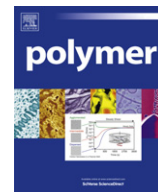


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Segmental mobility in the noncrystalline regions of nascent polyethylene synthesized using two different catalytic systems with implications on solid-state deformation

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ABSTRACT

Recently, it has been shown that using a single-site catalytic system it is possible to tailor entanglement density in the amorphous region of a semi-crystalline polymer, such as polyethylene, with a molar mass greater than 1 million g/mol. The synthesized polymer can be processed in its solid-state, along uniaxial and biaxial directions. It also shows strong heating rate dependence on melting invoking kinetics in randomization of chains from crystal to amorphous phase. With the help of solid-state NMR the distinction between amorphous regions of the synthesized and commercially available ultra-high molar mass polyethylene is made. For example, the polymer synthesized under the controlled conditions, using a homogeneous single-site catalytic system, shows faster motion of methylene units from the non-crystalline to the crystalline regions compared to commercially available nascent polyethylene synthesized using a Ziegler–Natta (Z–N) catalyst. The differences in chain diffusion, and the resultant ¹³C polarization transfer from the noncrystalline to the crystalline region, are attributed to the difference in entanglement density arising from the polymerization method employed. The two polyethylene samples investigated are of similar molar mass and crystallinity. Conformational changes caused by deformation of the two samples have been characterized and co-relationship with the entanglement density has been established.

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1. Introduction

In semi-crystalline polymers, entanglement formation in the amorphous region is a balance between thermodynamics and kinetics during crystallization. This will also be dependent on molecular characteristics, such as molar mass and molar mass distribution [1,2]. Two models depicting chain topology in the amorphous region, switchboard and adjacent re-entry, are often mentioned in literature [3,4]. It is well accepted that if crystallized from dilute solution, below the overlap chain concentration where the polymer chains are disentangled, platelet-like crystals are formed. Within these platelets the long polymer chains fold back

and forth where chain folding represents the noncrystalline regions. When the same material is crystallized from melt, chains are likely to freeze into several crystalline domains, and the switchboard morphology is more likely to establish. In nascent ultra-high molecular weight polyethylene (UHMWPE) with a molar mass above 1 million g/mol, the entanglement density during polymerization is expected to be strongly dependent on the polymerization conditions like pressure, temperature and the catalytic system used, which affect both crystallization and polymerization rates. Contrary to the heterogeneous polymerization conditions where the catalytic system is supported on a substrate and there is less control on the active sites, in the unsupported homogeneous single-site catalytic system polymerization and crystallization conditions could be better controlled [5]. For example, by lowering the polymerization temperature and catalyst concentration in the polymerization medium, the crystallization rate can be substantially higher than the polymerization rate. This leads to the extreme case of single crystal formed by a single chain.

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With varying polymerization conditions, entanglement density in the amorphous region is likely to vary, while the chain packing within the crystalline core of the semi-crystalline polymer remains the same [7–9] (schematically shown in Fig. 1). For example, for two different nascent UHMWPEs synthesized using homogeneous single-site and heterogeneous supported Ziegler–Natta catalytic systems the crystallite dimensions are found to be the same though crystallinity may differ (for further details please see the Supplementary section). Lippits et al. studied the difference in melting behaviour of nascent UHMWPE samples synthesized via these two catalytic systems [10]. For the nascent UHMWPE sample synthesized using the homogeneous single-site catalytic system an additional melting process has been reported. This process is assigned to the consecutive detachment of single chain stems from the crystalline substrate and their diffusion in the melt. The origin of this melting process is explained by invoking the melting kinetics arising from restricted chain mobility of chain segments on the crystal surface [11,12].

Investigation of the amorphous (noncrystalline) regions imposes a difficulty due to differences in the conformational order of the polymer chain segments, close and away from the proximity of the crystal surface. Here, the word “noncrystalline” refers to the chains packing between the crystalline and the amorphous regions. The normally used characterization methods, such as thermal analysis and X-ray measurement, often give indirect information on the conformational order [13,14]. In UHMWPE, ^1H NMR relaxation analysis has been successfully used to investigate structure and dynamics present in the noncrystalline region [15]. This technique is also capable of distinguishing and quantifying the noncrystalline region. However, simple ^1H NMR cannot provide enough information on the detailed characteristics of molecular dynamics, e.g. chain dynamics and its correlation in different phases.

In this publication, solid-state NMR has been used to follow subtle differences in the amorphous/noncrystalline regions and the resulting influence on the chain diffusion process of the two different nascent powders. These samples are synthesized using two different catalytic systems. Implications of entanglements on solid-state deformation are evident and are depicted in Table 1.

The distinct difference in processing window suggests differences in topological constraints (or chain entanglement) in the noncrystalline regions of the two samples, where the Z–N synthesized sample forms entangled and the single-site catalytic

Table 1

Distinction between processing and mechanical properties of the solid-state processed UHMWPE synthesized using Z–N and homogeneous single-site catalytic system (for details see Ref. [16]).

	Z–N synthesized (entangled, nascent)	Single-site catalytic system (disentangled, nascent)
Processing window	140–142 °C	120–145 °C
Tensile strength	2.4 GPa	3.6–4.3 GPa
Modulus	150 GPa	180–200 GPa
Biaxial film (without using solvent)	Not possible	Possible

system forms disentangled noncrystalline regions. We thus will address the differences in chain conformation of methylene units at different length scales for the noncrystalline regions of the entangled and the disentangled polyethylene. Combining solid-state ^{13}C -CP/MAS spectra and X-ray diffraction, differences in the noncrystalline regions of the nascent samples and during deformation have been explored. Moreover, from ^{13}C exchange NMR, the medium-range chain translation (or diffusion) between the crystalline and noncrystalline regions in the two nascent samples have been probed and correlation with solid-state deformation has been established. To our knowledge this is the first kind of its study that to some extent quantifies differences in the amorphous/noncrystalline regions to the synthetic conditions, and its implications on mechanical deformation.

2. Experimental section

2.1. Materials

UHMWPE samples studied in this publication include two nascent UHMWPE samples, two melt crystallized samples, and two series of drawn samples. The two nascent grades differ in synthesis conditions and catalyst type.

The nascent entangled sample is synthesized at ~ 70 °C using a heterogeneous Ziegler–Natta catalyst and named: “nascent entangled UHMWPE”. The nascent disentangled grade is synthesized at 20 °C using an unsupported single-site homogeneous catalytic system and named: “nascent disentangled UHMWPE”.

The melt crystallized samples were prepared on cooling the melt of the above mentioned samples from 160 °C to room

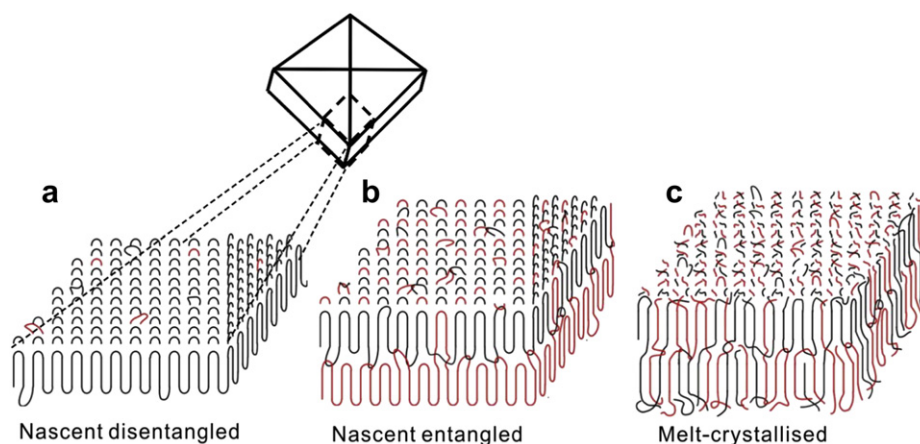


Fig. 1. Schematic representation of the crystal morphologies for (a) Nascent disentangled sample having re-entry chains with tight folds. (b) Nascent entangled sample having tight folds with re-entrant chains shared among several crystals, and (c) Melt crystallized sample having loose chain folding and loops with chains being shared among several crystals. To have the schematics of a nascent disentangled sample in agreement with the single crystal like morphology, a scenario of single chain forming single crystal is depicted. However, the sporadic occasions where a chain can be shared between different crystals cannot be ignored and such a possibility is shown by red folds on the crystal surface (reproduced from Ref. [6]). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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