NMR Analysis of Halogen Packing in Crystals of Precisely Substituted Polyethylenes. Toward Advanced Polyolefin Materials

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Introduction

We have studied the morphology and conformational changes upon controlled isothermal crystallization from the melt of a polyethylene with Cl atoms placed at an equidistant location along the chain backbone, PE15Cl. We found a unique sharp change in crystalline structure with decreasing undercooling.

Experimental

Solid state cpMAS ^{13}C NMR spectra were acquired at room temperature on an 11.75 Tesla (500 MHz 1H NMR frequency) Bruker Advance III NMR system with a 2.5 mm MAS probe at the NHMFL. Cp MAS were attained at 25 kHz MAS. Cross polarization was applied with a constant 50 kHz radio frequency field applied to the ^{13}C channel during the ^{1}H – ^{13}C spinlock (2 ms contact time) and ^{1}H radio frequency fields ramping linearly around 75+/- 25 kHz. A recycle delay of 5s was used for all NMR scans. The ^{1}H nutation frequency applied for decoupling was 110 kHz.

Results and Discussion

Figure 1 displays room temperature solid state ^{13}C NMR cpMAS spectra of PE15Cl crystallized at 45ºC (Form I) and 55ºC (Form II). Carbon resonances have been previously identified.[Error! Bookmark not defined.] The major differences between the spectra of Forms I and II are a 2 – 3 ppm upfield shift of the crystalline CH (from ~68 to 66 ppm) and crystalline CH_2 adjacent to the methine (from ~42 to 39 ppm). Following prior work,[1,2] the upfield shifts conform to shielding of CH and α CH_2 by the CH_2 that are gamma to them. Shielding takes place only when the CH-C bond is in a gauche conformation.[1,2] The ^{13}C NMR spectra provide evidence of a gauche conformation around the crystalline CH-Cl unit in Form II. The cpMAS spectra also provide useful qualitative information about the amount of C-CH gauche bonding from the pattern of the CH resonances of Forms I and II. While the resonance of amorphous CH is unchanged at 64.2 ppm, basically all crystalline CH resonance of Form II undergoes the ~2 ppm upfield shift indicating that the majority of the crystalline CH are gauche bonded to adjacent CH_2, as found from the FTIR spectra and in consonance with the schemes of Figure 2. In summary, all experimental data obtained from DSC, x-ray diffraction and vibrational and NMR spectroscopy support the suggested packing models of Figure 2.[3]

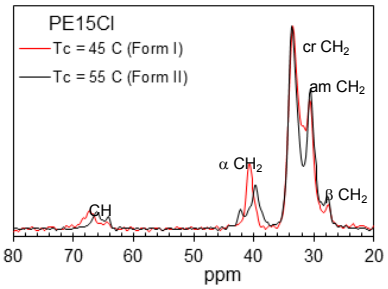

Fig. 1. Room temperature solid state ^{13}C NMR cpMAS spectra of PE15Cl crystallized at 45ºC (Form I) and 55ºC (Form II). Resonances of crystalline (cr) and amorphous (am) CH_2, methine carbons and methylenes α and β to the methine are identified.

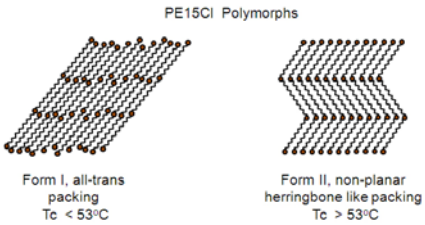

Fig. 2. Schematics of the crystalline packing in Form I and Form II. For clarity, chains protruding from the crystals to the amorphous regions are ommitted.

Conclusions

We have demonstrated that it is feasible to encode unique crystal microstructures using a precise placement of halogens, rather than the classical random distribution, in polyethylene-based polyolefin materials. Two different crystalline forms are enabled by controlling crystallization kinetics. Under relatively fast crystallization, the chains assemble in the all-trans packing accommodating ~9 repeating units. In this form, the inter-chain arrangement of the Cl atoms is layered but with some longitudinal disorder. Slower crystallization rates favor a highly ordered structure by intermolecular staggering of crystalline chlorines in highly symmetric layers possibly with a kinked or herringbone-like conformation.

Acknowledgements

A portion of this work was performed at the NHMFL supported by NSF (DMR-1157490), the State of Florida, and the U.S. Department of Energy. Additional support by NSF (DMR-1105129) to RGA.

References

[1] Tonelli, A.E., *et al.,* Macromolecules, **17**, 1946-1949 (1984). [2] Tonelli, A.E., *et al.,* Acc. Chem. Res.**, 14,** 233-238 (1981). [3] Kaner, P., *et al.,* Macromolecules*,* **47**, 236–245 (2014).