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Book Review

JOSEPH P. KENNEDY and ERNEST MARÉCHAL: Carbocationic Polymerization, John Wiley & Sons, New York, 1982

It is perhaps unrealistic to judge carbocationic polymerization by the criteria established for anionic polymerization. The advances in anionic polymerization pioneered by Szwarc, Milkovich, and others have led to a present control of the polymerization which can only be described as remarkable. One can today attain almost precisely a monotonic distribution of molecular species with an M_w/M_n almost equal to one. This condition is not obtainable in free radical polymerization due to the high reactivity of the active species. Thus monomer must compete for the active site with other important reactions interfering, such as chain transfer to polymer, solvent, or monomer. The growing free radicals do not exist long enough in time to allow equilibration to uniform molecular size with other molecular species. Only in this way can the monotonic distribution of species, as in anionic polymerization, be realized.

By contrast, in the case of anionic polymerization, the growing anionic center is relatively sluggish in reactivity. Furthermore, its reactivity is almost exclusively with monomer, so that tendencies to transfer with monomer, polymer, or solvent can be ignored or kept within acceptable limits. Furthermore, the familiar problems in free radical polymerization of bimolecular termination due to coupling or disproportionation are not problems in anionic polymerization. True, no other system exhibits such versatility in polymerization as free radical polymerization. Virtually all monomers exhibit a tendency to polymerize by free radical mechanisms to some degree. By contrast, in anionic polymerization only selected monomers such as methacrylates, styrene derivatives, conjugated dienes, vinylpyridines, and the like can be polymerized.

In the case of cationic polymerization, the range of polymerizable monomers is even more restricted than in anionic polymerization.

Polymerizable monomers are essentially limited to unsaturated hydrocarbons such as isobutylene and styrene and to the vinyl ethers. As a consequence, the only commercial cationic polymerization of note is that of polyisobutylene. More specifically, isobutylene is copolymerized with a small amount of butadiene or isoprene for the purpose of crosslinking. Very small amounts of vinyl methyl ether and other vinyl ethers are polymerized for limited uses as adhesives and water-soluble polymers.

Fifteen years ago it was reasonable to expect that, given a similar dedication to the task, control attained in anionic polymerization might be extended to cationic polymerization. As a result, not only were the talents of dedicated cationic polymerization specialists, such as Kennedy, dedicated to the study, but in addition, anionic experts endeavored to apply their techniques to cationic polymerization. It is tempting to conclude that, if the problem would submit to reasonable levels of diligence and ingenuity, it would have been solved by now. Some very recent studies by Kennedy are encouraging. If it has not been solved, it is undoubtedly a result of the extremely high reactivity of the active species not only with monomer to yield polymer, but in other ways that do not produce polymer. Nevertheless, some recent studies by Kennedy suggest the long-awaited result may be at hand.

Workers in the field have also directed much effort toward other means of obtaining, for example, block copolymers of cationic monomers with more conventional monomers. The problem of producing sequential block and graft copolymers is dealt with in Chapter 8 of the text. In one example, it was found by Kennedy that the polymerization of styrene could be initiated by a di-t-bromochloride compound under selected conditions such as only the t-chloride would be involved and the t-bromo substituent would survive the polymerization. The resulting polymer containing bromine was found to polymerize isobutylene in the presence of Et_2AlCl to yield a block copolymer of polystyrene and polyisobutylene.

By using variations of these procedures, BAB polymers of several types have been produced. These include poly(α-methylstyrene-b-isobutylene-b-α-methylstyrene). The sequential block copolymerization of poly(styrene-b-tetrahydrofuran) has also been accomplished.

The book Carbocationic Polymerization deals with essentially all of the active areas in cationic polymerization. Chapter 1 covers such interesting topics as advantages and usage of carbocationic polymerization and problems for the future. Chapter 2 deals with definitions, terminology, and nomenclature. Chapter 3 explores the nature of the polymerization active species, relative stability of carbocations, and structural effects influencing carbocation stability. Monomers and initiating systems are covered in great detail.

The book is unique in its unusually thorough treatment of copolymerization and reactivity in cationic copolymerization. Some 90 pages are devoted to this topic in Chapter 6.

The book is written in an easy, fluid style and should be of interest not only to academic scientists but to industrial research people as well. In the opinion of the authors, the area of cationic polymerization is undergoing a quiet revolution at the present time. This result is believed to proceed from the elucidation of the nature of cationic polymerization during the last ten years and the application of the information obtained to new products and processes.

It is with genuine admiration that I extend my compliments to Professors Kennedy and Maréchal for their comprehensive and stimulating treatise.

George E. Ham