590f Study of Ziegler-Natta and Single-Site Linear Low-Density Polyethylene by Fuming Nitric Acid Etching, Gpc and ^{13}C Solid-State NMR

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Fuming nitric acid etching, gel permeation chromatography (GPC) and ^{13}C solid-state nuclear magnetic resonance (NMR) spectroscopy were utilized to elucidate structural features of Ziegler-Natta (ZN) and single-site (ss) linear low-density polyethylene samples. High-resolution ^{13}C NMR spectra of unetched samples, obtained with cross polarization (CP), magic angle spinning (MAS) and high-power proton decoupling, showed that the resonance lines for the crystalline and non-crystalline components were chemically shifted from one another. ^{13}C spin-spin relaxation time (T_2) measurements of the non-crystalline region revealed that is consisted of an amorphous phase and an interfacial region, which was sandwiched between the amorphous and crystalline phases. Since the T_2 behavior of the two non-crystalline components differed, their ^{13}C NMR resonance lines were separately recorded so that the interfacial thickness and mass fraction of the interfacial phase were estimated. ^{13}C CP/MAS NMR spectra of the etched samples showed that both the interfacial and amorphous peaks disappeared, indicating that the etching process removed the non-crystalline components. The molecular weight averages of the etched samples were significantly reduced compared to those of the unetched samples, as demonstrated by the corresponding GPC data. The values of number average molecular weight of the etched samples imply that the acid etched away the interfacial region by breaking the chains at carbons that are located in the loop area of the folding crystallites. There exists a noticeable shoulder in the GPC chromatograms of the etched samples at a molecular weight value at about 2 to 3 times of the number average molecular weight of the etched samples, which is roughly the number average molecular weight of the stem of the corresponding crystallites. It is speculated that such higher molecular weight chains were the tie chains that connected the lamella initially present in the unetched samples and that they formed highly-ordered structure in the amorphous phase that made them, at least some of them, survive the 30-day fuming nitric acid etching. Our results showed that the chain length and concentration of the tie molecules of ZN-LLDPE were longer and lower than those of the ss-LLDPE, respectively.