Title:

Challenges During Design of Thermal Fractionation Protocols for Poly(propylene)-co-ethylene Resins

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Reference 7:
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Reference 9:
Reference 10:
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Reference 12:

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Abstract:

Commercially relevant resins of polypropylene random copolymers are prepared via copolymerization of propylene and α-olefins and typically display not only broad molecular weight, but also chemical composition distribution. Both need to be controlled via specific catalyst systems, comonomer content and distribution of comonomer within the resin in order to tailor relevant macroscopic properties like impact behavior, haze and clarity or slow crack growth performance. Analysis of these resins based on temperature rising elution fraction (aTREF, pTREF), size exclusion chromatography (SEC) and NMR is therefore a crucial step in providing a link among changes in molecular composition and structure upon changes in catalyst systems, comonomer content or reactor conditions. A comprehensive understanding of these aspects provides significant challenges to analytics, next to being a rather time-consuming task. In that respect, DSC based thermal fractionation in principle offers a complementary route that enables a rapid overview with regard to changes in molecular composition of the resins, based on the SSA (Successive Self nucleation and Annealing) protocol introduced by Mueller. These protocols need to be carefully designed, considering the temperature domains in which either annealing or self-nucleation takes place in such resins. Using DSC self-nucleation, we demonstrate that this behavior is very much determined by the presence of the broad chemical composition distribution of such resins.

Ultimately, the solidification of polypropylene-based resins yields a complex microstructure that is not only dependent on molecular composition, but also the conditions under which crystallization takes place. On one hand, rapid cooling may partially or completely suppress crystallization, yielding in the most extreme case mesomorphic structures, characterized by short range ordered helical segments that are formed by the isotactic sequences. Slow cooling, on the other hand, ensures full crystallization of such resins via long-range ordering of crystallizable segments, but typically yields a rich polymorphism with the monoclinic α- competing with the orthorhombic γ-phase.

We demonstrate in this contribution via DSC self-nucleation, 1-step isothermal annealing in conjunction with temperature- and time-dependent WAXD, that polymorphism strongly affects meting behavior and results after SSA treatment. Thermal fractionation even above the peak melting temperature causes melting and subsequent re-crystallization of long isotactic segments into very stable α-crystalline domains. On the other hand, shorter isotactic segments tend to re-crystallize at lower temperatures giving rise to a significant increase in the crystalline γ fraction under ambient conditions. While composition of the crystalline phase strongly depends on crystallization conditions, it is demonstrated that polymorphism affects lamellae morphology and thus the observed melting behavior under standard DSC as well as after SSA treatment.