Conventional and Living Carbocationic Polymerizations United.
I. A Comprehensive Model and New Diagnostic Method to Probe the Mechanism of Homopolymerizations

I. Majoros, A. Nagy and J.P. Kennedy
Institute of Polymer Science, The University of Akron, Akron, OH 44325-3909, USA

A closed-loop comprehensive model unifying impurity-induced and purposely-added initiator-induced isobutylene (IB) and styrene (St) polymerizations was developed. Both impurity-induced and purposely-induced olefin polymerizations can be both conventional or living, and the reaction conditions will determine whether the prevailing mechanism will be conventional or living. The model was used to elucidate the detailed mechanism of olefin polymerizations and to provide guidance toward preparative advances. The heart of the model is the Winstein ionicity spectrum which in its simplest form consists of three fundamental entities connected by two equilibria: a) a dormant species (in fact the initiator) which can be either a protic impurity or a purposefully added cationogen ("HX" or RX); b) a polarized covalent dipole (\( \sim C \cdots X \text{MtX}_n \)) which arises from the dormant species under the influence of excess Friedel-Crafts acid coinitiator (\( \text{MtX}_n \)) and is the source of living chains, and c) a dissociated ionic species (\( \sim C^+ + \text{MtX}^+_n \)) which yields conventional nonliving (i.e., transfer-dominated) chains. Under conventional conditions in charges containing a stoichiometric excess of \( \text{MtX}_n \) relative to the initiator (be this protic impurity or purposely-added cationogen), the contribution of the highly reactive ionic species to the polymerization rate is overwhelming and it is difficult to find evidence for the presence of the much less reactive dipole which is responsible for the relatively slow living propagation. Upon the addition of an electron pair donor (ED), hereafter electron donor, to a conventional charge, the ED and the excess \( \text{MtX}_n \) instantaneously form a complex \( \text{MtX}_n \cdot \text{ED} \), which in turn interacts with the carbocation (\( \sim C^+ \)) and thus yields an additional (fourth) species \( \sim C \cdots [\text{MtX}_n \cdot \text{ED}] \cdots \text{MtX}^+_n \) in the Winstein ionicity spectrum which becomes another source of relatively slowly propagating living chains. The new model led to a comprehensive diagnostic method which in turn led to new insight into mechanistic details of olefin polymerizations in respect of rapid/slow initiation, monomolecular/bimolecular chain transfer, impurity-induced/purposely-induced initiation, rates of ion generation/cationation, and to an examination of the constancy of various rate constants. All the elementary events, namely initiation (comprising of ion generation and cationation), propagation, monomolecular and biomolecular chain transfer and reversible (quasiliving) termination, are controlled by their individual Winstein ionicity spectra, the characteristics of which determine the rates, conversions, product molecular weights and molecular weight distributions (MWD). Specifically, the effects of ED (triethyl amine, TEA) and Friedel-Crafts acid (\( \text{TiCl}_4 \)) concentrations, medium polarity (mixtures of \( \text{CH}_2\text{Cl}_2/n-\text{C}_8\text{H}_{14} \)), temperature (from \(-20 \) to \(-82^\circ\text{C}\)), and reagent addition sequence (aging) on IB and St polymerization rates, and polyisobutylene (PIB) and polystyrene (PS) mol. wts. and MWDs were determined quantitatively and analyzed. The model shows the way toward the synthesis of controlled mol. wt. polyolefins of narrow MWD (\( M_w/M_n < 1.1 \)) by living polymerization.
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