Preface

At present, three-dimensional free-radical polymerization (TFRP) is a special field of radical polymerization. TFRP is characterized by specific kinetic regularities and mechanisms of processes for the formation of cross-linked or hyper-branched polymers, and they are different from the kinetics and mechanism of classical radical polymerization.

The fundamental studies of kinetics and mechanism of TFRP with formation of cross-linked polymers have been carried out in three stages. The first stage lasted from 1960 until 1983, and the main mechanisms of TFRP of oligo(acrylates) were established during this stage [1–3]. Condensation telomerization, being a universal oligo(acrylate) synthesis procedure, allows us to vary certain molecular parameters, such as length and flexibility of oligomeric blocks, number and type of reactive groups (methacrylic or acrylic groups), and chemical nature of atomic groups of an oligomeric block, which represent the centers of strong intermolecular interactions. For this reason, oligo(acrylates) were very convenient compounds for establishing the main kinetic regularities of TFRP and regularities of formation of polymer three-dimensional cross-linked structures, according to the so-called microheterogeneous mechanism (G.V. Korolev, 1977), at the topological and morphological levels. During the second stage, which lasted from 1983 until 1995, the kinetic regularities of TFRP were studied in depth, and additional evidentiary data in favor of the microheterogeneous mechanism of TFRP were found [4, 5]. The last, or third stage (from 1995 until 2005) involved exploration of TFRP under the "living" chains conditions and identification of new regularities associated with the implementation of these conditions [6], as well as the creation of the new gelation theory applicable to TFRP, investigation into physical and mechanical properties of cross-linked copolymers, and the interpretation of these properties within the framework of the physical network model [6].

The technical value of TFRP is generally known. Industrial use of oligo (acrylates), oligo(estermaleates) in styrene compositions, and oligo-esters modified by fatty acids of vegetable oils (alkyds) is based on TFRP with cross-linked polymer formation. The interest in TFRP throughout the world has markedly increased in the 1990s: by 2000 the number of publications on TFRP had grown tenfold. This growth is explained by the development needs of microelectronics, fiberoptics, and data storage and transmission devices. TFRP makes polymers highly attractive for

applications related to high-tech materials. The radical chain nature of TFRP enables performing curing of fluid polyunsaturated methacrylates in superfast time (seconds!) and an easily controlled mode at normal temperature.

It was found, in the middle of the 1990s, that in addition to cross-linked polymers TFRP can also lead to the formation of hyper-branched polymers (HBP) (non-cross-linked) that have a unique chemical structure and properties which are different from the structure and properties of all known linear and cross-linked polymers. Polymer chains of HBP diverge outward symmetrically in three-dimensional space from the point or linear center of symmetry and look like a branching tree. The unique properties of HBP turned out to be so popular that during the next decade these polymers found use in various applications for polymer materials from microelectronics to medicine. They caused a revolution in polymer materials technology. And, all this gave a new powerful impulse to the development of the entire TFRP field—the intensive and successful investigation into cross-linked polymers synthesized by TFRP conducted for many years did not betoken such a "burst" of interest. Judging by the trends in publications on this issue, this new subfield has developed extremely fast: before 1997, only a few publications appeared per year, during 1997–1998 the number of publications increased to 100, and during 2000–2005 more than 250 articles and patents per year have appeared.

The first part of this book deals with TFRP with formation of cross-linked polymers. It is based mainly on the results of systematic research of the authors and their colleagues.

This part (Chapters 1 through 6) includes all available data (plus analysis of these data) indicating the microheterogeneous character of TFRP. The microheterogeneous mechanism of TFRP includes both polymerization specifics at the initial, intermediate, and final stages (namely, initial formation, growth, and merger of polymer grains performing the function of autonomous micro-reactors) and structural and physical transformations in the course of TFRP (micro-syneresis, microredistribution, and local glass transition).

The interpretation of the main kinetic regularities of polyunsaturated oligomer polymerization in blocks and solutions and kinetic specifics of inhibited TFRP is given taking into account the microheterogeneous mechanism of TFRP. The main regularities of the polymerization of polyunsaturated compounds of vinyl and allyl types in a film under the conditions of oxygen diffusion were explained in the context of the proposed layer-by-layer TFRP model. A model of regular kinetically active associates intended for interpreting kinetic abnormalities of oligo(acrylates) and alkyl methacrylates polymerization is proposed: this model is substantiated both kinetically and via computer simulation. Basic kinetic features of the three-dimensional copolymerization of polyunsaturated (cross-linked) oligomers and monounsaturated (non-cross-linked) vinyl monomers were identified.

The main issues of the new branch in free-radical polymerization—namely, "living" chain three-dimensional free-radical polymerization—are analyzed. Also, exhaustive description is given for all studies on TFRP in the "living" chain mode and the role of this mode for the macromolecular design of cross-linked polymers.

The new theory of gelation in the TFRP process, which was developed by V. I. Irzhak and G.V. Korolev in 2000–2003, is described in depth. This theory is

alternative to the well-known Flory–Stockmayer theory, which is unjustifiably applied to TFRP. Critical conversion (gel point) for various modes of free-radical polymerization is determined in numerical form, and the obtained results are generalized in formulas.

Physical, mechanical, and thermo-mechanical properties of cross-linked (poly) acrylates and cross-linked copolymers of oligomers with vinyl monomers are analyzed in the context of the physical network model (i.e., intermolecular interactions system approximated by network of physical links). The predominant role of the physical network (i.e., a network of physical junctions) in proposed mechanisms for the transition of cross-linked copolymers into high-elastic and forced-elastic states is revealed. Problems of macromolecular design of cross-linked polymers and copolymers are also discussed.

The second part of the book [Chapters 7, 8] is devoted to methods of synthesis, properties, and application of hyper-branched polymers (HBP). An extensive array of information (about 400 publications) is systematized and reviewed. A classification of synthesis methods for HBP, which is based on mechanisms of synthesis reactions, is proposed. Methods for HBP synthesis by three-dimensional free-radical polymerization (with regulation of polymeric chains length due to the variation of initiation rate, employment of chain transfer agents and chain transfer catalysts, and intrachain reactions of radical chain carriers) are discussed in detail with examples. A mathematical model of HBP synthesis by the TFRP method under the conditions of unlimited supply of oxygen is proposed, and results of prediction obtained through the use of this model are presented.

The most successful and representative options of HBP synthesis by "living" chain free-radical polymerization are reviewed in depth because it is in just this case that the topological structure of HBP is distinguished by the maximum degree of regularity, which makes the HBP topological structure similar to the structure of regular HBP dendromers. Also, the method of "living" TFRP makes it possible to synthesize HBP with a sophisticated structure of macromolecules (nanostructured polymers).

Large amounts of information on practical application of HBP are systematized in this book in the form of generalized tables for the sake of convenience for readers. Particular emphasis is placed on HBP that are already produced industrially and on methods for modifying them in the context of specific applications.

Analytical reference materials for the subject matter of this book are given in the Appendix (Chapter 9). A short description of experimental methods that proved to be effective for studying the TFRP kinetics and mechanism, as well as the structure and properties of cross-linked polymers, is also given in the Appendix.

Thus, the authors have tried to give an integral description of scientific and applied aspects of three-dimensional free-radical polymerization with formation of both cross-linked and hyper-branched polymers as well as to outline the current state and trends of the development of this specific area of free-radical polymerization. The readers are to judge whether the authors have succeeded.

Chapters 1 and 2 were written by G.V. Korolev and M.M. Mogilevich, and Chapters 3, 4, 5, 6, 7, 8, and 9 were written by G.V. Korolev.

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To our deep sorrow one of the authors of the present book – Gennady Vladimirovich Korolev – passed away between its publication in Russian and in English. Therefore, publication of the English version, which was planned by him, is a tribute to the memory of the outstanding scientist he was and a solace for the members of his family and colleagues.

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