The crystallization behavior of poly(ethylene oxide) (PEO) was studied in the presence of an inorganic filler surface (sodium montmorillonite) with DSC, as well as isothermal cross-polarization optical microscopy. Crystallization of PEO is found to be inhibited, exhibiting a decrease of spherulite growth rate and crystallization temperature. However, the overall crystallization rate increases with silicate loading as a result of extra nucleation sites, which occur in the bulk PEO matrix (i.e., far from the silicate surfaces). PEO differs from other systems, where crystallinity is typically enhanced next to such surfaces, in that the polymer is amorphized near the montmorillonite surfaces. This behavior is attributed to the specific way that PEO interacts with Na+ montmorillonite, where strong coordination of PEO to the surface Na+ cations promotes noncrystalline (ether crown) PEO conformations.

Introduction

Polymer crystallization behavior near an inorganic surface has been the focus of extensive study. In most cases the inorganic surface is shown to produce a nucleating or epitaxial effect, which often stabilizes the bulk crystal phase or, in some cases, it promotes growth of a different crystal phase. The polymer mechanical and thermal properties can be enhanced through this mechanism, where the surface-nucleated crystalline phase has better mechanical and thermal characteristics than the bulk crystal phases. Fillers with large surface areas maximize these filler-induced enhancements of the material properties; a dramatic manifestation of such a response is found in nylon-6/montmorillonite nanocomposites. Less dramatic property enhancements are found in systems where the bulk crystalline phase is simply stabilized via the incorporation of heterogeneous nucleation sites, such as in polypropylene/organo-montmorillonite systems.

The nylon-6/inorganic hybrids show dramatic enhancements in their mechanical and thermal properties upon addition of a minute amount (2–10 wt %) of montmorillonite (MMT), a nanometer-thin mica-type layered silicate with a surface area of about 750 m²/g. This was later attributed to a filler-stabilized crystal-line phase of nylon-6 formed at the silicate surface. PVA/layered-silicate nanocomposites also possess such filler-induced property enhancements, which were also attributed to the existence of a non-bulk-like crystalline structure promoted when Na+ montmorillonite (MCT) is added to PVA.

The present work is inspired by the unique character of PEO, which exhibits crystallization enhancement in the presence of inorganic fillers, but at the same time, its crystallization is hindered by the addition of alkali cations. These two competing mechanisms are simultaneously present in PEO when Na+ MMT is added (since the polymer/MMT interactions are favorable to mixing and crystallization, whereas the polymer/Na+ interactions are favorable to mixing but not conducive to crystallinity). Thus, we aim to elucidate the crystallization behavior of PEO upon addition of Na+ MMT, where the general heterogeneous nucleation of polymers competes with the PEO coordination to Na+, which is known to destroy PEO crystallinity. We use differential scanning calorimetry (DSC) techniques (isothermal and scanning) as well as cross-polarization optical microscopy (CPOM) to investigate the crystallization behavior of PEO and PEO/Na+ MMT hybrid materials. We focus on the effect of the inorganic filler on the PEO crystallization behavior.
lization, and specifically on the morphology, nucleation, growth, and overall crystallization rate.

**Experimental Section**

**Materials and Sample Preparation.** Sodium montmorillonite (MMT) was obtained from Southern Clay Products (Cloisite Na⁺) with a cation-exchange capacity (CEC) of 0.95 mequiv/g, which corresponds to about one Na⁺ per 70 Å². MMT is a naturally occurring 2:1 phyllosilicate, capable of forming stable suspensions in water. This hydrophilic character of MMT also promotes dispersion of these inorganic crystalline layers in water-soluble polymers such as poly(vinyl alcohol)12,16 and poly(ethylene oxide).13,15 Films of neat PEO and PEO/ inorganic hybrids were prepared using a film-casting method.6 Hydrid films were cast from a MMT/water suspension where PEO was dissolved. Room-temperature distilled water was used to form a suspension of sodium montmorillonite at a concentration of ≤2.5 wt %. The suspension was stirred for 1 h and sonicated for 20 min. PEO (number-average molecular weight 136 000 g/mol, polydispersity 1.2) (PolySciences) was added to the stirring suspensions such that the total solids (silicate plus polymer) concentration was ≤5 wt %. The mixtures were then heated to 50 °C to ensure complete dissolution, again sonicated for 20 min, and finally films were cast from solution on top of glass substrates. Drying was done on a hot plate at 35–40 °C covered, for 24 h, followed by drying under vacuum at 40 °C. Samples were then melted at 100 °C for 30 min and allowed to cool slowly, to ensure good intercalation of the tactoid layers by the PEO. The nominal film thickness for the optical microscopy samples was 10–50 μm. Specimens for XRD and DSC studies of neat PEO and PEO/ MMT systems were prepared by the same method.

**Characterization.** Cross-polarization optical microscopy was carried out in a Olympus BH-2 optical microscope, equipped with a Mettler hot stage (RT-300 °C), and a video camera connected to a VCR. The crystallization behavior of all systems was recorded in real time video, which was used later for analysis. Differential scanning calorimetry (DSC) was performed in a Perkin-Elmer DSC7 at variable heating (or cooling) rates as well as at isothermal conditions under an argon atmosphere. Wide-angle X-ray diffraction (XRD) data were collected in digital form using a Rigaku Geigerflex powder diffractometer with a Dmax-B controller and a vertical goniometer. Operation was in the 0–0 geometry. The instrument uses radiation from a copper target tube (Cu Kα radiation λ = 1.541871 Å, including both the Kα₁ and Kα₂, whereas Kβ was eliminated with a graphite monochromator). The PEO molecular weight was characterized by aqueous GPC, bearing PH–aqulage–OH columns (OH 30, 8 μm, Polymer Laboratories), and calibrated with PEO standards.

**Results and Discussion**

**Results.** In this work we comparatively study the crystallization behavior of neat–unfilled–PEO and PEO/Na⁺–MMT hybrids. The structure of these polymer/inorganic hybrids is well-known (Figure 1), studied extensively both by experiment13–15 and by molecular simulations16,17 and is markedly independent of the filler loading. When enough PEO exists in the compos-
in isolation or in groups of tactoids (agglomerates, Figure 1b) separated by regions of pure polymer (Figure 1).

Cross-polarized optical microscopy (CPOM) was used to compare the crystal morphology between filled and unfilled PEO, and subsequently DSC studies were used to further quantify the relevant crystallization kinetics. We focus on systems with low silicate loadings ranging from neat PEO (0 wt % MMT) to PEO with 10 wt % MMT. In Figure 2 we compare the CPOM images of neat PEO and a PEO/5 wt % MMT intercalate, both crystallized at 45 °C. The morphology of the crystals is shown at an early stage (neat, Figure 2a; intercalate, Figure 2c) and at the final stage of crystallization (neat, Figure 2b; intercalate, Figure 2d). For the neat PEO, it can be clearly seen that the spherulites are similar in size, and prior to impinging upon one another, they appear circular, suggesting an isotropic (spherical) three-dimensional shape. For the intercalated system (Figure 2c,d) the spherulite sizes vary a lot, and they are typically much smaller than the ones seen in neat PEO. Moreover, in these systems the spherulites are characterized by very anisotropic, nonspherulitic shapes (Figure 2d) with jagged edges, even before impinging upon one another (Figure 2c).

A CPOM time series, following a crystalline growth front in the same intercalated material, can provide some clues on the origin of these crystal morphologies. In Figure 3 a progression of a growing crystallite is shown for the PEO/5 wt % MMT system. The early and late stages are shown in parts a and f of Figure 3, where silicate tactoids can be seen, manifested as either bright/white features (near the focused plane) or dark features (below and above the focused plane). Parts b–e of Figure 3 are a higher magnification of the selected area (shown as the box in Figure 3a/f) as the spherulite growth-front encounters an MMT agglomerate (or a large tactoid). As the growth proceeds, the lamellar pathways are interrupted and they are forced to grow around the tactoid, breaking the spherical symmetry of the crystallite, and crystallization is delayed in the region downfield from the tactoid. The same behavior is also observed for the smaller tactoids in the image, albeit at smaller scale. At the end of crystallization (Figure 3f), we see that the effect of the MMT on the crystallite growth resulted in “spherulites” grown in a haphazard fashion with tortuous lamellar pathways and jagged edges. Also, the crystallite size is markedly smaller than the spherulites developed in neat PEO (Figure 2b).
This difference in crystallite size can be quantified by enumerating the number of crystallites/spherulites per area. In Figure 4 we show the density of crystallites, as measured in the isothermal crystallization CPOM experiments at temperatures (T\textsubscript{iso}) of 45 and 50 °C. It is seen that the density of crystallites increases by more than an order of magnitude when MMT layers are introduced in PEO, even at very small silicate loadings. Moreover, CPOM reveals that almost all of the crystal nuclei initiate in the bulk PEO, i.e., far away from the MMT fillers. Albeit this huge difference in the number of crystallites between neat and intercalated PEO, the polymer crystalline fraction—as measured through DSC experiments—does not show a marked change between these two systems: In Figure 6 we plot the enthalpy of melting (ΔH\textsubscript{m}) as measured by DSC, showing no strong effect of the silicate loading and/or the crystallization temperature on the final crystallinity of the systems. One of these DSC experiments is shown in Figure 5a for neat PEO and PEO/5 wt % MMT. The onset and peak crystallization temperatures (T\textsubscript{c}) can also be measured from the cooling response (Figure 5b). The addition of MMT fillers in the PEO decreases the polymer T\textsubscript{c} for all cooling rates used, suggesting that the MMT hinders the PEO crystallization, a conclusion which is in concert with the behavior seen in Figure 3. As expected, the DSC-observed T\textsubscript{c} decreases with cooling rate, and the crystallization temperature of PEO/MMT composite deviates more from the neat polymer’s T\textsubscript{c} as more MMT filler is added. The fact that the dependence of T\textsubscript{c} on the cooling rate is similar for the neat PEO and the filled PEO suggests that these differences are due to genuine changes in the polymer crystallization, rather than changes of the thermal conductivity caused by the incorporation of the inorganic fillers. In the latter case, if the DSC-observed decrease of T\textsubscript{c} were actually due to changes in thermal conductivity, the difference in T\textsubscript{c} between the neat and filled PEO would have been a strong function of the cooling rate.

Finally, isothermal DSC measurements can be used to quantify the overall crystallization rate, which is the product of the nucleation rate and the crystal growth rate. Namely, in Figure 7 the crystallization half-time (t\textsubscript{1/2}) is plotted against the “undercooling” for various
isothermal temperatures ($T_{\text{iso}}$), for neat and filled PEO systems. The half time of crystallization ($t_{1/2}$) was defined as the time necessary to reach 50% of the total polymer crystallization, after the induction period. “Undercooling” is defined as the $T_C - T_{\text{iso}}$ temperature difference, where $T_{\text{iso}}$ is the temperature that crystallization was studied under isothermal conditions and $T_C$ is the DSC crystallization temperature. Due to the nature of these system’s crystallization behavior (Figure 5), different definitions of “undercooling”—or of $T_C$—will only shift the x-axis of Figure 7, but will not change the relative positions of the data points depicted in it. (18)

From Figure 7, it is obvious that the half-time of crystallization increases as $T_{\text{iso}}$ approaches the crystallization temperature, as expected; that is, crystallization becomes slower as $T_{\text{iso}}$ approaches the $T_C$ for each system. Furthermore, when silicate is added to the system, the half-life time is reduced for all undercoolings; thus, the overall crystallization rate increases with the addition of MMT in the polymer.

**Discussion.** Before we discuss our results, we outline the three main experimental observations to be explained:

1. The introduction of MMT fillers hinders the PEO crystallization, as observed directly by optical microscopy (Figure 3) and manifested in the decrease of the crystallization temperature (Figure 5).

2. The overall PEO crystallinity is not affected by the filler introduction (Figure 6) for small (<10 wt %) filler loadings, but the crystal morphology is strongly altered by the MMT presence, resulting in more, smaller, and nonisotropic crystallites (Figures 2 and 4).

3. The overall crystallization kinetics becomes faster with the addition of MMT (Figure 7).

At first glance, our first observation seems at odds with the last: Although crystallization is hindered by the introduction of MMT fillers, the overall crystallization kinetics becomes faster. This is a consequence of the much larger number of crystallites created in the presence of MMT compared to the neat PEO system (Figure 4). Because the overall crystallization rate—as measured by $t_{1/2}$—is the product of the nucleation rate and the crystal growth rate, it is actually possible for the overall kinetics to increase despite a slowing down of the crystal growth rate, when more crystals are nucleated, as is the case here (Figure 4).

The most interesting finding of this work is probably the fact that the introduction of MMT inorganic fillers slows down the polymer crystal growth in the vicinity of the filler. This contrasts the usual behavior of
The crystallization behavior of PEO in the presence of MMT surfaces should result in enhanced crystallization rates. The unusual behavior observed herein for PEO originates from the specific manner that MMT interacts with poly(ethylene oxide). Addition of small cations, in the form of salts, has been shown to reduce or completely destroy the crystallinity of PEO. This behavior is attributed to the strong coordination of PEO to small cations, such as Na⁺ and Li⁺, which promote “crown ether” type of backbone conformations coordinated to the cations. Such crown-ether conformations deviate from the helical PEO conformations—typically found in bulk PEO crystals—and therefore amorphize the PEO. Because the MMT surfaces bear large numbers of cations (approximately one Na⁺ per 70 Å²), PEO chains in their vicinity are highly coordinated to the Na⁺, adopting conformations with many crown-ether arrangements, which are highly amorphous. A similar behavior—with cations promoting an amorphous PEO structure—has also been seen in the interlayer gallery between the MMT layers in PEO/Li⁺-MMT composites by computer simulations, and we herewith find that this is also an important effect on the external surfaces of the tactoids.

We believe that the slowing of the crystal growth rate is due to this amorphization of the polymer in the vicinity of the silicate, which forces the spherulite to grow around the dispersed tactoids, resulting in “broken” lamellar pathways and geometrically anisotropic shapes. Scanning (cooling) DSC further corroborates these optical microscopy observations because it is found that the crystallization temperatures are shifted to lower values with MMT loadings. This Tc reduction is additional evidence that crystallization is inhibited with the addition of silicate fillers, as larger undercoolings are now needed to begin the crystallization process. If this is the case, reducing the surface density of Na⁺ cations on the MMT surfaces should result in enhanced PEO crystallization.

Finally, putting all these pieces together, we can trace the crystallization behavior of PEO in the presence of Na⁺-MMT fillers: primary nucleation takes place in the bulk—away from the MMT surfaces—and initially spherulites grow normally until they encounter a filler. At this point, because amorphous PEO structures are promoted in the vicinity of the MMT, there is a retardation of the spherulite growth front, resulting in jagged edges and nonspherulitic morphologies. This delay in covering space allows for the nucleation of other spherulites that grow in the same manner until all volume is filled. These additional nuclei cause the PEO to crystallize faster overall, despite the slower crystal growth rate, and allows for the total volume to crystallize more quickly, albeit with much smaller crystalite sizes than in bulk PEO.

Conclusions

Using scanning and isothermal DSC, and cross-polarization optical microscopy, we have investigated the differences of crystallization behavior in neat PEO films and PEO films filled by MMT inorganic layers. The coordination of PEO to the montmorillonite Na⁺ promotes the polymer-filler miscibility, but renders the PEO/MMT interface not conducive to crystallization because it promotes amorphous polymer conformations in the vicinity of the inorganic fillers. Thus, MMT causes a retardation of the crystal growth front and results in crystal morphologies that are characterized by nonspherical shapes with jagged edges. Moreover, this PEO crystal obstruction by the MMT allows for the “heterogeneous” nucleation of large numbers of crystallites, which grow to much smaller sizes than neat PEO spherulites. In the Na⁺-MMT-filled PEO, crystallization nucleation sites occur in the bulk of the PEO matrix, i.e., far from the silicate surfaces, in considerably larger numbers than in unfilled PEO at the same undercooling. This higher nucleation density is a manifestation of two effects: (a) the disruption of the spatial continuity by the inorganic layers, which allows for the independent nucleation of PEO crystallites in the spaces between the fillers, and (b) the characteristic PEO/Na⁺ coordination, which markedly inhibits “heterogeneous” nucleation by the MMT fillers. The absence of marked heterogeneous nucleation contrasts the PEO behavior against most of the other polymer/MMT systems studied, where heterogeneous nucleation and/or epitaxial crystallization are the dominant effects. Despite the different crystal morphologies between neat and filled PEO, there is no marked change in polymer crystal fraction for the small amounts of silicate (ϕ_{MMT} < 10%) studied here. For larger MMT loadings than studied here, the introduction of more PEO/MMT interfaces in the system decreases the PEO crystallinity proportionally to ϕ_{MMT}.

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