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How the restriction of sliding diffusion of comonomers affects crystallization and melting of homogeneous copolymers

Wenbing Hu [a],*, F.G. Karssenberg [b], Vincent B.F. Mathot [b],[c]

[a] *Department of Polymer Science and Engineering, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, China*
[b] *Laboratory of Polymer Technology, Department of Chemical Engineering and Chemistry, Eindhoven University of Technology, Eindhoven, The Netherlands*
[c] *DSM Research, P.O. Box 18, Geleen, The Netherlands*

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Dedicated to Prof. D.C. Bassett on the occasion of his retirement

Abstract

In ethylene-based copolymers, large comonomers/branches make the sliding diffusion difficult in the crystalline regions constituted by small monomers. We studied the influence of such a restricted sliding diffusion on the mechanisms of crystallization and melting of homogeneous copolymers, by means of dynamic Monte Carlo simulations. Comparing two extreme cases—no restriction and a hard restriction—we found that the hard restriction increases both temperatures of crystallization and melting on the temperature scanning. Moreover, during crystallization, the restriction weakens segregation of sequence lengths and decreases the lamellar-crystal thickness. These results can be attributed to a switch of the dominant crystal growth mode from longitudinal thickening to lateral growth due to the presence of a hard restriction.

Keywords: Crystallization; Melting; Homogeneous copolymers

1. Introduction

Crystallization and melting of ethylene-based copolymers are sensitive to the presence of large comonomers/branches because the latter tends to be excluded from the crystalline regions during crystallization [1–3]. From a thermodynamics point of view, such exclusion can be attributed to the low affinity of comonomers to monomers that may lead to a depression of the melting point compared to the crystals of pure monomers [4,5]. From a molecular-dynamics point of view, the exclusion appears to be caused by the restriction of sliding diffusion of comonomers in the crystalline region, since they are too bulky to be able to fit into the close-packed volume occupied by monomer sequences. Up to now, the way by which this restriction of sliding diffusion affects the kinetics of phase transitions as well as the metastability of polymer crystals has not been understood well.

Such a restriction is, of course, a stochastic event, and its probability depends upon the bulkiness of the comonomer. For instance, the comonomer 1-octene is expected to have a strongly restricted sliding diffusion, while the comonomer propylene may experience a weak restriction due to its relatively small size. However, in the experiments of reality, comonomers having variable restrictions of sliding diffusion usually also have different chemical affinities to the monomer. Therefore, it is very difficult, if not impossible, to separate the effect of variable restrictions from that of different chemical affinities. Recently, for three types of bulk statistical copolymers, we have reported dynamic Monte Carlo simulations that reproduced many basic facts of crystallization and melting of statistical copolymers [6]. The simulations assumed an athermal mixing between monomers and comonomers as well as a hard restriction with respect to the sliding diffusion of comonomers in the crystalline regions. In this paper, we will further study the extreme cases of on the one hand such a hard sliding diffusion restriction and on the other hand no sliding diffusion restriction, and focus on the impact on crystallization and melting of homogeneous copolymers. We will compare these two cases under a protocol of the same chain length, the same comonomer content, the same sequence-length

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* Corresponding author.
E-mail address: wbhu@nju.edu.cn (W. Hu).

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distribution, and the same conditions of athermal mixing. The results will show that the hard restriction of sliding diffusion significantly affects the appearance of crystallinity during cooling and heating; influences sequence-length segregation during crystallization; and results in quite different crystallite morphologies.

In the following, after an introduction of sample preparation and simulation techniques, we report the simulation results under variable conditions of temperature scanning, followed by discussion and conclusions.

2. Sample preparation and simulation techniques

In our simulations, the chain microstructures of homogeneous copolymers, especially the way by which the monomer and comonomer sequences are distributed along the chains, have been produced in such a way that they mimic copolymers synthesized recently in reality. These copolymers have been synthesized by copolymerization of ethene/ethylene (denoted as ‘1’) and propene/propylene (denoted as ‘2’) with six comparable, but slightly different metallocene catalysts [7]. The copolymerization kinetics of these systems can be well described by penultimate or second-order Markovian reactivity ratios r_{ijk} with i, j, k elements of {1,2} [8]. Here, we only pay attention to two typical catalysts: the alternating $Me_2Si(2\text{-}Me\text{-}Ind)_2Zr$ with $r_{112}=7.75$, $r_{121}=0.04$, $r_{212}=5.62$, and $r_{221}=0.08$; and the blocky $Me_2Si(4\text{-}Ph\text{-}Ind)_2Zr$ with $r_{112}=2.88$, $r_{121}=0.62$, $r_{212}=1.93$, and $r_{221}=1.01$. The feed composition $F=[1]/[2]$ (the concentration ratio of monomers to comonomers) has been properly chosen to make four samples with only two comonomer contents, as listed below.

Sample A: made by catalyst 1, $F=0.467$;
sample B: made by catalyst 2, $F=1.748$;
sample C: made by catalyst 1, $F=0.237$;
sample D: made by catalyst 2, $F=1.085$.

The propagation probabilities of copolymerization P_{ijk} are defined as [9]:

$$P_{112}=\frac{1}{1+r_{112}F};\quad P_{111}=1-P_{112};$$

$$P_{121}=\frac{F}{F+r_{121}};\quad P_{122}=1-P_{121};$$

$$P_{212}=\frac{1}{1+r_{212}F};\quad P_{211}=1-P_{212};$$

$$P_{221}=\frac{F}{F+r_{221}};\quad P_{222}=1-P_{221}.$$

The diad fractions x_{ij} and the mole fractions x_i can be calculated by solving the following equations:

$$x_{11}=x_{11}P_{111}+x_{21}P_{211}, \tag{1}$$

$$x_{12}=x_{11}P_{112}+x_{21}P_{212}, \tag{2}$$

$$x_{21}=x_{12}P_{121}+x_{22}P_{221}, \tag{3}$$

$$x_{22}=x_{12}P_{122}+x_{22}P_{222}. \tag{4}$$

$$x_1=x_{11}+x_{21}, \tag{5}$$

$$x_2=x_{12}+x_{22}. \tag{6}$$

As a result, both samples of A and B have a mole fraction of comonomers of 0.20, while both samples of C and D have 0.31. Both samples of A and C have more alternating sequences, while both samples of B and D have more blocky sequences.

Like in previous simulations [6], we put 1920 chains on a cubic lattice box that has a linear size of 64. Each chain contains 128 units, so the occupation density is as high as $1920\times128/64^3=0.9375$ to mimic a bulk (co)polymer system. Then, as a pre-condition, an athermal situation was realized (meaning an infinitely high temperature), by which the chains relaxed to the equilibrium-coil state before performing the cooling step. The dynamic relaxation was realized by applying the micro-relaxation model [10], which allows single-site jumping accompanied with a partial sliding diffusion along the chain if necessary, and with a hard volume exclusion among chain units and their bond connections. The bonds can stay either along the lattice axes or along the (face and body) diagonals, and accordingly, the coordination number of this cubic lattice is $6+12+8=26$. The periodic boundary conditions were employed as usual.

As mentioned above, we prepared four samples of homogeneous copolymers. In each sample, we defined all the sequences of chains consecutively along a long-chain macromolecule. On generating the sequence of this macromolecule from one chain end, the first two sequences were determined by the probability according to the diad fractions x_{ij}. Subsequent sequences along the macromolecule were defined by simulating a continuous copolymerization process with the propagation probabilities P_{ijk} corresponding to each sample.

The attraction between parallel packing of monomer bonds has been known to be responsible for the crystallization of monomer sequences [11], and contributes to a penalty of the potential energy pE_p in Metropolis sampling, where p is the net change of the number of parallel-packing pairs for those monomer bonds in each step of micro-relaxation, and E_p is the potential-energy change for each pair of monomer bonds losing parallel packing. For the sake of simplicity, we assumed fully flexible chains and, in addition, athermal mixing between monomers and comonomers.

In each step of micro-relaxation, partial sliding diffusion may bring the comonomer into a position of parallel-packing pairs of monomer bonds. To introduce a hard restriction in such kind of sliding diffusions, realization of such trial move is rejected in that case. In the no-restriction case, we allowed such kind of sliding diffusions to be realized. Below, for both extreme cases we will compare the cooling and heating curves of crystallinity, the sequence-length segregation during crystallization, and the resulting crystallite morphologies.

3. Results

3.1. Cooling and heating curves of crystallinity

We first performed a program of cooling followed by heating in order to monitor crystallization and melting of our sample systems. The temperature–time ramps consisted of stepwise decrease (or increase) of the temperature $T/E_p/k_B$ with a step length of 0.01 and a step period of 500 MC cycles. Here, k_B is the Boltzmann constant, and one Monte Carlo (MC) cycle is defined as one trial move for each chain unit summed over the sample system. To trace the phase transitions, we made use of the absolute crystallinity defined in Ref. [6], which is the number fraction of monomer bonds containing more than five parallel neighbors of the same type, in the total amount of monomer bonds. This definition of absolute crystallinity is quite precise at the molecular level and the chosen criterion of five allows the crystalline phase to include the bonds on the surfaces of the crystallites [12]. Therefore, the reported values are apparently higher than the relative crystallinity as defined in reality [6]. The results, as calculated at the end of each temperature step, are shown in Fig. 1.

Fig. 1(a) summarizes the results of the alternating copolymers with (solid lines for A, dot lines for C) and without (dash lines for A, dash–dot lines for C) a hard restriction in the sliding diffusion of comonomers. Fig. 1(b) is for the case of the blocky copolymers. One can see that, using the same type of catalyst, and by that the same type of sequence-length distribution, higher comonomer contents lead to lower temperatures of crystallization and melting. For the same comonomer contents but different types of sequence distributions, the blocky copolymers show higher temperatures of crystallization and melting than the alternating copolymers. These observations are in accordance with our previous simulations [6] as well as reality [13,14].

Furthermore, the curves in Fig. 1 demonstrate that the non-restricted homogeneous copolymers undergo crystallization and melting at lower temperature regions than the corresponding hard-restricted samples with the same comonomer content and the same sequence-length distribution. Meanwhile, upon the temperature scanning, their phase transitions appear to be more gradual and with smaller hysteresis.

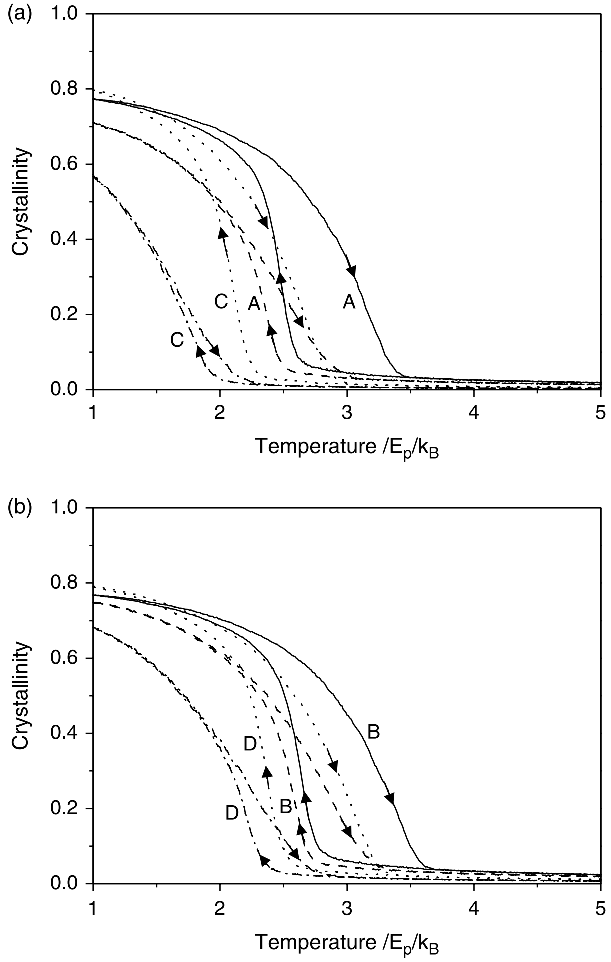

Fig. 1. Cooling and heating curves of absolute crystallinities for homogeneous alternating copolymers (part (a): samples A and C) and homogeneous blocky copolymers (part (b): samples B and D). Solid lines (A or B) and dot lines (C or D) represent restriction cases, while dash lines (A or B) and dash–dot lines (C or D) stand for no-restriction cases. Samples A and B contain 20% comonomer and samples C and D contain 31% comonomer. Pairs of arrows located at the same altitudes indicate the directions of temperature scanning for the same sample.

It is difficult to make direct comparisons of the simulation results with experiments on account of the chemical dissimilarity of comonomers in the comparable real samples. Moreover, relevant measurements on homogeneous copolymers having different comonomer types but produced with the same catalyst have seldom been reported. Fortunately, for the hysteresis feature we found an example. According to the report in Ref. [13], an ethylene-based (E) homogeneous copolymer containing 10.6% of propylene (P) has the onset of crystallization on cooling at about 70 °C and the end of melting on heating at 90 °C, so the hysteresis is about 20 °C. Another homogeneous copolymer, produced with the same catalyst, containing 11.5% of 1-octene (O) shows the onset of crystallization at about 50 °C and the end of melting at 80 °C, so its hysteresis is 30 °C, much larger than the EP copolymer. In general, this feature of hysteresis has been confirmed by experiments reported in Ref. [14]. According to the prediction of our simulations, this difference of hysteresis can be attributed to the fact that the size of 1-octene is larger than that of propylene and hence gives rise to a stronger restriction on its sliding diffusion in the crystalline region. However, also reported in Refs. [13,14], the EP copolymer shows higher temperature regions for crystallization and melting. This result is contradictory to the expectation from our simulations. It has to be remarked that the statistics of the comonomer inclusion into the chains during polymerization of the EP and the EO copolymers reported in Refs. [13,14] was not very different: the products of the reactivity ratios $r_{\mathrm{monomer}}r_{\mathrm{comonomer}}$ have been calculated as being 0.55 and 0.48, respectively. Most probably, this small difference has a negligible effect on the chain statistics, and thus it cannot explain the differences in the temperature shifts of crystallization and melting found from simulations and in reality. Rather, the found discrepancy may be associated with the different affinities of propylene and 1-octene to the monomer sequences. The chemical affinity is related to the structural similarity and indeed, on the chemical structures, propylene is closer to ethylene than 1-octene; therefore, EP copolymers are expected to experience a less depression of the melting temperature than EO copolymers.

3.2. Sequence-length segregation during crystallization

Recently, molecular simulations have identified the segregation behavior of sequence lengths during crystallization of homogeneous copolymers, with the hard restriction in the sliding diffusion of comonomers [15]. It will be interesting to study this segregation behavior in the no-restriction case and to make a comparison. To this end, we decreased the temperature of sample A with a step length of 0.02 through the temperature region $1 < T/E_p/k_B < 3$ where the crystallization takes place. In the meantime, we traced the crystallinity as well as the mean length of crystalline sequences that contains crystalline bonds more than half of the sequence length. Here, as defined before, 'crystalline bonds' are those monomer bonds having more than five neighboring monomer bonds in parallel. The cooling curves in both cases with (solid lines) and without (dash lines) restriction are shown in Fig. 2.

Fig. 2 shows that the restricted copolymer appears to have a weaker segregation of sequence lengths upon crystallization than the non-restricted copolymer. The scatter of the mean crystalline sequence-length at high temperatures can be attributed to the scarcity of data, since at the beginning of crystallization the crystallites are few in number and small due to thermal fluctuations.

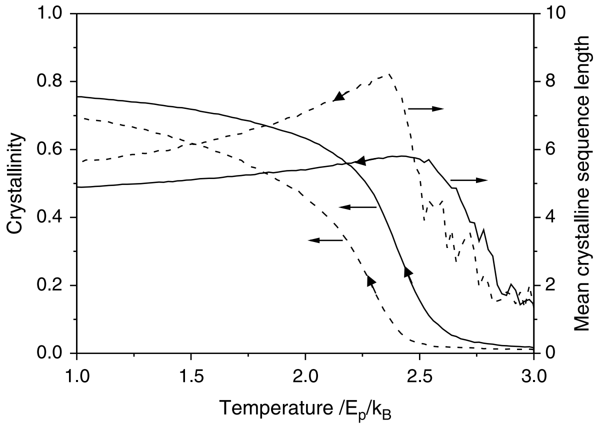

Fig. 2. Cooling curves of absolute crystallinities (left axis) and of mean crystalline sequence-lengths (right axis) for sample A in the restriction case (solid lines) and in the no-restriction case (dash lines). Arrows on the curves indicate the directions of temperature scanning, and arrows next to the curves point to the relevant axis.

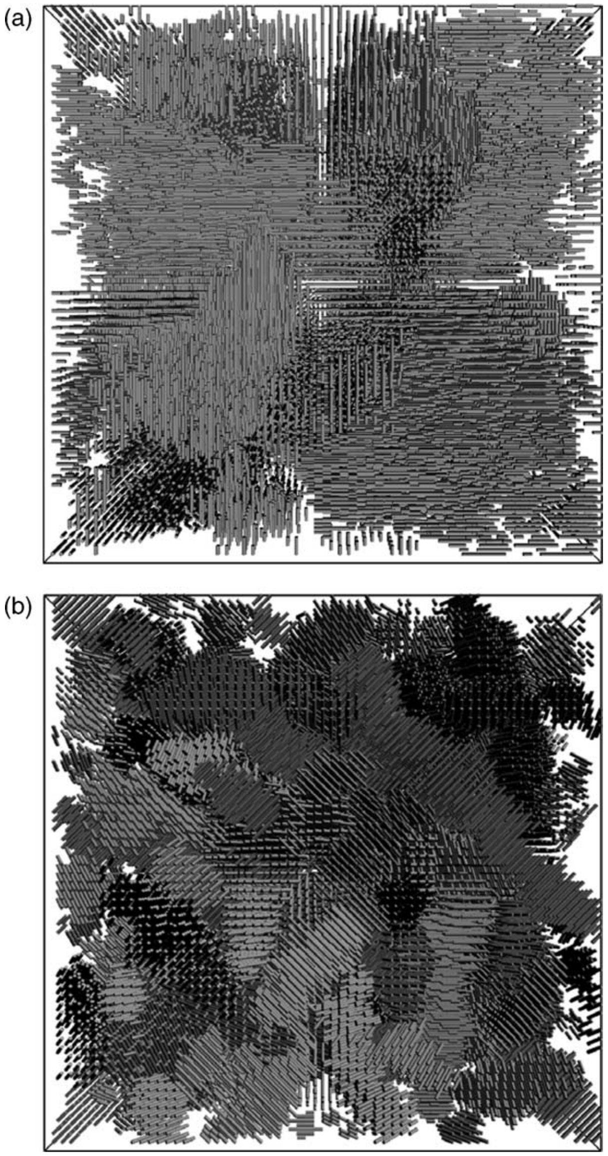

Fig. 3. Snapshots of sample A in a cubic box with periodic boundary conditions at the reduced temperature of one, for the no-restriction case (a) and the restriction case (b). The samples were cooled from the melt as in Fig. 2. Only the crystalline bonds (the monomer bonds having more than five parallel neighbors of monomer bonds) are shown, as cylinders.

3.3. Crystallite morphologies

A comparison of the crystallite morphologies may provide us more insight in the effects of the sliding diffusion restriction of comonomers. Fig. 3 shows snapshots of crystallites produced during the cooling process demonstrated in Fig. 2. A significant difference in crystallite morphology is observed in these two cases. In Fig. 3(a), one can see that the crystallites of non-restricted copolymers are quite thick, implying a strong tendency towards chain extension, similar to those in the case of homopolymers as demonstrated in Ref. [6]. In contrast, in Fig. 3(b), the crystallites of restricted copolymers show only thin lamellae, whose thickness is clearly confined by the sliding diffusion restriction of comonomers, pinning crystallites down at their fold surfaces. In the latter case, the crystal growth mainly happens at the lateral surfaces of crystallites, while in the former case the crystal longitudinal (thickening) growth seems to be faster than the crystal lateral growth.

We also traced the time evolution of crystallite morphology on the cooling of these two kinds of copolymers. Both showed that the crystallization was spontaneously initiated by a multiple primary crystal nucleation that led to a random stacking of crystallites without a higher-level organization. We provide movies for these processes as Supporting information of this paper.

4. Discussion

Usually, thick lamellar crystals have higher melting temperatures than thin ones. However, comparing Figs. 1 and 3, the non-restricted copolymers in spite of having thick crystallites shows lower melting temperatures on heating than the restricted copolymers having thin lamellae. The reason can be found from the well-known Gibbs–Thomson equation describing the depression of the melting temperature (T_m) of polymer crystals due to the limited sizes,

$$T_\mathrm{m} = T_\mathrm{m}^0\left[1-\frac{(2\sigma_\mathrm{e}/l + 4\sigma_\mathrm{s}/\alpha)}{\Delta h_\mathrm{m}}\right], \tag{7}$$

where T_m^0 is the equilibrium melting temperature, σ_e, σ_s the surface free energies of the fold-end surface and of the lateral surface, respectively; l the crystal thickness; a the crystal lateral size, and Δh_m the heat of fusion per unit of crystal volume. According to this equation, the smaller the crystallite dimension, the higher the depression of melting point will be. On the other hand, the equation also tells us that not only the crystal sizes but also the heat of fusion are relevant to the melting-temperature depression. Without the sliding diffusion restriction of comonomers, an appreciable amount of comonomers will be embedded into the crystalline regions as defects that will decrease the heat of fusion. Therefore, even in the case of thick crystals these may have low melting temperatures if they contain many defects. In other words, imperfect crystals will result from the inclusion of defects during crystallization at all temperatures. As evidences of imperfection, Fig. 1(a) and (b) have shown lower crystallinities at low temperatures for the non-restricted copolymers although their crystal sizes appear larger. These crystals will melt early on subsequent heating due to their smaller heat of fusion. Thus, crystallization and melting of non-restricted copolymers will proceed quite gradual and reversible, and hence give rise to a small hysteresis.

The hard restriction of sliding diffusion of comonomers impedes lamellar thickening and offers an additional stability to the metastable folded-chain crystals. This additional stability will affect both phase transitions on cooling and heating. On crystallization, crystal nuclei may survive in thermal fluctuations more readily, and hence the onset of crystallization on cooling shifts to higher temperatures compared to the case of non-restricted copolymers. On melting, in addition to the effect of more perfection, the effect of hard restriction makes the crystallites more capable to resist heating than those of non-restricted copolymers, and therefore, melting occurs at higher temperatures and in a more abrupt way. The latter stabilizing effect thus contributes to a large hysteresis for phase transitions of restricted copolymers.

As discussed above, the thermal stability of crystals depends on the amount of crystal defects. Therefore, the thickening growth of crystallites at the fold-end surface swallows chain units in a probability according to their content of comonomers. When longer ethylene sequences accumulate together, the local area on the fold-end surface should contain less amount of comonomers, and this situation favors further thickening growth. By this mechanism, a selection of sequence lengths is realized in the thickening growth of crystallites for non-restricted copolymers. The thickening growth measures the length of monomer sequences simply through the sliding diffusion process. On the contrary, restricted copolymers have only thin lamellar crystals that measure the length of monomer sequences on the lateral surface of crystals through chain folding. From a molecular-dynamics point of view, making a chain fold is expected to be more difficult than realizing a sliding diffusion. Therefore, the lateral growth shall be much less efficient in the selection of sequence lengths than the thickening growth. This explains why the crystallization of restricted copolymers gives rise to a weak segregation of sequence lengths.

In reality cases of homopolymers, the thickening growth of crystallites is mainly impeded by a frictional restriction in the sliding diffusion process of monomers in the crystalline region [16,17]. The same situation also exists in the crystallization of real statistical copolymers. With respect to factors hindering crystal thickening, we expect to see a cooperative effect of the frictional restriction of monomers and the sliding diffusion restriction of comonomers. Therefore, in reality, most of ethylene-based copolymers will undergo the crystal growth on the lateral sides of thin lamellae. Only under high pressure will their thickening growth be a dominant process with mesophase formation at high temperatures [18,19].

5. Conclusion

In practice, it is very difficult, if not impossible, to separate the effect of comonomers with their variable restrictions of sliding diffusion in the crystalline regions, from the effect of comonomers with their variable chemical affinities to monomers. The dynamic Monte Carlo simulations reported here make a study of the sole effect of sliding diffusion restrictions of comonomers in the crystalline regions possible. This restriction appears to have a very significant effect on crystallization and melting of homogeneous copolymers. It enhances crystallization on cooling and retards melting on heating, explaining the variations of hysteresis found in reality. It also leads to a change from the usual dominant mode of crystal growth by thickening in the longitudinal direction, to the mode of crystal growth in the lateral direction. Thus, it leads to thin lamellar crystals as well as to a weak segregation of sequence lengths. The disagreement found between simulations and reality with respect to the crystallization and melting temperatures of the non-restricted and restricted copolymers may be associated to the different chemical affinities of propylene and 1-octene to the monomer sequences. In reality, with respect to crystal thickness, the sliding diffusion restriction of comonomers is expected to play a cooperative role with the frictional sliding diffusion restriction of monomers.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.polymer.2005.02.134. Movies of the cooling of the restricted sample A for $2.3 < T/E_p/k_B < 3.0$ and of the non-restricted sample A for $1.9 < T/E_p/k_B < 2.7$ are available via Internet at http://www.elsevier.com.

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