

# Polymorphism and Crystallization Kinetics of Polyethylenes with Precise Chlorine Substitution.

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Polyethylenes with halogen substitution at a precise distance along the methylene backbone are unique models to study the effect of nano-structured chain-defects on folding and crystallization of polymers. Prior work has shown that the halogen is accommodated in the crystal disrupting the unit cell symmetry, crystallization and melting proportionally to the halogen's size [1, 2]. Furthermore, packing of the chlorine units in the crystallites of a polyethylene with chlorine substitution on every 15<sup>th</sup> backbone carbon was found to undergo a transition which is controlled within one degree of undercooling [3]. At high undercoolings the chains pack in an all-trans planar conformation (Form I) with layered crystalline chlorines that present some longitudinal disorder as demonstrated by FTIR and WAXD. The crystals formed at higher temperatures pack in a non-planar herringbone-like structure with a TGGT....TG'G'T backbone conformation around the substitution, while conserving the trans packing of the methylene sequence (Form II). We have extended the structural analysis to a set of precision samples with chlorine on the 9<sup>th</sup>, 19<sup>th</sup> and 21<sup>st</sup> carbons, and compared the polymorphic behavior to analogs with the random substitution. The unique polymorphic transition found in the system with chlorine between 15 carbons is also found in all members of the precision series, making the planar and non-planar packing with respect to undercooling a general feature of crystallization of polyethylenes with chlorine substitution. Polymorphism is absent when the chlorine is randomly distributed. Especial emphasis is given to the analysis of the overall crystallization kinetics measured by DSC of Forms I and II and to the temperature range of stability based on rate data. With decreasing crystallization temperature, the rate of Form I follows the usual negative temperature coefficient, while the overall rate of form II shows a maximum at crystallization temperatures where both forms coexist. The inversion of the rate coefficient with decreasing temperature is associated with a blocking effect on the growth of Form II by the presence of crystallites in Form I, hence, the magnitude of the effect increases with content of Form I. The polymorphic transition and equilibrium melting temperatures of both forms scale linearly with chlorine content.

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## References:

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