The phase composition and lamellar morphology of linear and branched polyethylene: Morphology interpretation of TD-NMR and SAXS studies over broad range of crystallinity

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The semi-crystalline structure of polyethylene (PE) strongly affects its physical properties and also the transport of small-molecule penetrants in PE. The diffusion of penetrants in PE is important not only in PE manufacturing and down-stream processing, but also affects its application properties, such as permeability of PE membranes. As a semi-crystalline polymer, PE is composed of thin lamellar crystals with characteristic thickness approx. 10 nm. These lamellae are arranged into stacks and separated by an amorphous phase. The lamellae grow from a nucleation center, branch and twist, until they impinge on other lamellae growing from adjacent nucleation centers. Thus, the space filling spherulitic structure is formed.

Although the morphology of PE is extensively studied, most studies are focusing only on the crystallinity. Thus, they often non-critically adopt the classical three-component model of PE, which considers a crystalline and an amorphous phase separated by an interfacial component. However, this can lead to very high interfacial component content, with unrealistic values above 40 wt. % reported for PEs with lower crystallinities. To address this issue, we used low field ^{1}H NMR and small-angle X-ray scattering (SAXS) to obtain the phase contents and characteristic lamellar dimensions of PE samples with a wide crystallinity range, ranging from VLLDPE (35 wt. %) to HDPE (82 wt. %). Evaluating the ^{1}H NMR data measured for the HDPE samples, we observed only one amorphous component – a rigid amorphous phase, which consists of chains constrained between the neighboring lamellae in the lamellar stacks. However, a second amorphous component with significantly higher mobility was observed in the PE samples with crystallinity lower than 60%. We believe that this mobile amorphous phase, referred to as "free amorphous", consists of chains outside of the lamellar stacks. To support our hypothesis, we used SAXS to estimate the thicknesses of amorphous and crystalline domains in the stacks. These data were then used to calculate the fractions of the free amorphous chains outside of the lamellar stacks, obtaining excellent agreement with our ^{1}H NMR results and with a large set of literature data. Finally, the obtained experimental data were also compared with model predictions based on reconstructed 3D replicas of PE spherulites.