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### Preface

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## Preface

Living polymerizations, i.e., polymerizations proceeding in the absence of chain transfer and termination, are certainly among the most effective methods in the armamentarium of the macromolecular engineer. Living polymerizations are on the top of his list when he wants to prepare certain polymers (e.g., polybutadienes) with precise molecular weights and narrow molecular distributions, predictable microstructures and endgroups. Preparative polymer science will always remain in debt to Professor Michael Szwarc et al. who first recognized the synthetic power of this technique and demonstrated its use by preparing the first of a new family of sequential copolymers, i.e., block copolymers of styrene-isoprene [1, 2]. Unfortunately, living polymerizations can be used only with a rather limited number of monomers under rigorously controlled conditions.

Since the discovery of living anionic polymerizations, polymer synthetic chemists all over the world have strived to find other living polymerization systems and thus to broaden the field of precisely tailored macromolecules. Over the past two decades numerous living polymerizations have been diagnosed, e.g., in the field of Ziegler-Natta coordination polymerizations, ring-opening polymerizations; however, in spite of claims to the contrary and sustained investigations, living carbocationic systems have not been found. (The term living polymerization has been, regrettably, quite often abused by thoughtless workers who misused it to describe all kinds of polymerizations that do not proceed by chain transferless/terminationless mechanisms.)

The collection of papers in this special issue on Quasiliving Carbocationic Polymerizations is the result of extended fundamental research commenced in 1979. Investigations started by postulating and then demonstrating that kinetics resembling that of living polymerizations (hence the terminology quasiliving polymerization) can be obtained in typical carbocationic polymerization systems, e.g., "H<sub>2</sub>O"/BCl<sub>3</sub>/α-methylstyrene, under controlled conditions [3]. Specifically, it was found that the molecular weight of poly(α-methylstyrene) increased linearly with the amount of monomer added provided the

monomer was introduced slowly and continuously to a stirred active charge. Thus  $\bar{M}_n$  versus monomer input plots were linear starting from the origin (a diagnostic proof of living polymerization) and  $\bar{M}_w/\bar{M}_n$ 's were much below 2.0 (another indication of a living system). These findings were followed up by demonstrations that under carefully controlled conditions, di- and triblock copolymers, e.g., poly(isobutyl vinyl ether-*b*- $\alpha$ -methylstyrene-*b*-isobutyl vinyl ether), can be obtained by sequentially feeding monomers to an active charge (another proof positive of living polymerization) [4, 5]. Simultaneously with block copolymerizations, carbocationic olefin polymerizations of isobutylene [6], styrene [7], *p*-tert-butylstyrene [8], indene [9], and isobutyl vinyl ether [10] were also carried out, demonstrating the general validity of the underlying quasilinging carbocationic mechanism.

Having convinced ourselves of the veracity and breadth of the quasilinging phenomena, a broad theory of living polymerizations was developed encompassing the basic principles involved in living polymerizations in general and quasilinging polymerizations in particular [11].

A most promising consequence of quasilinging polymerizations is "forced quasilinging copolymerizations" [7]. Thus the possibility exists to produce by the quasilinging technique new copolymers by forcing monomers to copolymerize with each other which under conventional conditions would not copolymerize. The composition and the molecular weights of the copolymers can be controlled, at least to the extent permitted by the quasilinging mechanism. For example, it has been demonstrated that the molecular weight of poly(styrene-co- $\alpha$ -methylstyrene) obtained under forced quasilinging conditions may be higher than that of the respective homopolymers obtained under the same conditions. Investigations in this field are continuing.

The final paper in this issue concerns molecular weight dispersities and demonstrates that in contrast to truly living systems in which  $\bar{M}_w/\bar{M}_n = 1$  can be obtained, the limiting distribution in quasilinging systems tends toward 1.33 [12].

Even a cursory glance at this special issue indicates the international and interdisciplinary nature of these investigations, the cooperation between American, Hungarian, and Japanese investigators, between chemists, kineticists, and mathematicians. All of us are grateful to the NSF (Grants DMR-77-27618, INT-76-03952, and INT-78-27245), Hungarian Academy of Science, and the PRF administered by the ACS for financial support without which this research could not have been accomplished.

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