

SAXS-WAXS INVESTIGATION OF THE TRIGONAL MODIFICATION IN C3/C5 RANDOM COPOLYMERS

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Since the middle of the past century a wide spectrum of polymeric materials has been developed in order to find suitable substitutes for replacing natural products. Important advances have been attained in the development of new synthesis and new catalysts which enable an unprecedented control of chain microstructure and, in turn, provide an ideal base for understanding the relationship between structure and properties in semicrystalline polymers, the large family of polyolefines being one of the most widely used and studied. In the framework of a comprehensive investigation of microstructure-properties correlations in random copolymers of propene with α -olefines,^{1,2} our interest is here focused on the crystallization and melting behaviour of propene/1-pentene random copolymers obtained with isospecific methylaluminoxane activated *ansa*-zirconocenes catalysts.

In line with the expected behaviour, it has been found that presence of randomly distributed constitutional defects initially depress development of α -crystallinity, while slightly favouring the formation of a small fraction of α -crystallinity. However, when the concentration of co-units exceeds a minimum limit, a sudden appearance of three rather sharp reflections is observed at $2\theta =$ ca. 10, 18 and 21° in the WAXD pattern, which correspond to the (110) (300) and (220+211) planes of the trigonal modification recently found in propene/1-hexene copolymers.³⁻⁵ This new polymorph being the only crystalline modification developing in copolymers with 1-pentene contents up to, at least, 50 mol.%. Inclusion of the bulky side group of pentene in the lattice enables stabilization of a 3-fold helical symmetry of the chains in a 3-fold crystallographic symmetry, a situation which is not permitted in the homopolymer because of the too low density of the resulting lattice.³ Alike in the copolymers with hexane,⁵ the lattice constants *a* and *b* related to the interchain distance increase linearly with the comonomer content. However, due to the smaller size of the lateral group, at a given comonomer content the cell dimensions are slightly smaller with 1-pentene than with 1-hexene co-units.

Thermal analysis and simultaneous SAXS-WAXD experiments, performed at room temperature and during heating, reveal that the trigonal modification melts at low temperature, around 50-60°C, independent from the content of comonomer units, and slowly forms upon cooling from the molten state and during aging at room temperature.

A common feature in all collected WAXD patterns is the sharpness of the diffraction peaks, in particular of the (110) reflection. This suggests that the crystallographic order in the trigonal modification extends over large distances in the plane perpendicular to chain axis. On the other hand, very weak signals can be appreciated in the small angle scattering range at spacing around 17 nm, indicating that the density difference between the amorphous and the ordered phase is small.

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