I - Mechanisms of Polymerization

Considered in this discussion were mechanisms of chain growth polymerization including the following:

a) radical
b) cationic
c) anionic
d) group transfer
e) coordination

All the participants emphasized the important requirement of indentifying and controlling the active center structure. This is certainly necessary to prepare well defined "living" polymers. Transfer and termination reactions must be also controlled, so as to allow for the preparation of predictable molecular weights and narrow molecular weight distributions. The various mechanisms listed above may be considered to represent a continuum where various polarizing conditions can be achieved either by electrophilic or nucleophilic activation of covalent bonds.

In recent years, it has become clear in a number of polymerization systems that the control of the active center can be best achieved by "moderating" its nature. For example, reliable data have been produced that demonstrate living polymerizations in the field of carbocationic polymerization as well as earlier anionic systems. Thus Higashamura and coworkers have recently described living polymerization of vinyl alkyl ethers by HI/I₂ combinations and Kennedy et al of isobutylene and other olefins by certain ester or ether/Lewis acid complexes. By skillful selection of specific alkyl vinyl ethers, for example, amphiphilic block and graft copolymers have been assembled. Also linear and three-arm star telechelic polyisobutylene capped by tert.-chlorine end groups have been conveniently obtained in the -30 to

172°C range. These advances in synthetic techniques together with the availability of these and similar well-defined new products bring carbocationic polymerizations again center-stage among the best-controlled polymer preparative methods.

The fundamental difference between conventional carbocationic polymerization systems and the recently described carbocationic living systems is that chain transfer and termination are absent in the latters. As conventional carbocationic polymerizations (i.e. polymerizations initiated by $\text{H}_2\text{O}.\text{BF}_3$, $\text{H}_2\text{O}.\text{TiCl}_4$, $\text{t-BuCl.Et}_2\text{AlCl}$, etc... combinations) are believed to proceed by solvated free ions or strongly ionized species, the recent living systems must involve different active species and most likely do not contain free ions or highly dissociated ion pairs.

While the fundamental differences in the kinetic profiles of conventional nonliving and new living polymerizations indicate some profound phenomenological differences, the nature of these differences remains obscure. Among our first objectives should be to gain increased insight into these differences, particularly in regard to a better definition of the active species involved. Our task however is rendered enormously difficult on account of the elusive and transient nature of the carbenium ion, carbanion or coordination intermediates, and because the activity of the true propagating species is determined not only by its primary structure but also by secondary external parameters, such as counter ions medium polarity, impurities, concentrations, aggregation states, temperature, addition sequence of ingredients and by the mutual interdependence of these factors.

In the past, researchers in the field of carbocationic and anionic polymerizations tended to concentrate on the exploration of highly ionic systems, which overemphasized the effect of traces of moisture. They were compelled to operate at cryogenic temperatures in order to "freeze out" undesirable side-reactions. These measures rendered ionic polymerizations rather cumbersome for the academic experimentalist and uneconomical for the industrialist. It now appears that the new living systems emerging in Japan and the U.S. not only provide heretofore unattainable synthetic-preparative advantages (i.e. new functional polymers, blocks, grafts) but also ease of operations in terms of relatively low moisture sensitivity and experimentation at close to or above ambient temperatures.