Abstract

During the cold crystallization of poly(trimethylene terephthalate), PTT, multistage preordering activities associated with hierarchically structural evolution and origin of mesomorphic domains were investigated with time-resolved Fourier transform infrared (FTIR), photoluminescence (PL) and dielectric spectra (DS), and simultaneous small- and wide-angle X-ray scattering (SAXS/WAXS). The observed fluorescent emission at 390 nm and an absorption band at 874 cm⁻¹ associated with the CH out-of-plane bending mode of the phenyl rings indicate that the ground-state dimers resulting from the phenyl rings of PTT chains via π–π interactions are formed in supercooled amorphous liquids. The time dependences of the increase of the fluorescent intensities, the wavenumber shift from 874 to 872 cm⁻¹, the conformational transformation of the trimethylene glycol units from trans to gauche for the cold crystallization at 50°C. Herein, we propose a preordering mechanism of cold crystallization in which the π–π interactions among the dimers serve as ordering bonding forces to drive intermolecular cooperativity before intramolecular changes of conformation, and the dimer aggregation triggers the phase-separated mesomorphic domains before the growth of crystalline nanograins (non-lamellar crystals). As distinct from the hierarchical structure of nanograins within mesomorphic domains, the formation of lamellar crystallites within spherulites without underwent the dimer aggregation were observed form the melt crystallization at 200°C.

Keywords - cold crystallization; mesomorphic domains; poly(trimethylene terephthalate).

Introduction

Polymer crystallization is a series of sequential and cooperative chain activities among inter- and intramolecular assemblies. These chain activities prior to crystallization, so-called “preordering”, are one of the most important subjects for understanding a relationship between structural formation and physical properties. Over the past few decades, a considerable number of studies have been conducted on formation of mesomorphic phase or liquid-liquid phase separation (via nucleation-and growth or spinodal decomposition mechanisms) during the preordering process. [1-4] Although it is a wide agreement with that intermediate structures for the preordering are generally referred to a more or less ordered peaking of parallel chains with significantly favored conformations and slight high density in zones of semi-ordered arrangements and observed form crystallization under a deeply supercooling degree (a far from equilibrium condition), their nature and origin were still a controversial issue and no universalism, and varied interpretative models or mechanisms were proposed for different polymers. [1-4]

In our preceding work, we investigated the isothermal cold crystallization of poly(trimethylene terephthalate) (PTT) using simultaneous small- and wide-angle X-ray scattering and differential scanning calorimetry (SAXS/WAXS/DSC) and transmission electron microscope TEM. [3] An atypical hierarchical structure of nanograins within mesomorphic domains prior to cold crystallization was firstly evidenced. The formation of the mesomorphic domains indicated the transient coexistence of liquids in two forms in the induction stage of cold crystallization. In this study, we attempted to investigate the inner structure of the mesomorphic domains and to probe their origin using time-resolved measurements of SAXS/WAXS, FTIR, PL and DS. FTIR and PL spectroscopies are powerful and effective tools for studying real time changes of microstructures and chain conformation during the crystallization process. On the basis of experimental results, we demonstrated that the supercooled liquid of quenched PTT sample does not have a homogeneous random structure, but has existence of phenyl-phenyl dimers via π–π interactions. [5] From integration of time-resolved data, we proposed that the dimer aggregation drives the phase-separated mesomorphic domains during the induction stage of PTT cold crystallization. We also measured the temperature dependence of dimer formation by FTIR, and suggested that the phenyl-phenyl dimer is a kind of locally metastable structure prompted by instability.

Experiments

Poly(trimethylene terephthalate) (PTT) (Tg ≈ 45°C ,Tm ≈ 252°C) pellets of specific gravity 1.34, with an intrinsic viscosity 0.92 dL/g (60/40 phenol/tetrachloroethane, 160°C), were kindly supplied by Shell Chemicals Co Taiwan. Glassy amorphous samples were prepared by melt-pressing at 270°C for 5 minutes before quenching.
into ice-water. Fluorescence emission spectra were collected by fluorescence spectrometer (FLS920). In-situ SAXS/WAXS were performed at the beamline 23A1 of the National Synchrotron Radiation Research Center (NSRRC), Taiwan. FTIR measurements were determined at the beamline 14A1 of NSRRC. Dielectric loss measurements were performed by using Solartron 1260 Impedance Analyzer with 1296 Dielectric Interface for highly resistive samples.

**Results**

To understand the relation among the dimer aggregation, mesomorphic domains and nanograins during the cold crystallization at 50°C, we show in Fig. 1 all time-resolved data derived from SAXS, FTIR, DS and PL, allowing us to elucidate the multistage preordering of the cold crystallization from various points of view of structural and conformational changes and chain dynamics. Before stage III (the two phases only), we estimated the fraction of amorphous domains from the ratio between the dielectric strength $\Delta \varepsilon_a$ and total dielectric strength ($\Delta \varepsilon_a + \Delta \varepsilon_m$) as well as the fraction of mesomorphic domains on the basis of the unity conservation. In Fig. 1b, the two fractions as function of time indicate that the conversion from the regular amorphous to mesomorphic domains occurred mainly in the induction stage I and then approached a plateau about 65% in stage II. Figs. 11c and 11d show the time dependence of the intensity of fluorescence emission of the dimers, the wavenumbers of bands associated with the CH out-of-plane bending mode of the phenyl rings and the intensities of bands at 815 and 936 cm$^{-1}$ corresponding to the trans and gauche conformers, respectively. These results reveal that the preordering chain activity in stage I involved dimer aggregation with a large proportion of the trans conformers; in nucleation stage II the transformation from trans to gauche accompanied the increasing phenyl-phenyl distance, verified from the shift of wavenumber of the band from 874 to 872 cm$^{-1}$ (Fig. 1c) and the decrease of the dimer fluorescence (Fig. 1c). In Fig. 2, the time dependences of the lamellar structural parameters determined from the SAXS data and the crystallinity $W_c$ obtained from the WAXS data are compared with the intensity changes of the trans and gauche conformers revealed by FTIR data for the melt crystallization at 200°C.

**Discussion**

Our experimental results indicate that the dimer aggregation is responsible for the greatly disparate morphological features between the melt and cold crystallizations, which have different kinetic routes. The π-π interactions, which constitute a weak force but which exist to a considerable extent among the dimers, serve as ordering bonding forces to assemble neighboring segments in which the system is trapped under supercooled amorphous liquids for the cold crystallization. In the case of melt crystallization at 200°C, the large thermal fluctuations are disadvantageous for dimer aggregation, whereas a large mobility of chains allows formation of large lamellae through chain sliding diffusion and disentanglement of chains for chain folding.

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**References**