Historical Perspectives on Living Anionic Polymerization*

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SUMMARY: The discovery by Michael Szwarc that radical anions of aromatic hydrocarbons in ethereal solvents can transfer electrons to vinyl monomers to yield two-ended living polymers led to a global resurgence of anionic polymerization. Lack of spontaneous termination of the propagating ends provided a path for the construction of block, star and graft copolymers, telechelics, and other polymeric materials with a well- defined architecture. The numerous studies by Szwarc, which started in 1955 and continued until his death on August 2, 2000 were chiefly concerned with the reaction mechanism. A variety of techniques were utilized to explore the kinetics and thermodynamics of anionic polymerization and of electron transfer processes, as well as the structure of ion pairs and their solvation complexes.

This paper is focused on the role of various ionic species in the polymerization mechanism, particularly that of tight and loose ion pairs, free ions and triple ions. Their relative preponderance in ethereal solvents turns out to be a sensitive function of temperature, pressure, solvent structure, nature of the counter cation, and the presence of salts or complexing agents. The findings make it possible to rationalize observed retardation effects on adding salts, peculiar temperature phenomena such as regions of negative activation energies, and a host of other phenomena observed in these living polymerizations as a function of the above parameters.In the presence of ruthenium complexes divinyldiorganosilicon compounds undergo de-ethenated coupling polycondensation yielding under optimum conditions *trans-tactic* polysilylene(siloxylene, silazanylene)vinylenes and poly(silylene-arylene-vinylenes). Rhodium- ($[RhX(cod)]_2$ X = Cl, $OSiMe_3$) catalyzed ring closure of oligomeric (dimeric, trimeric) products of intermolecular condensation opens a new route to synthesizing organosilicon exo-cyclic methylenes. In the presence of Ru-complexes the cross-coupling (poly)condensation of di- and trivinylsilicon monomers with organic dienes allows syntheses of a series of linear and dendrimeric poly(arylene-silylene-vinylene)s.

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*The full paper will appear in an issue of the "Journal of Polymer Science" which will contain the papers presented at the one day symposium on Ionic Polymerization in honor of Dr. Szwarc.

CCC 1022-1360/00/$ 17.50+.50/0