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Six types of spherulite morphologies with polymorphic crystals in poly (heptamethylene terephthalate)

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ABSTRACT

Six types of spherulite morphologies packed with polymorphic crystals and their growth kinetics in melt-crystallized poly(heptamethylene terephthalate) (PHepT) were characterized using polarized-light optical microscopy (POM), Fourier transformed infrared microspectrometry (micro-FTIR), differential scanning calorimetry (DSC) and atomic-force microscopy (AFM). Two maximum melting temperatures (T_{max}), a higher 150 °C and a lower 110 °C, were used to melt the initially crystallized PHepT of either α- or β-crystal. The high T_{max} was enough to melt all nuclei, but the lower T_{max} was considered as near or slightly below the equilibrium melting temperatures of these two cells (if estimated by nonlinear methods). When crystallized at various T_c from these two T_{max}'s, PHepT can exhibit as many as six types of spherulites (Ring Type-I, -II, -III, Maltese-cross Type-1, -2, and -3) owing to different nucleations. Ring Type-I, Maltese-cross Type-1 and -3 spherulites are packed of the sole β-crystal, while Ring Type-II, -III and Maltese-cross Type-2 spherulites are attributed to the sole α-crystal. However, as the PHepT polymorphic cells are related to T_c, such correlations between the crystal cells and spherulite types (ring or ringless) cannot be ruled out to be a coincidence.

1. Introduction

Semicrystalline polymers exhibiting polymorphism and different types of spherulite morphology have been studied, such as in poly(vinylidene fluoride) (PVDF) [1–3], poly(1,4-butylene adipate) (PBA) [4–6], poly(hexamethylene terephthalate) (PHT) [7–9] and isotactic poly(1-butene) (i-PBu-1) [10–13]. Polymorphic behavior in PVDF, PBA, or PHT is dependent on crystallization temperature (T_c); besides, the spherulite morphology in these three polymers depends on not only T_c but also polymorphism [1,2,4–9]. Melt-crystallized PVDF shows the α-crystal at T_c lower than 160 °C; however, upon scanning from 160° to melt, the α-crystal transforms to the γ-crystal and the γ-crystal reaches a maximum amount at 170 °C then melts at temperature higher than 185 °C. In the temperature range of 160–185 °C, both the α- and γ-crystal of PVDF exist simultaneously [1], and two kinds of spherulites are observed, where one is ringless and the other is ring-banded. Kressler et al. [2] have characterized the correlation between the spherulite morphology and the polymorphism of PVDF using Fourier transformed infrared microspectroscopy (micro-FT-IR) and indicated that the ringed and ringless spherulites are attributed to the α-crystal and the γ-crystal, respectively. Spherulite morphology and polymorphic behavior in melt-crystallized poly(1,4-butylene adipate) (PBA) have also been well-studied. PBA shows the α-crystal (monoclinic) and β-crystal (orthorhombic) when crystallized at T_c higher than 31 °C and lower than 28 °C, respectively. At T_c lower than 28 °C, where only the β-crystal is crystallized, the spherulite morphology is highly crystallization temperature dependent. At T_c lower than 25 °C, PBA is crystallized into the Maltese-cross (ringless) spherulites, while at $T_c = 26–28$ °C, PBA exhibits the ringed ones. The mechanism in the formation of ring bands in melt-crystallized PBA at $T_c = 28$ °C has been recently reported [14], and the great change of the steepness in height is considered to be the dominant mechanism. Unlike the β-crystal produced at lower T_c (lower than 28 °C), PBA melt-crystallized at T_c higher than 31 °C exhibiting the α-crystal is packed into the Maltese-cross ringless spherulites independent on T_c [4,5].

PHT, an aryl-polyester with six methylene groups between two terephthalate groups, exhibits complex polymorphic behavior upon melt crystallization. PHT contains both the α- and β-crystals when melt-crystallized at T_c lower than 140 °C, whereas when T_c is higher than 140 °C, crystallized PHT contains only the β-crystal. Upon

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crystallization at $T_c = 100$ °C, PHT possesses mixed α- and β-crystal cells, and PHT can be crystallized into mixed morphologies composed of Maltese-cross ringless spherulites and dendrites. An earlier investigation has pointed out that there may be a correlation between the spherulite morphology and the polymorphism in PHT [7]. The normal Maltese-cross spherulites correspond to the α-crystal and the dendritic morphology is associated with the β-crystal. Apart from the effect of the crystallization temperature, polymorphic behavior in semicrystalline polymers is also influenced by crystallization condition, such as cold crystallization, melt crystallization, solvent-induced crystallization or presence of nucleating agent. Isotactic poly(1-butene) (iPB-1) is a polymorphous semicrystalline polyolefin exhibiting four types of crystals, form I, form I′, form II and form III [8]. Form I′ is crystallized from a certain dilute solution or in thin film at elevated temperature (150 °C, 5 days), while Form I, the most stable crystal form in iPB-1, is produced through transformation from Form II when kept at ambient temperature for long time. These four types of crystals in iPB-1 have been claimed to assume different spherulite morphology corresponding to each crystal form, in which the spherulites of Form I and -II are ringless and those of Form III are ring-banded [8].

Polymers mentioned above are all polymorphous and exhibit different spherulite morphology corresponding to each crystal form. In this study, poly(heptamethylene terephthalate) (PHepT) served as a model polymer to go further on investigations of the spherulite morphology of a polymorphous polymer. PHepT exhibits polymorphism (α- and β-crystal) in melt crystallization depending the crystallization temperature (T_c) and maximum melting temperature (T_{max}) [15–17]. When heated at a lower T_{max} (110 °C) containing some traces of α- or β-nuclei and quenched to T_c, the crystallized PHepT shows the sole α-crystal or the mixed $\alpha+\beta$ crystal, respectively. In contrast, when heated at a higher T_{max} (150 °C) and quenched to T_c, the crystallized PHepT is packed of the sole β- and α-crystal at T_c higher than 35 °C and lower than 25 °C, respectively. Although the polymorphic behavior in PHepT has been well analyzed and proven [15], the corresponding spherulite morphology in association with each of these two crystal forms (α- or β-crystal) has yet to be characterized. The lower T_{max} (110 °C) might be superficially over the equilibrium melting temperatures of the α or β-crystal cells of PHepT ($T_m{}^\circ$= 98 and 100.1 °C, linear Hoffman-Weeks extrapolation method) [18]. However, the conventional linear extrapolation procedures for obtaining the equilibrium melting temperatures of polymers might have underestimated the true equilibrium melting temperatures. The equilibrium melting temperatures of the α- and β-crystal according to the nonlinear Hoffman–Weeks method are 121 °C and 122.5 °C, respectively [18]. Thus, the reason of using $T_{max} = 110$ and 150 °C for melting the PHepT samples was based on the result of $T_{max} = 110$ °C being lower than and $T_{max} = 150$ °C being higher than $T_m{}^\circ$= 121 °C – 122.5 °C (nonlinear method). By subjecting PHepT in thin-film forms to T_{max} = 110 or 150 °C, respectively, the spherulitic morphology and growth kinetics in melt-crystallized PHepT packed of either of α- or β-crystal or both crystal cells were characterized using polarized optical microscopy (POM), atomic-force microscopy (AFM), Fourier transformed infrared micro-spectrometry (micro-FTIR) and differential scanning calorimetry (DSC) in order to reveal the exact natures of multiple types of spherulites packed with polymorphic crystal cells.

2. Experimental

2.1. Materials

Poly(heptamethylene terephthalate) (PHepT) was not commercially available and was synthesized in-house using a catalyst (butyl titanate) by following the method described earlier in the literature [19]. Characterizations showed basic physical data for PHepT, whose $T_g = -1.6$ °C, $T_m = 96$ °C, $M_w = 37{,}500$ g/mol (gel permeation chromatography, GPC, Waters), and polydispersity index (PDI) = 1.7 (GPC).

PHepT was heated to a maximum temperature (T_{max}), held to ensure equilibrium, then quenched rapidly to a crystallization temperature (T_c) for various times to ensure full crystallinity. Two maximum melting temperatures (T_{max}), 150 °C and 110 °C, were used to melt the initially crystallized PHepT crystals of either α- or β-crystal. PHepT is polymorphic and samples could be prepared to contain solely α or β-type crystal, prior to being subjected to heating to the prescribed T_{max}. The higher T_{max} (150 °C) was capable of erasing all prior nuclei, and upon crystallization at T_c higher than 35 °C, only β-crystal was found [15]. Samples treated at $T_{max} = 150$ °C are coded as **PHePT-150**.The other T_{max} (110 °C) would permit presence of trace nuclei of either α- or β-crystal, depending on the crystal forms prior to heating to T_{max}. PHepT originally of β-form was heated at T_{max} = 110 °C so that they contained β-form nuclei at this T_{max}; upon crystallization at any $\underline{T}_c$ by quenching from T_{max} = 110 °C would lead to crystals of both α- and β-forms. PHepT samples treated at T_{max} = 110 °C and crystallized with β-nuclei are coded as PHepT-110β. On the other hand, PHepT originally of α-form was heated at same T_{max} = 110 °C so that they contained α-form nuclei at this T_{max}; upon crystallization at any T_c by quenching from T_{max} = 110 °C would lead to only α-crystal. Samples treated at T_{max} = 110 °C and crystallized with α-nuclei are coded as PHepT-110α These crystallization procedures were performed either in DSC cells or on microscopic hot stages, both with precision temperature control, depending on characterization to be followed.

2.2. Apparatus

2.2.1. Differential scanning calorimetry (DSC)

DSC measurements were made in a Perkin–Elmer DSC-Diamond equipped with a mechanical intracooler under dry nitrogen purge. Temperature and heat flow calibrations at different heating rates were done using indium and zinc. Considerably slow heating rates of 0.1 °C/min and 0.5 °C/min were used to completely separate the overlapped melting peaks of the α- and β-crystals.

2.2.2. Fourier transform infrared microspectroscopy (micro-FTIR)

Micro-FTIR measurements were performed at a resolution of 2 cm^{-1} on a Varian 600 UMA microscope with a Varian 3100 FTIR spectrometer equipped with an MCT detector. The lateral resolution of micro-FTIR is 11 μm × 11 μm. Samples for micro-IR measurements were thin PHepT films of 4–5 μm thickness, which were prepared by dissolving the polymer in chloroform (~2 wt%) and cast onto KBr pellets at ambient temperature. The films on KBr pellets were dried in vacuum at 40 °C for 2 days to remove the residual solvent.

2.2.3. Polarizing-light optical microscopy (POM)

A Nikon Optiphot-2 polarized-light optical microscope (POM) equipped with a charge-coupled device (CCD) digital camera and a Linkam THMS-6000 microscopic heating stage with TP-92 temperature programmer was used to observe the crystal morphology of the isothermally crystallized samples. The CCD equipped with automated image software was used to capture the morphology of the isothermally crystallized samples at preset time intervals. Thin-films specimens for POM were sandwiched between two glass slides.

2.2.4. Atomic-force microscopy (AFM)

AFM characterizations were performed in intermittent tapping mode (Caliber, Veeco-DI Crop., USA), using a silicon tip (ν = 70 kHz,