

The effect of temperature on nascent morphology of polyethylene polymerized over solution-phase flat model catalysts

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ABSTRACT

The structure and morphology of polyethylene (PE) produced during solution polymerization using bis(imino)pyridyl metal catalysts supported by flat SiO₂/Si(100) wafers were investigated by atomic force microscopy (AFM) and electron diffraction. Depending on the polymerization temperature, ranging from RT to 85 °C, different morphologies of the nascent PE have been observed. “Sea weed” like super-molecular structures are the predominant nascent morphologies of the PE polymerized at low temperatures. This should be associated with the high PE yield and high nucleation rate at low temperature; the catalyst is highly active and the PE macromolecules have low solubility in toluene and nucleate immediately after formation. With increasing polymerization temperature, e.g. at 60 or 70 °C, larger single crystals with roughly a lozenge shape but saw-tooth-like facets have been created. The multilayer overgrowth of the PE crystals demonstrates that the generated PE materials exceed what is required for single layer crystal growth. At 85 °C, decreasing crystal growth rate results in the formation of small PE single crystals. At the same time, the high solubility of the PE in toluene results in continuous diffusion of the macromolecules to the existing PE crystals and therefore single crystals in regular truncated lozenge shape have been formed. Electron diffraction indicates that in the whole temperature range, PE crystallizes in flat-on crystals in chain-folded structure with different chain folding stem length.

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1. Introduction

The morphology and structure of crystalline polymers have been extensively studied during the past several decades. The morphological development of polymers during crystallization from quiescent states is relatively well understood on the lamellar as well as on the spherulitic scale [1]. However, these investigations have been limited almost exclusively to crystals obtained by crystallization from the solution and melt of pre-synthesized polymers. In the early 1980s, Geil and coauthors have found that the particle morphology, including the size and shape, has significant effect on the properties of a processed polymer [2,3]. It has also been recognized that the defects in the crystals of the nascent polymer also plays an important role in the physical properties and processing behavior of the final products [4]. Understanding the

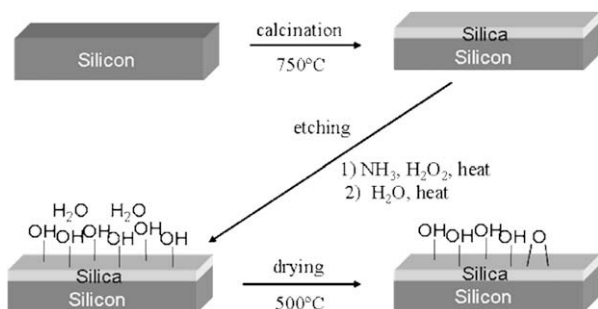
morphological development during polymerization, especially the effect of the catalyst and polymerization conditions, is the main topics in the study of the nascent polyolefin morphology. To date, several papers have been published on the morphology of nascent polyolefin. The development of nascent state morphology of PE is documented reasonably well on the micrometer level [5–16]. However, in contrast to the process of melt crystallization, the nascent state and the associated polymerization–crystallization processes which govern morphology development, are not well understand.

A number of morphologies for nascent polyolefin have been observed depending on catalyst systems and polymerization conditions. The polymers produced with heterogeneous Ziegler–Natta catalysts were found to have a fibrous texture similar to shish-kebabs [17]. Fibrillar structures are even observed in samples polymerized under quiescent conditions [18]. Polyethylene prepared with the soluble catalyst system bis-(cyclopentadienyl)-titanium dichloride under a variety of polymerization conditions has, however, a chain-folded lamellar structure over a wide range of catalyst concentration, as described by Georgiadis and Manley [11].

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Scheme 1. Preparation of the SiO₂/Si (100) model surface.

In the case of another soluble catalyst system VOCl₃/(C₂H₅)₂AlCl, dual morphological structures, including folded-chain lamellar crystals and fibrillar crystals, have been reported [19]. It has been concluded that in heterogeneous systems, owing to the close proximity of active sites on the surface of the catalyst substrate, fibrillar crystals are grown by an intermolecular crystallization of polymer chains emanating from adjacent active sites. Moreover, subsequent stretching of the just formed crystals caused by catalyst fragmentation and polymer particle growth is another factor that causes formation of fibrillar crystals during heterogeneous polymerization.

The overall particle morphology, as prepared in the reactor by the important industrial processes such as catalyst replication, is difficult to characterize on the molecular scale using microscopy techniques [20–22]. Recently, flat Phillips model catalysts have been introduced [23–25]. They are based on silicon (100) single crystals covered with a thin layer of silica (20 nm) with a surface roughness below 1 nm. These single crystals are used to support the flat Phillips model catalysts [26]. As a result, the nascent morphology of polyethylene polymerized by this flat Phillips model catalysts has been investigated [15,27]. Through scanning electron microscopy (SEM) investigations, it was found that the nascent morphology of PE samples polymerized by this flat Phillips model catalysts at 25 °C and 70 °C consists of pillar-like stacked spherical entities, which are loosely connected with each other.

Recently, the flat model silica-supported bis(imino)pyridyl iron(II) polyolefin catalyst has been successfully developed [16]. In

this case, since the iron catalyst is covalently anchored onto the flat SiO₂/Si(100) surface, it shows a very high activity towards ethylene polymerization. The concentration of the surface-silica-supported bis(imino)pyridyl iron(II), which is the active site, can be controlled independently by adjusting the concentration of the catalyst in solution. Since the number of active sites on the model catalyst surface is well controlled, it can prevent interference between the growth of neighboring nascent islands or crystals. On this basis, a proper amount of polymers are formed on the silica surface that are suitable to study the initial nascent morphology of individual crystals by AFM observation.

In the present paper, we examine the morphology and structure of nascent polyethylene polymerized with the silica-supported bis(imino)pyridyl Iron(II) polyolefin flat model catalysts. Polymer samples were prepared at different temperatures and studied by AFM combined with electron diffraction. The effect of polymerization temperature on the nascent morphology and structure of PE is discussed based on the morphological features obtained.

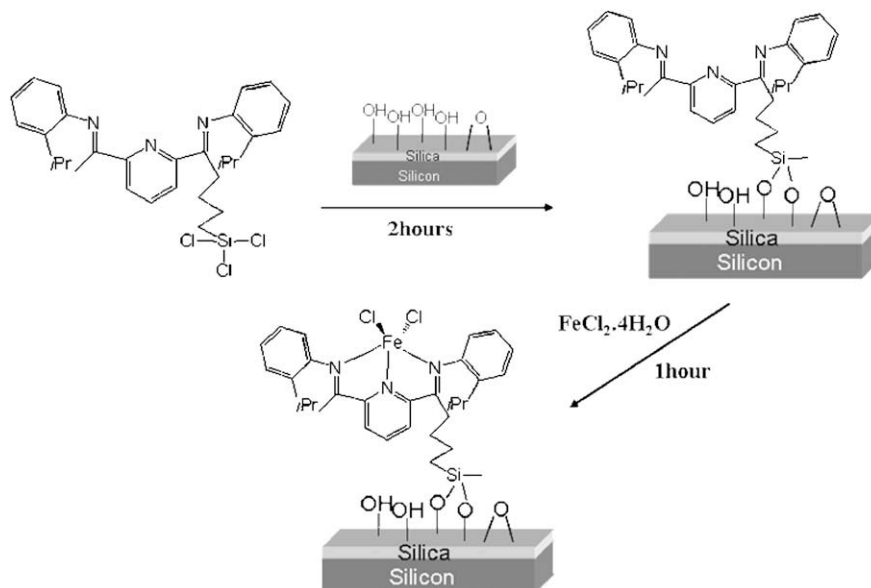
2. Experimental details

2.1. Materials

All manipulations of air or water-sensitive compounds were performed using standard Schenk or glovebox techniques. All chemicals were purchased from VWR or Aldrich and used as received. Initially HPLC-grade solvents were taken from an argon flushed column packed with aluminum oxide. The solvents were stored with 4 Å molecular sieves. The allyl-modified bis(imino)pyridine ligand was prepared according to the procedure described in the literature [28].

2.2. Catalyst preparation and polymerization procedure

The synthesis of the immobilized iron(II) catalyst precursor is summarized in Ref. [16]. As shown in Scheme 1, the SiO₂/Si(100) wafer was prepared as described in the literature (calcination at 750 °C, followed by etching with H₂O₂/NH₃) to obtain a layer of amorphous silica (20 nm) on a single-polished silicon (100) wafer [29]. The wafer was then partially dehydroxylated at 500 °C in hot



Scheme 2. Preparation of anchored bis(imino)pyridyl iron(II) complex.

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