

Melt-memory of polyethylenes with halogen substitution: Random vs. precise placement

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HIGHLIGHTS

- Model precision and random ethylene-vinyl halides generalize the strong melt-memory observed in random copolymers.
- Random halogen polyethylenes show enhanced crystallization rate from melts 60° above observed melting.
- Precision halogen polyethylenes show negligible change in crystallization rate above observed melting.
- Crystallization rate is insignificantly altered by annealing heterogeneous random copolymers melts for up to 1000 min.
- Recrystallization of precision halogen polyethylenes depends on polymorph that melts prior to crystallization.

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ABSTRACT

Polyethylenes with Br, Cl, or F atoms placed at an equal distance of 21 or 15 backbone carbons are known to crystallize as homopolymers, accommodating the halogen in layered crystallites. In contrast, analogs with a random distribution display a crystallization path dominated by sequence-length selection. A consequence of the sequence selection of random copolymers is a constrained interlamellar region and broader melting peaks displaced at higher temperatures than analog systems with the precise placement. Precision and random ethylene-vinyl halides are excellent models to substantiate as a general behavior the strong melt-memory observed in random ethylene 1-alkene copolymers, which contrasts with a much weaker or lack of melt-memory seen in linear polyethylene. While precision polyethylenes with Br, Cl, or F placed on each 21st or 15th backbone carbon show negligible deviation in crystallization rate above the observed melting, the increase in crystallization rate of analogs with the random distribution is observed even from melts 60° above the observed melting point. These data give further evidence of the sharp difference of melt-memory behavior between homopolymers and random copolymers, regardless of whether the co-unit participates in the crystalline regions. Differences in melt-annealing behavior, and a recrystallization of precision polyethylenes that depends on the polymorph that melts prior to a subsequent cooling, are also highlighted.

1. Introduction

The influence of a crystalline structure on recrystallization after melting often arises in the form of enhanced recrystallization kinetics and thus, higher crystallization temperatures. More specifically, the term melt-memory, often referred to as self-nucleation, is used to discuss increases in crystallization rate that occur when cooling from melts above the observed melting temperature but below the equilibrium melting temperature of the polymer. Strong melt-memory occurs when the increase in crystallization rate happens upon cooling from above the equilibrium melting temperature of the polymer. The term self-seeding is usually applied to polymers that display an increase in crystallization

rate when cooled from temperatures slightly below their final observed melting temperature. Therefore, the manifestation of melt-memory as an increase in recrystallization kinetics is a feature that can be easily followed by differential scanning calorimetry [1–9]. Melt-memory is associated with the process of dissipation of the order upon heating crystals above their melting point.

In a recent work, we demonstrated that linear polyethylene only displays melt-memory when it is heated to temperatures very close to its observed melting temperature [1]. Linear polyethylene showed only a slight increase in peak crystallization temperature, indicating that its crystallization is approximately independent of the melting temperature. On the other hand, a series of hydrogenated polybutadienes

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(HPBD), analogous to random ethylene co-1-butene copolymers, showed a significant dependence of peak crystallization temperature on melt temperature for copolymers above a molecular weight of 7000 g/mol. Below this threshold molecular weight, the crystallization of random copolymers displays the same independence from melting temperature as linear polyethylene. The increases in peak crystallization temperature with decreasing melt temperature occur at temperatures $\sim 65^\circ$ above the observed melting, and well above the copolymer's equilibrium melting temperature, indicating the presence of strong melt-memory.

We concluded from the study that the melt-memory effect found in the random copolymers, which was absent in linear polyethylene, must be due to the ethyl branches, as they are the only structural difference between the two. Since branches longer than methyl are excluded from the crystal, the crystallization of random copolymers evolves through a process of sequence selection by which branches and other topological constraints are rejected and accumulated in the intercrystalline regions, especially at the higher levels of transformation [10–12]. It is the constrained topology of branches, knots, ties, loops, and other entanglements surrounding the copolymer's crystallites that is believed to hinder segmental diffusion at temperatures below a critical (onset) melt temperature. Hence, the strong melt-memory found in the copolymers is associated with clusters of molten ethylene sequences from the initial crystals that remain in close proximity, unable to diffuse quickly to a randomized melt state. The clusters only fully dissolve into a homogeneous melt at very high temperatures, well above the equilibrium melting point [2,13–18]. On the other hand, when the branch content is increased above a certain value, melt-memory disappears altogether. We attributed reduction in melt-memory with increasing branch content to the shortage of crystallizable sequences that exist when more branches are present. When fewer crystallizable sequences exist, the level of crystallinity decreases, the crystals produced are thinner, and the system is therefore more readily randomized to a homogeneous melt at lower temperatures.

A set of homopolymers and equivalent random ethylene copolymers, containing halogens instead of alkyl branches, is available via novel synthetic routes [19–22]. These samples are ideal systems to test the generality of the strong melt-memory effect in crystalline random copolymers, and to probe the differences in melt-memory between homopolymers and random copolymers observed in prior works. The novel polymers comprise a polyethylene backbone and halogens (Br, Cl, or F) that are either placed precisely at the same equal distance along the backbone [19–21], or randomly distributed [22]. Hence, unlike the linear polyethylene and random ethylene co-1-alkene copolymers, the new polymers have analogous backbones with pendant halogens, and the only difference between the two is the location of the halogen substituents along the chain. We have shown in previous works that polyethylenes with precisely placed halogens have the melting and crystallization behavior of homopolymers [23–25]. Therefore, in the present work we study comparatively the melt-memory behavior of the precision and random halogen-containing polyethylenes and treat the precision samples as the homopolymer reference for the behavior of each random copolymer.

Unlike the ethyl branches of the ethylene co-1-butene copolymers, the halogen substituents have a relatively small volume, such that some of the co-units can participate in the crystalline region [25–31]. In this case, crystallization begins with the most crystallizable sequences, or long ethylene sequences with few halogens, and proceeds to the shorter chain lengths that contain more co-units, a process which is analogous to the sequence selection mechanism for excluded co-units discussed above. Although a portion of the co-units become trapped within the crystalline region upon crystallization, they act as defects in the crystalline structure, resulting in lower degrees of crystallinity [25]. Additionally, it becomes more difficult for the halogens to be accommodated within the crystalline region with increasing size. This further reduces the degree of crystallinity as the content of halogen in the chain

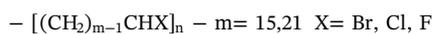
is increased.

A conclusion in our earlier work was that sequence selection leads to a complex intercrystalline melt topology, which is responsible for the strong melt-memory observed in random copolymers with co-units excluded from the crystals [6]. If this conclusion is general for all semi-crystalline random copolymers, including those with co-units partially included in the crystals, then the polymers with randomly placed halogens will display melt-memory, while the polymers with precisely placed halogens will not. To test this hypothesis, the series of polymers with precisely and randomly placed halogens is studied by differential scanning calorimetry (DSC). The comparative analysis from this study indicates that not only is the effect of melt-memory on recrystallization drastically different between random and precision analogs, thus corroborating previous observed differences between homopolymers and random copolymers, but also that recrystallization of precision samples depends on the thermal stability of the polymorph that melts upon heating.

2. Experimental

2.1. Materials

In this work, we compare the melting and crystallization behavior of polyethylenes with halogens precisely placed on each and every 15th and 21st backbone carbon to that of polyethylenes with analogous, randomly distributed, halogen content. The polyethylene samples with precisely placed halogens are labeled PE15Br, PE21Br, PE15Cl, PE21Cl, PE15F, and PE21F. The number following PE indicates the precise placement of the halogen on the backbone. The configuration of the halogen is atactic. The polyethylene samples with precisely placed halogens are considered homopolymers with the repeating unit:



The polyethylene samples with randomly distributed halogens are labeled RPE15Br, RPE21Br, RPE15Cl, RPE21Cl, RPE15F, and RPE21F. The number following RPE indicates that the average molar content of halogen in the random copolymer is identical to the halogen content of the precision sample. In other words, for every 100 carbon atoms, PE15X and RPE15X both contain 6.67 halogen atoms, while PE21X and RPE21X contain 4.76 halogen atoms. The only difference is the distribution of the halogens along the backbone. The polyethylene samples with randomly placed halogens are considered random copolymers of ethylene and vinyl halide.

The synthesis and chain characterization for all the polyethylene samples used herein have been reported previously [19–22]. The weight-average molar mass (M_w), molar mass distribution (M_w/M_n), and relevant thermal characteristics obtained using DSC are shown in Table 1.

2.2. Methods

A TA Q2000 differential scanning calorimeter (DSC) was used to investigate the crystallization and melting behavior of each sample listed in Table 1. The DSC operates under flow of nitrogen and is connected to a TA Refrigerated Cooling System 90, which permits temperature control below ambient conditions. Indium was used to calibrate the DSC for static temperature, thermal lags, and heat of fusion. A film with a thickness of approximately 150 μm was prepared from the original sample powder using a Carver press. Approximately 4 mg of the film was cut and placed in an aluminum DSC pan.

Each sample was brought first to a temperature sufficiently high to erase its thermal history. Samples with randomly placed halogens were heated at $10^\circ\text{C}/\text{min}$ to 200°C , held isothermally for 5 min, and cooled at $10^\circ\text{C}/\text{min}$ to 0°C (or -50°C in the case of RPE15Br). Samples with precisely placed F followed exactly the same procedure, while samples with precisely placed Cl or Br were heated only to 120°C . Melting and

Table 1
Molecular mass and thermal characterization of precision and random halogen-containing polyethylenes.

Sample	mol% (halogen)	$M_w \cdot 10^3$ (g/mol)	M_w/M_n	T_c peak (°C) ^c	T_{melt} peak (°C) ^c	ΔH_m (J/g) ^c
RPE21Br	4.76	55.5 ^b	1.7	65.0	75.6	72.9
RPE15Br	6.67	72.1 ^b	1.8	37.0	34.4	48.2
PE21Br	4.76	94.1 ^b	2.2	53.9	69.2	70.5
PE15Br	6.67	27.6 ^b	1.7	26.6	48.9	44.5
RPE21Cl	4.76	118.5 ^b	2.2	76.8	88.0	106.0
RPE15Cl	6.67	73.6 ^b	2.1	57.7	70.4	78.9
PE21Cl	4.76	31.1 ^b	4.4	72.1	81.0	117
PE15Cl	6.67	51.4 ^a	1.8	54.4	64.0	79.1
RPE21F	4.76	21.6 ^a	1.6	119.8	127.2	172.1
RPE15F	6.67	7.9 ^a	2.5	108.2	119.3	154.3
PE21F	4.76	7.6 ^a	1.8	113.6	123.9	165.8
PE15F	6.67	10.4 ^a	2.2	115.2	124.3	171.8

^a GPC vs PE in DCB.

^b GPC vs PS in THF.

^c Crystallization peak (T_c peak), second melting peak (T_{melt} peak), and heat of fusion (ΔH_m) obtained by DSC at 10 °C/min.

cooling protocols for each sample were derived from those previously used for testing melt-memory by DSC [6,8]. A schematic diagram depicting part of the thermal protocol used for RPE21Br is shown in Fig. 1a. Following the clearing of thermal history, each sample was heated to a given melting temperature, held isothermally for 5 min, cooled to 0 °C, held isothermal for 5 min, and heated to the next melting temperature. All heating and cooling proceeded at 10 °C/min. The peak crystallization temperature was recorded from each crystallization exotherm. To avoid annealing of melt-memory or systematic errors in determination of the crystallization temperature, the samples were heated to random melting temperatures well above and slightly below the observed melting temperature. When the sample was heated to values within the region of melt-memory or close to the observed melting temperature, the subsequent melting was at a temperature above the onset temperature to observe melt-memory.

In addition to the thermal protocol described above, random and precision samples were kept at a given temperature above the observed melting temperature for various periods of time prior to cooling to record crystallization. The temperature used to anneal each sample was selected such that the melt would be heterogeneous, i.e. from the self-seeding region, or from the region wherein melt-memory was observed. The purpose of these experiments was to investigate the effect of annealing time on the melt-memory. Each sample with randomly placed halogens was first heated to 200 °C and held isothermal for 5 min to ensure that the thermal history would be erased. The precision samples were heated only to 120 °C as before. This step was followed by preparation of the crystalline state by cooling to 0 °C and holding isothermal for 5 min. Next, the sample was melted to its chosen heterogeneous melting temperature, T_{melt} , and held for the specified time. Finally, after annealing at T_{melt} , each sample was cooled to 0 °C. This

cycle is depicted schematically for the random copolymers in Fig. 1b and was repeated for various times ranging from 5 to 1200 min (5–300 min for precision) for each sample. All heating and cooling proceeded at 10 °C/min. The peak crystallization temperature from 200 °C (120 °C for precision) and from each T_{melt} were recorded for all cycles.

3. Results and discussion

3.1. Equilibrium melting temperature

To determine if random ethylene vinyl halide copolymers display strong melt-memory, or memory of crystallization at temperatures above the equilibrium melting point, a characteristic of random ethylene co-1-alkene copolymers, we first estimated the equilibrium melting temperature (T_{mco}^0) of the copolymers analyzed. Due to the relatively small volume of the Br, Cl, and F pendant groups, the halogens are known to be partially included in the crystalline regions [25–31]. The Sanchez-Eby [32,33] theory accounts for the possibility that some co-units exist inside the crystallites through incorporation of an excess free energy, ϵ . The depression of the equilibrium melting point from the homopolymer reference (in this case polyethylene) is:

$$\frac{1}{T_m} - \frac{1}{T_{mco}^0} = -\frac{R}{\Delta H_u} \left[\epsilon \frac{X_C}{RT_m} + (1 - X_C) \ln \left[\frac{(1 - X_C)}{(1 - X_B)} \right] + X_C \ln \left(\frac{X_C}{X_B} \right) \right] \quad (1)$$

ΔH_u is the enthalpy of fusion per mole of crystalline repeating unit, X_C is the concentration of co-units in the crystallites, and X_B is the concentration of co-units in the chain. The value of X_B is known from the synthesis, and X_C can be obtained via solid-state ¹³C NMR for the copolymers of interest. Values of X_C for RPE21Cl and RPE15Cl were obtained in a prior work [24].

The excess free energy associated with the incorporation of co-units into the crystallites (ϵ) can be calculated under the assumption that, for slowly crystallized copolymers, the experimentally accessible average concentration of co-units in the crystallites is close to the equilibrium value X_C^{eq} [32]. The expression derived by Sanchez and Eby for ϵ is the following:

$$\epsilon = -RT_m \ln \left[\frac{X_C^{eq}}{X_B} \left(\frac{1 - X_B}{1 - X_C^{eq}} \right) \right] \quad (2)$$

Using values of ΔH_u and T_m^0 for polyethylene (970 cal/mol and 145.5 °C, respectively) as well as the ¹³C SS NMR values of X_C obtained in the previous work (shown in Table 2) [24], we calculated the equilibrium melting temperatures, T_{mco}^0 for RPE21Cl and RPE15Cl. Low signal to noise ratio of the ¹³C SSNMR spectra of RPE21Br did not allow a quantitative measurement of X_C . Hence, the equilibrium melting temperatures for random copolymers with Br were assumed equal to those obtained for Cl analogs (see spectra in Figure S11 and Table S11 for justification of this assumption). Due to the larger size of Br, the parameter ϵ is expected to be larger, and T_{mco}^0 for random Br samples may be somewhat lower than the values of Cl analogs given in Table 2. Since F is much smaller than Cl, the T_{mco}^0 for the random F samples is

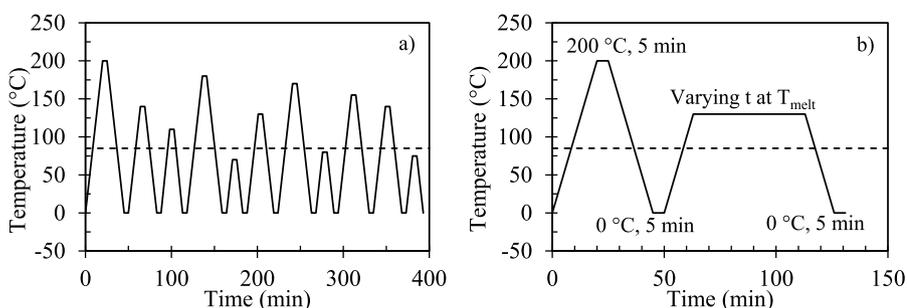


Fig. 1. (a) Example of a DSC thermal protocol used for RPE21Br. Melting and cooling took place at 10 °C/min. The dashed horizontal line corresponds to the observed melting temperature of RPE21Br. (b) DSC thermal protocol used to test the time dependence of melt-memory for RPE21Br. The dashed horizontal line represents the observed melting temperature of RPE21Br.

Table 2

Data used to estimate the equilibrium melting temperature of the Br and Cl substituted copolymers in this study.^a Mole fraction of CHCl or CHBr in the crystalline regions.^{24b} Mole fraction of methine carbons in the copolymer molecule.

Sample	x_{Cl}^{c}	x_{Br}^{c}	ϵ cal/mol	$T_{\text{m copo}}^{\text{o}}$ (Sanchez-Eby) °C
RPE15Cl	0.054	0.067	290	138.3
RPE15Br				
RPE21Cl	0.033	0.048	310	140.2
RPE21Br				

expected to be higher than that for the random Cl analogs. It has been found previously that F is small enough to be incorporated into the crystalline region with minimal lattice strain [22]. It is reasonable then, to assume that the depression of $T_{\text{m copo}}^{\text{o}}$ from polyethylene in the F analogs will be negligible. For this reason, the value of $T_{\text{m copo}}^{\text{o}}$ was not estimated for the random F copolymers studied here.

3.2. Melt-memory of random vs. precision copolymers

Shown in Fig. 2 are selected crystallization exotherms (Fig. 2a), and the subsequent melting endotherms (Fig. 2b) for RPE21Br following the protocol of Fig. 1a. To display the most dramatic effect on crystallization, the exotherms and corresponding endotherms are reported only for T_{melt} values at and slightly above the onset temperature, $T_{\text{m onset}}$, wherein deviation from repeatable kinetics begins.

Cooling from melts of 155 °C and above results in identical exotherms as indicated by the dashed, vertical line drawn in Fig. 2a. Conversely, when cooling from temperatures below 155 °C, the exotherms start at increasingly higher temperatures, reflecting the advent of melt-memory. This feature is independent of cooling rate (Figure

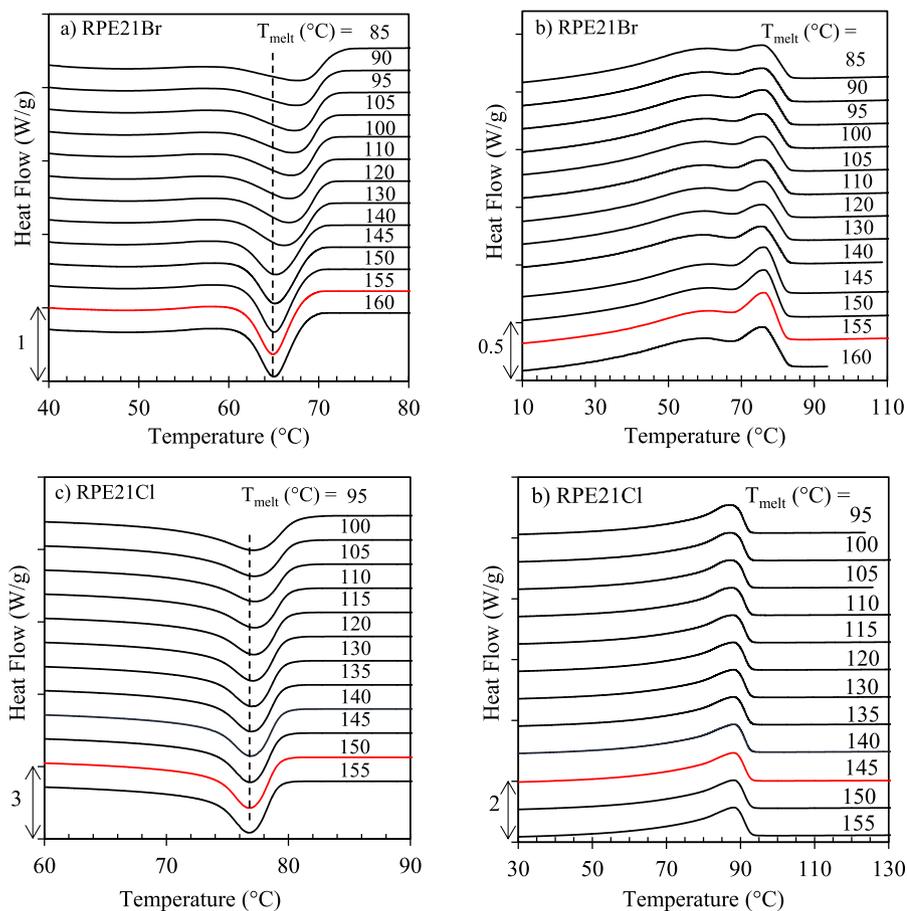


Fig. 2. Crystallization exotherms (a, c) and subsequent melting endotherms (b, d) for RPE21Br and RPE21Cl. The temperature in the legend indicates the temperature to which the sample was melted before crystallization in (a, c) took place. The thermograms have been vertically shifted for clarity. All thermograms for T_{melt} above 160 °C (for RPE21Br) or 155 °C (for RPE21Cl) are equivalent and therefore are not shown here. The red thermograms demarcate the onset of melt-memory. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

SI2). The shift toward higher crystallization temperatures is approximately 2–3° and corresponds to an increase in crystallization kinetics when cooling from temperatures well above the observed melting temperature of 85 °C, and above the equilibrium melting temperature, estimated at 140.2 °C (Table 2). These unique recrystallization features are remarkably similar to those found in model ethylene co-1-butene random copolymers (HPBD) with 2.2 mol% branches [6].

As shown in previous works, melt memory is observed when approaching T_{melt} from below, but not when reaching the same melting temperature from much higher temperatures, indicating a relation between the heterogeneous nature of melts with memory and the formation of crystallites [6]. The difference is that the content of pendant Br atoms in RPE21Br is 4.76 mol%, while HPBD with > 4.5 mol% ethyl branches do not display the effect of melt-memory on crystallization. Therefore, we must conclude that due to the partial inclusion of the halogen in the crystallites, random ethylene vinyl halides display strong melt-memory of crystallization at co-unit contents significantly higher than copolymers with co-units excluded from the crystallites. We observe a similar rightward shift of the crystallization peak in the exotherms of RPE21Cl, as shown in Fig. 2c. As expected, the melting endotherms for crystals formed from melts with or without memory are identical (Fig. 2b and d).

A peculiarity of the melting endotherms of RPE21Br shown in Fig. 2b is that they are bimodal. This is a feature often observed for random copolymers, which is attributed to the nature of the sequence-length selection process during crystallization. It has been posited that two populations of crystals develop, one from the long sequences that can fold to form crystallites of a given thickness, and a second that develops from short sequences without folding, and hence, with more accumulation of branches at the basal surface [34,35]. Although the average crystal thickness may not change broadly, the nature of the interface differs between the two populations of crystals and may cause

the difference observed in melting. The double melting of Fig. 2b may also be explained if the distribution of content of Br in the RPE21Br copolymer is bimodal. Due to the synthetic route used [22], the ethylene sequence length between Br is limited to ≥ 17 CH₂. Hence, the random distribution of Br differs somewhat from the expected statistical distribution in a random copolymerization of ethene and a vinyl halide monomer.

The melting endotherms of the random Cl analog, RPE21Cl, are broad, and also unchanged regardless of the crystallization from melts with or without memory, as shown in Fig. 2d. RPE21Cl crystals do not display the double melting feature in spite of the same sequence length limitation in the lower side of the distribution [22]. Therefore, it appears that the reactivity ratio of the starting monomers is different, which leads to a distribution of content of Cl that is more homogeneous in RPE21Cl than the distribution of Br content in RPE21Br.

The random F-containing copolymer, RPE21F, gives relatively sharp crystallization and melting peaks with similar trends to those observed for Br and Cl analogs (thermograms shown in Figure SI3). All crystallization and melting data indicate a general behavior of random ethylene copolymers with a co-unit that is partially (Br, Cl, F) or fully (ethyl and longer branches) rejected from the crystallites.

The comparative effect of melt-memory on crystallization for the three halogens studied is given in Fig. 3 where the temperature of the initial melt (T_{melt}) is plotted versus the temperature at the peak of the exotherm ($T_{\text{c peak}}$). Vertical continuous lines are drawn over the invariant $T_{\text{c peak}}$ obtained by cooling from melts above the onset of melt-memory. The discontinuous horizontal lines represent the observed final melting temperature. The inset has expanded plots of the data for RPE21Cl and RPE21F that more clearly show the shift of $T_{\text{c peak}}$ to higher values, which for these two samples takes place in a smaller temperature interval. Individual, expanded graphs for each of the three halogens studied are provided in Figure SI4. The onset (strength) of melt-memory, or beginning of the increase in crystallization temperature for the three copolymers, is observed at temperatures 25–60° above the observed crystal melting, and above the equilibrium melting point. As shown in Figure SI4, we choose $T_{\text{m onset}}$ to be the final point which remains on the vertical continuous line (155 °C for RPE21Br, 150 °C for RPE21Cl, and 160 °C for RPE21F). RPE21Br shows the greatest extent of melt-memory, 2–3 °C, while the increase is less than one degree in Cl or F analogs. We see from Fig. 3 that with decreasing halogen size, the extent (range of $T_{\text{c peak}}$ shift) of melt-memory decreases, indicating that

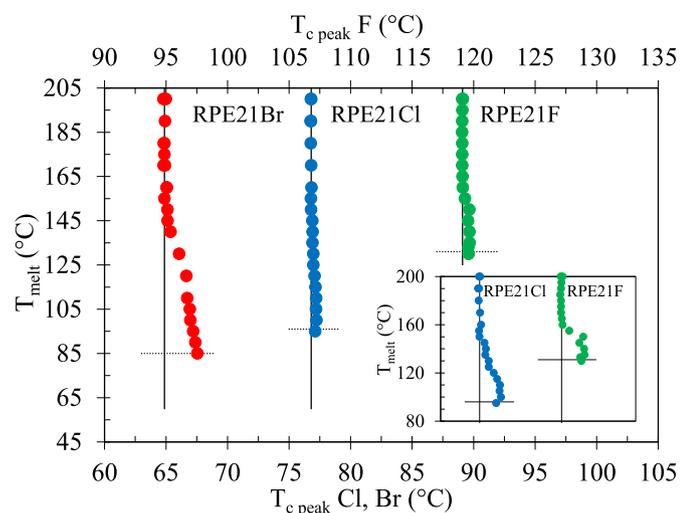


Fig. 3. Plot of the peak crystallization temperatures ($T_{\text{c peak}}$) as a function of the initial melt temperature (T_{melt}) for RPE21Br, RPE21Cl, and RPE21F (top X scale). The discontinuous horizontal lines correspond to the observed final melting temperature. The inset contains expanded plots for RPE21Cl and RPE21F.

the remaining clusters in the melt dissipate more easily in the copolymers with smaller halogen size. Moreover, some differences in heterogeneous nucleation between these samples cannot be ruled out.

Our interest is not only to demonstrate that smaller side groups of random ethylene copolymers display the type of melt-memory observed in random ethylene co-1-alkene copolymers, but also that the corresponding homopolymers, or polymers with equivalent halogen content placed at a regular, equal distance along the backbone, are not subjected to the strong melt-memory effect. Fig. 4 displays crystallization exotherms from the indicated initial melting temperatures, and melting endotherms of precision PE21Br (Fig. 4a and b) and of PE21Cl (Fig. 4c and d). It is clear from the identical thermograms of PE21Cl in Fig. 4c and d, that the rate of crystallization is not affected by the initial melt temperature up to temperatures corresponding to the final crystal melting of 83 °C. Therefore, these data are direct supporting evidence that melting crystallites from a homopolymer leads to melts that are, basically, free of melt-memory.

The crystallization and melting thermograms of PE21Br (Fig. 4a and b) are more complex. At first glance, it appears that the rightward shift in the crystallization exotherms of Fig. 4a may indicate melt-memory, as discussed for RPE21Br. However, this is not the case. Firstly, the increase in crystallization temperature does not begin until values of $T_{\text{melt}} \leq 76$ °C, or at temperatures very near the observed final melting, as seen in Fig. 4b. Therefore, the increase in crystallization kinetics occurs predominantly below $T_{\text{m obs}}$ or from a melt self-seeded by the un-molten crystallites. Second, contrary to the behavior of PE21Cl, the melting endotherms of PE21Br are not equivalent. The double melting of crystallites formed from $T_{\text{melts}} \geq 77$ °C are due to the melting-recrystallization-melting behavior previously discussed [24,25,36–39]. For many precision polyethylenes, the crystal reorganization on melting is associated with the formation of different polymorphs. As shown, for Br or Cl-containing precision polyethylenes, two polymorphs develop depending on crystallization kinetics and display different thermal stabilities [24,25,36–39].

From homogeneous melts, PE21Br and PE21Cl develop crystals of Form I, a kinetically favored *all-trans*, planar, low melting polymorph, while cooling from heterogeneous melts results in crystallization at higher temperatures and thus, development of Form II, a thermodynamically more stable phase that, on further heating, melts at a higher temperature. Form II crystals have a non-planar herringbone type structure [25,36–39]. The complex melting behavior of Fig. 4b is explained as follows. From $T_{\text{melt}} \geq 77$ °C, at a cooling rate of 10 °C/min, PE21Br crystallizes in a mixture of Form I, that melts at 64 °C (the low temperature melting peak of Fig. 4b), and Form II that melts at ~ 72 °C. Upon heating, Form I crystals melt and quickly recrystallize into Form II [38]. At heating rates of 10 °C/min, this recrystallization upon melting of Form I into Form II is unavoidable, thus, any $T_{\text{melt}} \leq 75$ °C will be seeded with remains of Form II crystallites. Because planar Form I crystals cannot grow from the non-planar surface of Form II, any further crystallization must proceed in Form II. This unique polymorphism of PE21Br, characterized by the formation of crystals with drastic differences in conformational packing on cooling from the melt, explains the unusual melting. From melts where some order of the more stable Form II crystals remain, (73 °C $< T_{\text{melt}} < 76$ °C), crystals develop of pure Form II polymorph and melt at ~ 72 °C, while if some fragments of pure Form II crystals remain unmolten ($T_{\text{melt}} < 73$ °C), crystal annealing and further growth at these high temperatures lead to a sharp higher melting endotherm, as seen in Fig. 4b for $T_{\text{melt}} < 72$ °C. The red and blue thermograms of Fig. 4 demarcate the onset of self-seeding ($T_{\text{melt}} = 76$ °C), and the onset of Form II crystal annealing ($T_{\text{melt}} < 72$ °C) respectively.

Form I crystals also develop during dynamic crystallization from the melt of PE21Cl at a rate of 10 °C/min. However, Form I crystals from PE21Cl do not undergo melt-recrystallization at the same heating rate. Therefore, the only possible order or seeds that may remain in the melt are from Form I crystals. Moreover, lack of any increase in the

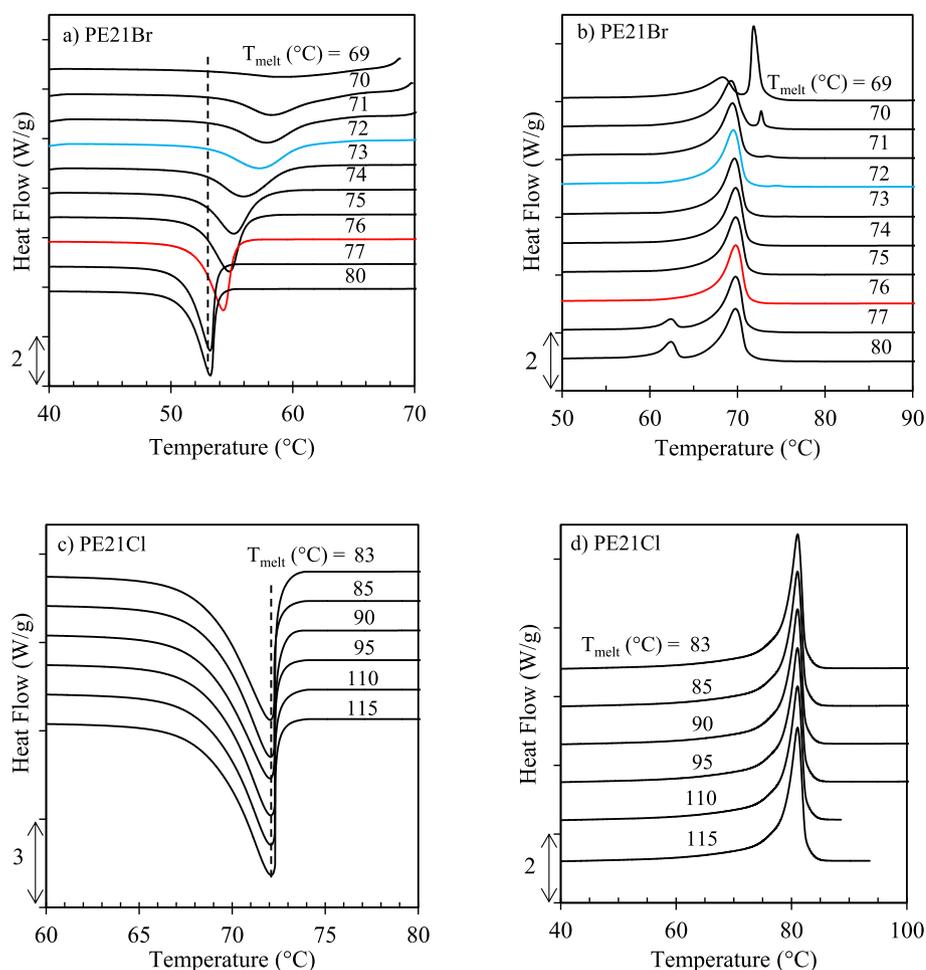


Fig. 4. Crystallization exotherms (a, c) and subsequent melting endotherms (b, d) for PE21Br and PE21Cl. The temperature in the legend indicates the temperature to which the sample was melted before recrystallization in (a, c) took place. The thermograms for T_{melt} above 80 °C (for PE21Br) or 115 °C (for PE21Cl) are equivalent and are therefore not shown here. For PE21Br, red thermograms indicate the onset of self-seeding, and blue thermograms indicate the onset of annealing of Form II crystals. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

crystallization temperature, as seen in Fig. 4c, indicates a fast randomization of the molecules of PE21Cl after melting Form I crystallites. Hence, it appears that randomizing all chain segments that build the more stable herringbone-type Form II crystals requires higher thermal activation than to randomize the *all-trans* sequences of Form I. As found in Fig. 4b, the segments that form Form II crystals retain some order at temperatures 2–3° above their final melting (T_{melt} between 73 and 76 °C). A similar seeding phenomenon has been found in poly (lactic acid) [40], isotactic polypropylene [41], and isotactic polybutene [42]. One can then conclude that the ability for self-nuclei to survive temperatures 3–4° above a homopolymer's observed final melting point depends on the nature and thermal stability of the initial crystallites. Self-nuclei are more prominent upon melting crystallites with strong hydrogen bonding or dipolar interactions, as recently pointed out in a study of the crystallization behavior of poly (ϵ -caprolactone) [43].

Quantitative evidence of the difference between the strong melt-memory effect on crystallization observed in random copolymers and a much weaker or self-seeding effect displayed by the homopolymer is given in Fig. 5a and b. Here, the temperature of the initial melt is plotted vs. the peak crystallization temperature comparatively for samples with random or precision distribution with a composition of 4.76 mol% of Br (Fig. 5a) or Cl (Fig. 5b). While the onset of melt-memory for the random systems is found ~70 °C above the observed final melting point of RPE21Br, and ~55 °C for RPE21Cl, the crystallization temperature of PE21Br, and PE21Cl is unchanged and independent of the initial melt at temperatures very near and above the final melting point.

The data of Fig. 5 clearly confirm the role of sequence selection that occurs during crystallization of random copolymers in building a more

constrained intercrystalline chain topology, such that upon melting, memory of the clustering of long sequences, required to form crystallites, remains up to very high temperatures, even above the equilibrium melting point of many random copolymers. The increase of $T_{\text{c peak}}$ in the homopolymer PE21Br is restricted to values of T_{melt} only ~2 °C above the final melting of Form II crystals; the observed increase of $T_{\text{c peak}}$ when cooling from temperatures below the final melting is indicative of self-seeding, as previously discussed. These results are analogous to what we found when comparing the behavior of linear polyethylene fractions and hydrogenated polybutadienes [6]. We previously deduced that sequence selection leads to a complex, heterogeneous, melt topology which is responsible for the strong melt-memory observed in random copolymers with co-units excluded from the crystals. Since the halogens Br, Cl, and F are not preferentially excluded from the crystalline regions in RPE21Br/Cl/F, we can now surmise that the results in previous works [6–9] are general for random copolymers, irrespective of the moieties' presence in the crystals.

In the following section, we analyze the role of halogen concentration on the strong melt-memory effect of crystallization of halogen substituted polyethylenes. Comparative data for the crystallization behavior of random and precision samples with 6.67 mol% halogen are shown in Fig. 6 for PE15Br/Cl and RPE15Br/Cl. Unlike the behavior of copolymers with lower halogen content, RPE15Br and RPE15Cl show no apparent shift of $T_{\text{c peak}}$ toward higher temperatures for crystallizations from melts above the observed final crystal melting. The same invariance of $T_{\text{c peak}}$ is found for crystallizations of the random analog with F (data shown in Figure S15). The exotherms and endotherms are independent of the temperature of the initial melt, indicating lack of melt-memory in these random systems. Moreover,

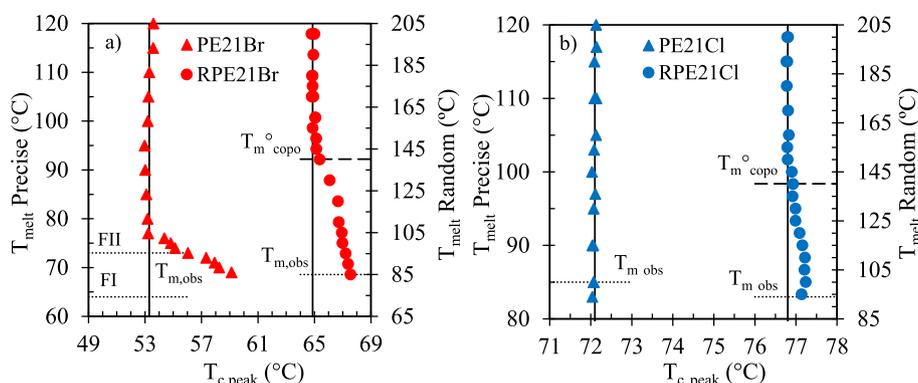


Fig. 5. Peak crystallization temperature plotted as a function of the initial melting temperature for Br (a) and Cl (b) containing polyethylenes with precision (left Y axis) or random (right Y axis) distribution. $T_{m,obs}$ represents the observed melting temperature, $T_{m,ocopo}$ is the equilibrium melting temperature of the copolymer.

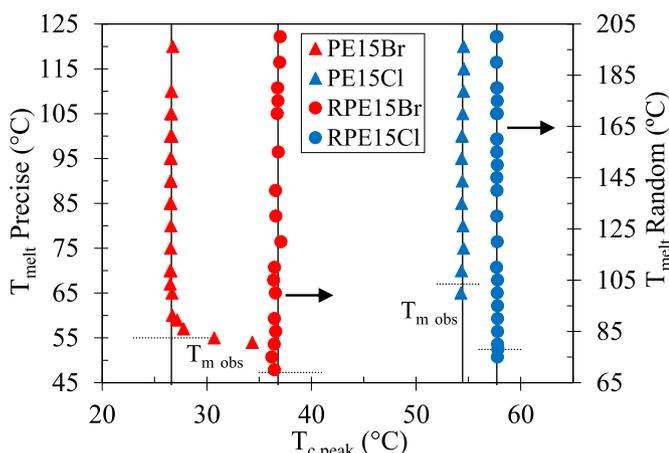


Fig. 6. Peak crystallization temperature plotted as a function of the initial melting temperature for precision (left Y axis) or random (right Y axis) polyethylenes with 6.67 mol% Br or Cl pendant atoms. The horizontal dotted lines represent the observed melting temperature of each sample.

based on the data obtained with model ethylene co-1-butene random copolymers, and the effect of level of crystallinity on melt-memory, the observed dissipation of melt-memory with increasing content of co-unit is expected [6,8]. With increasing comonomer content, the reduced level of crystallinity leads to a topologically less constrained inter-crystalline region, which facilitates dissolution of melt-memory. For alkyl branches excluded from the crystals, melt-memory dissipates at a branching content of 4.5 mol% [6]. The halogen is partially accommodated in the crystals of RPE15Cl and RPE15Br, hence, these copolymers develop a higher degree of crystallinity than ethylene co-1-butene copolymers with equivalent co-unit content. Accordingly, the effective halogen content to enable melt-memory will correspond to the chain's halogen content that remains uncrystallized, which is lower than the content of halogen in the copolymer. In other words, differences in co-unit partitioning between crystalline and non-crystalline regions explain why melt-memory is observed in random copolymers with a halogen content of 4.76 mol%, while memory is dissolved in the melts of ethylene co-1-butene copolymers at a content of ethyl branches ≥ 4.5 mol% [6]. Melt-memory is expected to dissipate at a halogen content > 4.8 mol%.

For comparative purposes, the crystallization data of precision analogs with Br or Cl atoms regularly spaced by 15 backbone carbons (PE15Br, PE15Cl) are also added in Fig. 6. As shown, the data for PE15Cl fall on a vertical line for any T_{melt} above the observed final melting temperature. This invariance is largely equivalent to the behavior of PE21Cl. The slight increase of $T_{c,peak}$ from temperatures 2° above the observed melting of PE15Br is, as discussed for PE21Br,

associated with the development of Form II crystals on cooling. Clusters from this polymorph remain in melts slightly above the observed final melting, thus increasing the crystallization rate on a subsequent cooling. Conversely, the crystals formed on cooling PE15Cl from any T_{melt} are of the less stable Form I, which on melting randomize instantaneously to a homogeneous, memory-free melt.

In addition to documenting the absence of melt-memory in random ethylene co-vinyl halide copolymers with 6.67 mol% comonomer, the data of Fig. 6 make relevant the effect of halogen size on crystallization temperature. The straining effect of the large Br atom in the crystal lattice decreases the crystallization and melting temperatures to a large extent compared to Cl analogs, a 28° decrease in $T_{c,peak}$ between precision samples, and $\sim 21^\circ$ decrease in $T_{c,peak}$ between the random polymers.

For any given composition, the random copolymer crystallizes and melts at higher temperature than the corresponding precision analog, as seen in Figs. 5 and 6. The increased melting temperature of the random copolymer is attributed to the presence of long ethylene sequences in the chain that generate crystallites including a low content of Br or Cl which therefore melt at higher temperatures. Conversely, the layered crystals from precision homopolymers have the same content of halogen as the chain. The difference in melting between precision and random analogs is the highest for Br containing samples ($\sim 10^\circ$), followed by Cl ($\sim 4\text{--}5^\circ$) and by the smallest halogen, F ($1\text{--}2^\circ$). The data for F are not shown [21,22].

We previously quantified the strength of melt memory as the difference between the temperature at the onset of melt-memory and the equilibrium melting temperature of the copolymer ($T_{m,onset} - T_{m,ocopo}$) [6]. Data of the strength of melt-memory for hydrogenated polybutadienes from our prior work and the present data for random copolymers with Cl and Br are plotted versus the content of ethyl branches, and versus the content of halogen, in Fig. 7. For copolymers with ethyl branches excluded from the crystals, the strong melt-memory effect of crystallization vanishes when the ethyl branch content exceeds 4.5 mol%, as shown by the intersection of the line describing the variation of experimental data with the zero value of $T_{m,onset} - T_{m,ocopo}$. The disappearance of strong melt-memory is attributed to the limited availability and shorter length of crystallizable methylene sequences that occur in the chain as the branch content increases. When the amount of crystallizable sequences is reduced, the crystallinity is lowered, and thinner crystallites are produced. Each of these factors contributes to the facilitation of sequential diffusion during melting. The data for RPE21X are represented by the solid circles in Fig. 7. Even for a halogen content higher than 4.5 mol%, the strength of melt-memory is above zero and hence, higher than for ethylene co-1-butene copolymers. However, the same vanishing of melt-memory with increasing halogen content is indeed present in the copolymers studied here, as evidenced by the lack of melt-memory seen in Fig. 6 for the random copolymers with 6.67 mol% halogen (RPE15Br/Cl).

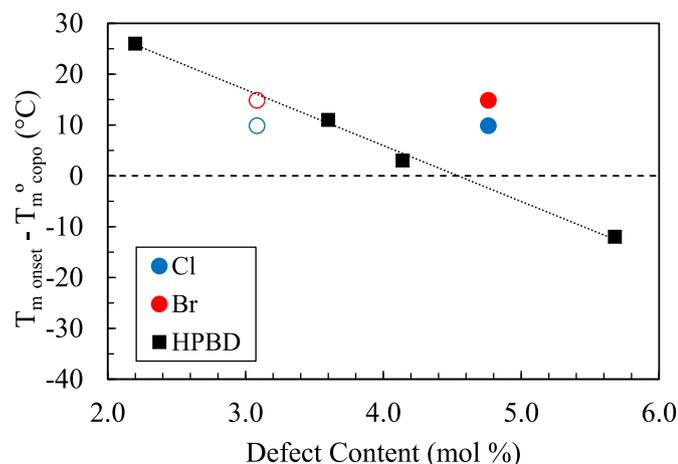


Fig. 7. Strength of melt-memory, the difference between the onset temperature for observation of melt-memory and the equilibrium melting temperature, versus the content of pendant halogen and the content of ethyl branches (defect content in the X label). “HPBD” refers to model random ethylene co-1-butene copolymers from our previous work [6]. Open markers represent the chain’s effective content of Cl or Br for melt-memory (see text).

Because the halogen substituents can partially participate in the crystalline region, the average length of crystallizable sequences is longer in the random copolymer with halogens than in the copolymer with the equivalent content of ethyl branches. Hence, of interest for a comparative effect on melt-memory is the content of halogen in the chain that is non-crystallizable, or effective content for melt-memory. One could then test if the effective halogen content shifts the halogen data in Fig. 7 to the values that describe the random ethylene co-1-butene behavior. The effective halogen content is the content in the chain (4.76 mol% in the data of Fig. 7) minus the content of halogen in the chain that is incorporated in the crystals. The latter can be calculated from the NMR value of content of halogen inside the crystals (out of 100% pure crystals) and the level of crystallinity as [44]:

$$[\text{CH}]_{\text{effective}} = [\text{CH}]_{\text{total}} - [\text{CH}]_{\text{CR}} \cdot X_{\text{cryst}} \quad (3)$$

In writing Equation (3) we note that the content of halogen is given by the methine content. $[\text{CH}]_{\text{total}} = 4.76$ mol%, the content of halogen in the crystalline regions $[\text{CH}]_{\text{CR}}$, termed X_c in Equation (1), is listed in Table 2, and the NMR-based degree of crystallinity, X_{cryst} is 0.52 for RPE21Cl [24]. Since we assumed that the X_c for RPE21Cl is the same as for RPE21Br, as discussed previously, we also use the same X_{cryst} for this calculation. Due to the larger size of Br, X_{cryst} is likely slightly lower than that for RPE21Cl, which would reduce the $[\text{CH}]_{\text{effective}}$ somewhat, however assuming equivalency is sufficient for a baseline estimation. With these data, the value of $[\text{CH}]_{\text{effective}}$ is 3.08 for RPEBr/Cl. The open symbols in Fig. 7 correspond to this effective value and, as shown, fall very close (within experimental error) to the line for the ethylene co-1-butene copolymers. Hence, the constraint effect of the co-units that are

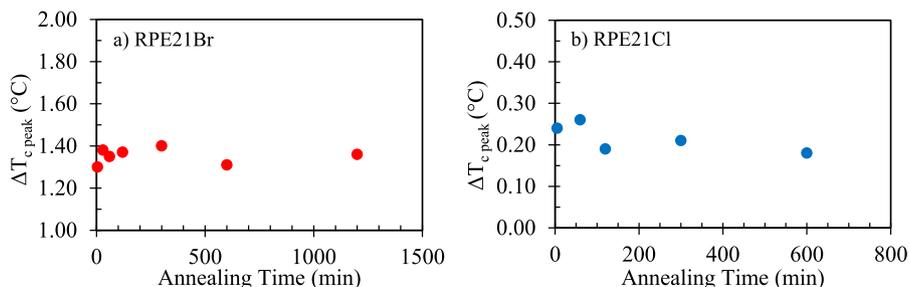


Fig. 8. Difference in peak crystallization temperature after melting to 200 °C (homogeneous) and to a heterogeneous T_{melt} of a) 130 °C and b) 125 °C as a function of annealing time at T_{melt} .

accumulated in the intercrystalline regions of random copolymers is of the same nature regardless of the comonomer type.

3.3. Effect of annealing time on melt-memory

Previously, our group found that melt-memory does not completely disappear upon annealing for a series of hydrogenated polybutadienes (HPBD), even after annealing times of up to 1200 min. Further studies pointed to a strong effect of molar mass on the kinetics of dissolution of melt-memory [9]. During the initial stages of annealing, the melt-memory is reduced for copolymers with $M_w < 50,000$ g/mol, but it never dissipates completely. Instead, an asymptotic value of melt-memory is approached with increasing annealing time. To investigate whether this is the case for the random halogen substituted polyethylenes that showed clear evidence of strong melt-memory, we used the thermal protocol depicted earlier in Fig. 2. The results are reported in terms of the difference between the crystallization peak which occurred after melting to a fully homogeneous state (200 °C), and that which occurred after annealing at the chosen heterogeneous melting temperature. Crystals formed after annealing at the heterogeneous melt temperature were heated to 200 °C and cooled to record the crystallization peak. This procedure was carried out to subtract the effect of heterogeneous nucleation, and to account for any drift the homogeneous melt may experience. The crystals were subsequently heated to the heterogeneous melt where they were kept for a selected annealing time, prior to cooling. Thus, each annealing at the chosen heterogeneous melt temperature had a homogeneous melt reference. The difference between the value at T_{melt} and the reference’s value is labeled $\Delta T_{c\ peak}$.

In Fig. 8, the $\Delta T_{c\ peak}$ is plotted as a function of annealing time for RPE21Br (a) and RPE21Cl (b). It is evident that the change is negligible over prolonged melt annealing times (less than 0.2 °C). Given that the M_w of both random copolymers is greater than 50,000 g/mol, the negligible variation of $\Delta T_{c\ peak}$ with time follows the invariance found for ethylene co-1-butene copolymers of high molar mass [9]. It is worth mentioning that in our previous work, the heterogeneous melting temperature was kept above the equilibrium melting temperature [9]. In this work, the heterogeneous melting temperatures used were 130 °C for RPE21Br and 125 °C for RPE21Cl, which are both below the estimated equilibrium melting temperature of 140.2 °C. We selected lower T_{melt} values for annealing to allow for changes of $T_{c\ peak}$ over a wider temperature range for increased resolution in the experimental data. However, as mentioned, the temporal change of $T_{c\ peak}$ is negligible. Hence, with respect to melt annealing, the data of Fig. 8 indicate a behavior of random copolymers with halogens, identical to the annealing behavior of copolymers with ethyl branches. It is also reasonable to assume that the diffusion coefficient at lower temperatures is lower, and coupled with a relatively high molecular weight, randomization of melt-memory is further hampered in the halogen containing random copolymers. Moreover, annealing at a higher T_{melt} , the change in $T_{c\ peak}$ will be too small to be measured. Note from Fig. 3 that the total change in $\Delta T_{c\ peak}$ at T_{melt} of 140 °C is < 0.2 °C and any change

within this range will be almost impossible to quantify.

As shown earlier, the homopolymers, or precision polyethylenes with halogens, are free of melt-memory, or display a self-seeding effect on crystallization at melt temperatures only 2–3° above the observed final melting. We have associated the self-seeding effect with remains of the order adapted by the most thermally stable polymorph (Form II) of these systems. Conversely, all order of Form I crystals quickly dissipates on heating, and the chains randomize at the observed melting point, as per the invariance of $T_{c \text{ peak}}$ obtained on cooling from any T_{melt} above the final melting (Figs. 5 and 6). Hence, annealing experiments in the precision homopolymers are only relevant for samples that crystallize in Form II on cooling, such as PE15Br, or samples that crystallize in Form I (or a mixture of Forms I and II) but are subject to melting-recrystallization-melting on heating at the standard rate used in this work of 10 °C/min. The latter is the behavior found for PE21Br.

As discussed in the previous section, melt annealing of RPE21Br and RPE21Cl does not result in dissolution of melt-memory. The situation is different for the residual order of Form II at melt temperatures close to the final melting of PE21Br. Notice from the thermograms of Fig. 4a and b that homogeneous melts of PE21Br or invariant crystallization, are reached at melt temperatures ≥ 77 °C. Hence, the sample was annealed at 76.5 °C, or just below the transition from homogeneous to seeded (Form II) melt. The corresponding crystallization and melting thermograms for annealing times up to 300 min at 76.5 °C are given in Fig. 9a and b. Upon increasing the annealing time, we observe that the melting peak for Form I (~63 °C) gradually returns, indicating that the ordered segments, or seeds of Form II that were left in the melt are dissolving with time and increasingly adding isotropic melt for Form I to grow on further cooling. This randomization is possible in the precision samples since they lack the extra complexity in the interlamellar regions characteristic of the random copolymers. To demonstrate the difference between this dissolution of self-seeding and annealing of Form II,

PE21Br was also annealed at 70 °C, a temperature where a small fraction of crystals remain unmolten, for increasing time. The results are shown in Fig. 9c and d. It is evident by the increase in heat of fusion of the melting peak at 73–75 °C, that the amount of annealed crystals increases with time, but no Form I is ever formed. Similar annealing experiments on PE15Br lead to analogous results.

4. Conclusions

Polyethylenes with halogen substitution (Br, Cl, or F), either at a regular, equal distance along the backbone or with a random distribution, are excellent models to contrast the distinctive effect of melt-memory on their recrystallization behavior.

Random polyethylenes with 4.76 mol% halogen content display strong melt-memory up to melting temperatures ~55–70 °C above the observed melting point, and up to nearly 15 °C above their equilibrium melting temperature. This behavior is equivalent to the strong melt-memory previously observed in ethylene 1-alkene copolymers. Due to the partial accommodation of halogen in the crystals of random copolymers, the level of crystallinity is higher than the crystallinity developed by ethylene 1-alkene copolymers with the same co-unit content. Accordingly, melt-memory is observed up to a higher content of halogen in the chain. Copolymers with the biggest pendant halogen (Br) display the highest increase in recrystallization rate, or largest extent of melt-memory. Melt-memory dissipates for copolymers with 6.67 mol% halogen.

In contrast, polyethylenes with precise halogen substitution, which are known to crystallize as homopolymers, showed no significant deviation in crystallization kinetics when cooled from temperatures near or above the observed melting point. This invariance of crystallization kinetics with changing initial melt temperature was also the result found for linear polyethylene fractions. Hence, the data on the halogen

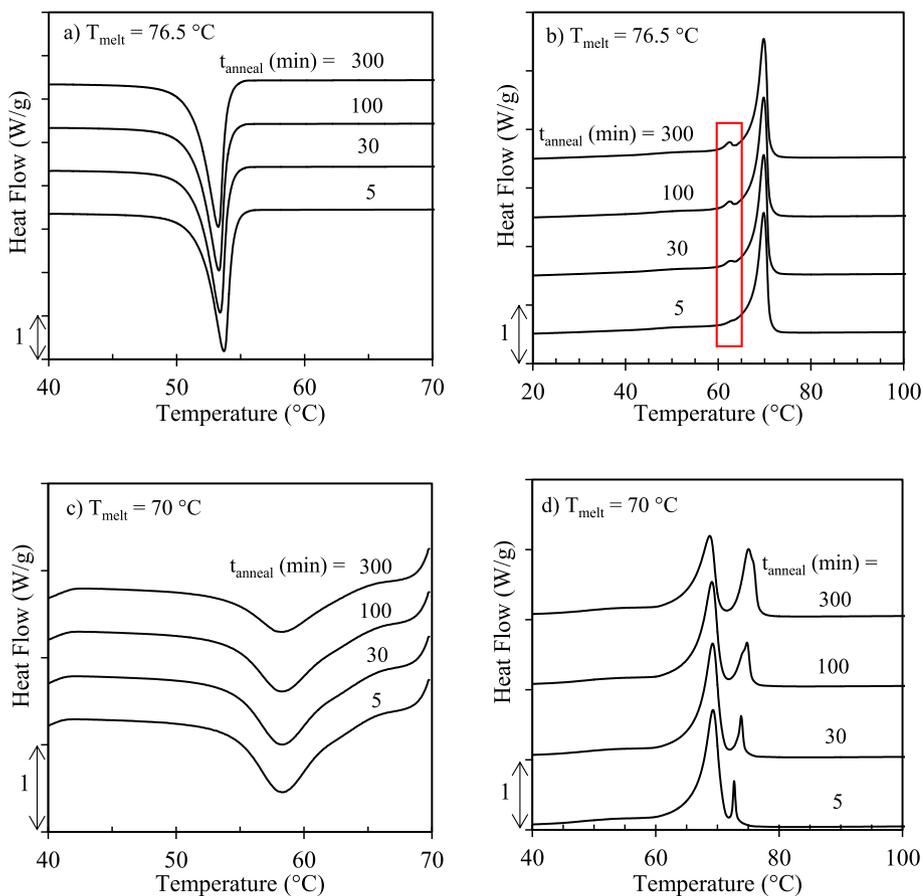


Fig. 9. Crystallization exotherms a), and subsequent melting endotherms b) after annealing PE21Br at T_{melt} of 76.5 °C. The red box highlights the small but gradual formation of Form I crystals upon increasing annealing time. c) and d) are corresponding crystallization and melting thermograms for annealing PE21Br at T_{melt} of 70 °C. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

substituted polyethylenes give strong supporting evidence of the distinctive melt-memory behavior between random copolymers and homopolymers. The strong melt-memory of the random copolymers is attributed to a sequence partitioning during crystallization that leads to a more topologically constrained intercrystalline region, especially around the basal crystal surface. Conversely, sequence selection is not operative in the crystallization of homopolymers. Melt diffusion of chain segments of the homopolymer crystals is less restricted than for copolymer crystallites.

Annealing heterogeneous copolymer melts for times up to ~1000 min made insignificant changes to the crystallization rate, indicating a very slow process for the dissipation of memory. These slow kinetics for dissolution of memory parallel the high activation energy found to dissolve melt-memory of random ethylene co-1-butene copolymers.

The recrystallization of precision polyethylenes with halogens depends on the polymorph that melts prior to recording crystallization on a subsequent cooling. A weak memory effect on recrystallization, which extends to just 2–3° above the observed final melting, is found in precision polyethylenes that crystallize in the most stable polymorph, Form II. In these samples, chain segments from the crystallites retain the symmetry of Form II just above melting, and serve as self-nuclei to increase the crystallization kinetics of this phase on a subsequent cooling. Conversely, precision samples crystallized in the metastable Form I are free of any melt-memory effect, as these less thermally stable crystals melt instantaneously into a homogeneous, isotropic melt.

For random and precision samples, annealing at temperatures below the observed melting leads to self-seeding by which unmolten crystal fragments speed up the rate of crystallization on subsequent cooling from the seeded melts.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.polymer.2019.02.030>.

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