle N(t) \rangle \sim 1/3$  nearly equal to the results from Sukumaran *et al.*<sup>19</sup> for N=200 homopolymer chain melts.

In this regime,  $\langle N(t) \rangle$  grows more rapidly than  $N_e(t)$ , and the growth process of each chain interacts with a stochastic background associated with the ensemble of growing chains. Thus, in this Rouse-like regime, topological constraints do not play a significant role and one may expect that chains with average length  $\langle N(t) \rangle < N_e \sim N/3$  dominate the polymerization, following a Rouse-like chain dynamics.

Following this regime, while  $\langle N(t) \rangle$  still grows, a stabilization of the same ratio is observed. In this regime,  $N_e(t)/\langle N(t) \rangle < 1/3$ , and a slowing down is observed during chain growth dynamics. This new reptationlike regime corresponds to a dynamics where the surrounding medium topology limits transverse chain displacements around their own contour length. Chains with mean size  $\langle N(t) \rangle > N_e$  $\sim N/3$  follow this reptationlike dynamics, and the polymerization process is slowed down. While the longest chains are still growing, the average entanglement length does not vary drastically, as one can see once the generation stage is finished, where the ratio  $N_e(t)/\langle N(t) \rangle \rightarrow N_e/N$ .

From all these results, it appears that our approach is validated as a method for generating equilibrated configurations of homopolymer melts. In the following section, the radical-like algorithm will be used to generate block copolymers in a lamellar configuration.

# **IV. APPLICATION TO COPOLYMER GENERATION**

In this section, generation of block copolymers will be performed: the radical-like polymerization algorithm will be modified to get a lamellar structure.

Modeling the demixtion itself is not an easy task. Adjusting force fields and replicating basic units of the previously assembled copolymers, Srinivas *et al.*<sup>20</sup> managed to obtain large scale demixtion in biological systems (self-assembled copolymers in water). Zhang *et al.*<sup>21</sup> used full-atomistic simulations based on dynamics density functional theory but their approach is limited to small system sizes. May be more adapted to block copolymer generation, semi-particle based methods such as single chain in Mean field<sup>22–25</sup> seem to be promising.

Other methods have been proposed for generating diblock copolymers: Grest et al.<sup>26</sup> and Murat et al.<sup>27</sup> proposed a method, which consists in grafting chains on two parallel planes facing each other. The coverage density of each plane is as low as  $0.1\sigma^{-2}$ . Then, the two planes are brought together such that the overall density between the plates reaches the desired value, requiring an equilibration stage. Finally, the mirror image of each chain about its grafting point is constructed and considered as the second phase. In the following, we present an alternative method based on an adaptation of the radical-like method to the particular case of a symmetric AB diblock where  $N_A = N_B$  and  $N = N_A + N_B$ .  $L_x$ ,  $L_y$ , and  $L_z$  are the box sizes along the x, y, and z directions. Values for excluded volume potentials [Eqs. (1) and (2)] have been chosen as,  $\epsilon_{AA} = \epsilon_{BB} = \epsilon_{As} = \epsilon_{Bs} = \epsilon = 1.0$  and  $\sigma_{AA} = \sigma_{BB} = \sigma_{AB} = \sigma = 1.0$ , while potentials are truncated and shifted at  $r_c = 2.5$ .

### A. Generation of a lamellar diblock

Generation of a diblock copolymer with an interface lying in the (xy) plane is performed as follows, starting from a LJ liquid of monomers:

- (1) Each monomer *i* has a probability *p* to be a radical of type *A* if, say,  $z_i > L_z/2$  and B otherwise.
- (2) As long as the chain does not reach the size N/2 (N(t) < N/2), growth is performed as in a homopolymer with a supplementary condition: addition of a new monomer *j* is possible only if it lies in the same region  $(z_j > L_z/2 \text{ for } A \text{ chains and } z_j < L_z/2 \text{ for } B \text{ chains})$ . Interfaces situated at z=0 and  $z=L_z/2$  are then impermeable: no chain can cross them.



FIG. 12. (Color) Snapshots of diblock and triblock copolymers generated using the radical-like copolymerization method for M=215 chains of length N=200 under periodic boundary conditions. Chains are unfolded according to the position of the first bead of the chain. Two macromolecules are highlighted and the simulation box is shown in black. *AB* diblock:  $n_A=n_B=100$  and  $\epsilon_{AB}=0.01$ . *ABC* triblock:  $2n_A=n_B=2n_C=100$ ,  $\epsilon_{AA}=2\epsilon_{BB}=\epsilon_{CC}=1$  and  $\epsilon_{AB}=\epsilon_{BC}=\epsilon_{AC}=0.01$ .

(3) Once a chain reaches the size N/2, the growth within a lamella is stopped. A force is applied to attract the chain ends to the closest interface (either z=0 or  $z = L_z/2$ ), and the condition above is reversed: addition of

a new monomer *j* is possible only if it lies in the opposite region  $(z_j < L_z/2 \text{ for } A \text{ chains and } z_j > L_z/2 \text{ for } B \text{ chains})$ . Under this new condition, and once a radical combines with a new monomer in the opposite region,

it turns into the opposite species (A radical becomes B radical and B radical becomes A radical). For chains with N(t) > N/2, the growth is then continued with the impermeable interfaces condition: addition of a new monomer j is possible only if it lies in the same region  $(z_j > L_z/2 \text{ for } A \text{ chains and } z_j < L_z/2 \text{ for } B \text{ chains})$ . Growth of a chain occurs until its length reaches the size N.

- (4) As for homopolymers, a number  $n_{bG}$  of MD steps is performed between each growth step, during which the systems is coupled to the heat bath at  $k_BT=2$  and P = 0.5 (cubic simulation box).
- (5) The process is stopped when each chain has reached the desired size  $N=N_A+N_B$  and  $N_A=N_B$ .
- (6) Residual monomers are then eliminated and system is equilibrated at  $k_B T = 0.5$  and P = 0.5 during  $10^6$  MD steps.<sup>28</sup>

# **B.** Lamellar spacing

The order-disorder transition temperature is governed by the product  $\chi N$ , where  $\chi$  is the Flory–Huggins parameter. In this paper, we use the reduced interaction parameter  $\tilde{\epsilon} = (0.5\epsilon_{AA}+0.5\epsilon_{BB}-\epsilon_{AB})/\epsilon$ . On a lattice with only the nearest neighbor interactions,  $\chi$  would be equal to  $\tilde{\epsilon}/(k_BT)$ . Note that Grest *et al.*<sup>26</sup> proposed a linear relation between  $\chi$  and  $\tilde{\epsilon}$ , and both  $\chi$  and  $\tilde{\epsilon}$  characterize the incompatibility between A and B chains. In this paper, for the sake of simplicity, we computed  $\tilde{\epsilon}$  instead of  $\chi$  (see Ref. 26 for a detailed discussion). The order-disorder transition temperature is then closely related to the product  $\tilde{\epsilon}N/(k_BT)$ .

From a theoretical point of view, symmetric diblock copolymers are homogeneous at small  $\chi N$  value, but strongly heterogeneous with ordered structure when  $\chi N$  exceeds, in mean-field theory, the critical order-disorder transition value  $\chi N_{\rm ODT}$ , which separates two limiting cases:<sup>24</sup> the weak segregation limit, valid at temperatures near the order-disorder temperature, and the strong segregation limit (SSL) at temperature well below. In the weak limit, Leibler's random phase approximation<sup>29</sup> predicts a lamellar ordering at a critical value ( $\chi N$ )<sup>L</sup><sub>ODT</sub>=10.5. In the SSL limit of a symmetric diblock, the two halves of the chains are well separated, with lamellar layers containing one type of monomer except inside a small interface layer of width  $w \propto \chi^{-1/2}$ . The periodicity of the layer  $d_l(\chi N)$  is then predicted to scale as  $N^{2/3}\chi^{1/6}$ . As discussed previously,  $d_l$  scales also as  $N^{2/3}\tilde{\epsilon}^{1/6}$ .

Hence, as a first application of the radical-like *copolymerization* algorithm, we simulated diblock copolymers with various values of the  $\tilde{\epsilon}N/(k_BT)$  parameter ranging from 4 (( $\epsilon_{AB}$ =0.99) to 396 ( $\epsilon_{AB}$ =0.01)).

Note that, after termination stage, this procedure does not generate the correct lamellar spacing, which is arbitrary chosen as half of the (cubic) simulation box size. Therefore, as in Grest *et al.*,<sup>26</sup> an additional 10<sup>7</sup> MD step have been simulated using an isotropic Nosé–Hoover barostat, in such a way that  $P_x = P_y = P_z = 0.5$ ,<sup>30</sup> while the temperature was fixed to  $k_B T = 1.0 \epsilon_{\alpha\alpha}$ .

In Fig. 11, the period  $d_l(\tilde{\epsilon}N)$  of the lamellar structure at the end of the isotropic equilibration process is plotted as a

function of the product  $\tilde{\epsilon}N$ . For each value of  $\tilde{\epsilon}N$ , the distance  $d_l(\tilde{\epsilon}N)$  is measured using the *z* dependence of the concentration function for the *AB* diblock perpendicular to the separating interface. This one is defined as  $C_A(z) = C_B(z)/(C_A(z) + C_B(z))$ .

From Fig. 11, it can be observed, that the distance between lamellas  $d_l$  scales as  $\tilde{\epsilon}^{1/6} N^{2/3}$  as expected from theoretical<sup>27-32</sup> arguments and experimental<sup>33-39</sup> results.

Note that below a value of  $\epsilon N \approx 10-15$ , a trend towards mixing with a diminution of  $d_l$  is observed. Equilibrium is not completely achieved, even after  $10^7$  MD steps. A loss of translational order is therefore expected on larger timescales.

### C. Toward the generation of triblocks

The above mentioned method has been applied to the generation of *ABC* triblock copolymers with  $2n_A = n_B = 2n_C = 100$  monomers. Each chain links the three phases *A*, *B*, and *C*. For that purpose, the system is divided into three regions and chains grow as follows: (i) simultaneous nucleation and growth within *A* (and *C*) region until  $n_A = 50$  (and  $n_C = 50$ ); (ii) pulling chain ends to the *AB* (and *BC*) interface; (iii) growth of all chains in *B* region until  $n_B = 100$ ; (iv), pulling chain ends to the *BC* (and *AB*) interface; and (v) growth within *C* (and *A*) region until  $n_C = 50$  (and  $n_A = 50$ .

Snapshots of *AB* diblock and symmetric *ABC* triblock configurations are shown in Fig. 12, where simulations have been performed on M=215 chains with a polymerization degree of N=200 for both triblocks and diblocks.

The stability of the lamellar morphology and the lamellar spacing of generated diblocks and triblocks copolymers led to the validation the radical-like copolymerization technique. The advantage of this technique resides in the control of the geometry of simulated copolymers as well as the possibility to generate in a flexible way, configurations with various topologies and chain architectures.

# **V. CONCLUSION**

The radical-like polymer chain generation method is inspired by radical polymerization in which the reactive center of a polymer chain consists of a radical. The free radical reaction mechanism can be divided in to three stages: (i) initiation (creation of free radicals), (ii) propagation (construction of the repeating chain), and (iii) termination (radical is no longer active).

Performing a relatively important number of MD relaxation steps between each growth step (typically 300) leads to well equilibrated chains (in terms of radius of gyration, MSID and PPA), for chains of N=200 and N=1000monomers.

The main advantage of the radical-like generation algorithm is that equilibration occurs simultaneously with growth. Indeed, chains are relaxed before they become too long (and then too entangled). In particular, we have shown that the relatively long chains (N=1000) can also be well equilibrated.

The radical-like generation method is particularly adapted to generate polydisperse polymer melts (branched polymers, star polymers, copolymers,...). Nanostructured lamellar di- and triblocks copolymers have been successfully generated with the radical-like method (*n*-blocks could be straightforwardly generated).

Physical and mechanical properties of diblock and triblock copolymers generated using this algorithm will be the subject of a future paper.

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