Physico-Chemical Principles for Processing of Oligomeric Blends

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To

the memory of my teacher and friend
Alfred A. Berlin

INTRODUCTION TO THE SERIES

This series will provide, in the form of single-topic volumes, state-of-the-art information in specific research areas of basic applied polymer science. Volumes may incorporate a brief history of the subject, its theoretical foundations, a thorough review of current practice and results, the relationship to allied areas, and a bibliography. Books in the series will act as authoritative references for the specialist, acquaint the non-specialist with the state of science in an allied area and the opportunity for application to his own work, and offer the student a convenient, accessible review that brings together diffuse information on a subject.

(oligomer feed) to a solid body (final polymer product), which are inherent to all classes of oligomers, were not systematized. This also pertains to common and specific features of the mechanisms of formation of heterogeneous structure during the curing of various oligomers and to the correlation between the structure of initial liquid formulation and the properties of the final solid material. In the excellent book *Reactive Oligomers* by Entelis et al. (1985), in spite of the very general title, only some aspects of the synthesis of oligomers with specified functionality and methods for determining functionality type distribution and molecular weight distribution were discussed.

Moreover, there have been no serious publications devoted to oligomer blends, although during the last decade oligomer blends (oligomer–monomer, oligomer–oligomer and oligomer–polymer) have come to dominate in industrial practice. It is the oligomer blends that initiated the progress in RIM processes, interpenetrating polymer networks, hybrid binders and gradient glasses. The principle of "temporary plasticization" and other effective modification procedures in rubber and plastics technology are also associated with oligomer blends. Monographs and collections of papers dealing with this trend [e.g., *Vzaimopronikayushchie polimernye setki (Interpenetrating Polymer Networks)* by Yu. Lipatov and L. Sergeeva, 1979; *Interpenetrating Polymer Networks and Related Materials* by L. Sperling, 1981; *Reaction Injection Molding*, edited by J. Kresta, 1982, 1985; *Fizikokhimiya mnogokomponentnykh polimernykh sistem (Physical Chemistry of Multicomponent Polymer Systems)*, edited by Yu. Lipatov, 1986; and *Khimicheskoe formovanie polimerov (Reaction Molding)* by A. Malkin and V. Begishev, 1991] only partially cover the physico-chemical aspects of the problem and, moreover, mostly those aspects that are related to the final (polymeric) state of a blend.

In this monograph, we make an attempt to give a comprehensive treatment of the modern state-of-the-art in theoretical and experimental studies of oligomeric systems. The aim of this undertaking was to supply process engineers with a quantitative approach to formulation of liquid oligomer compositions and selection of the regimes for their processing to materials and articles.

From this standpoint we discuss the classification of oligomers and oligomer blends and analyze their structural organization in the liquid state. In terms of statistical thermodynamics we consider equilibrium and nonequilibrium properties of oligomeric systems. On molecular, supermolecular, topological, and colloidal levels of structural hierarchy, we trace the relationships between phase organization and the kinetics of chemical and structural transformations during the cure of oligomers. Previously reported and predicted correlations between structural parameters of cured systems and their macroscopic properties are summarized. Most sections of the book are supplemented by practical recommendations that describe the application of the discussed physico-chemical regularities to real technological practice. The last chapter deals with physico-chemical aspects of oligomer technology and materials science, including the physico-chemical analysis of the relationship between the ingredients of the formulation and the properties of the resultant material.

This book is based on research of the author and other studies of the scientific school founded by Prof. Alfred A. Berlin, conducted at the Institute of Chemical Physics of the Russian Academy of Sciences in cooperation with other research groups headed by Prof. A. Chalykh (Inst. Phys. Chem., RAS), Prof. V. Lantsov (Kuibyshev Institute of Construction Engineering), and Dr. R. Frenkel' (R&D Technological Institute of Rubber Industry). I am pleased to acknowledge their cooperation. In addition, results of studies at other research centers are also discussed—in particular, studies headed by Profs. S. Entelis, Yu. Lipatov, G. Korolev, B. Rozenberg, L. Sperling, S. Krause and T. Kwei. I have tried also to give the most comprehensive coverage of the most important results discussed at five National Conferences on Oligomer Chemistry and Physical Chemistry held in the USSR (later CIS) between 1977 and 1994 which, because of the language barrier, have been unknown to foreign scientists.

This is the reason for the prevalence of Russian editions in the lists of references. However, realizing the difficulties the reader may encounter in gaining access to the Russian publications, wherever possible I have tried to cite current monographs and reviews. The reader is referred to the original publications only where absolutely necessary.

I dedicate this book to the memory of my teacher and friend Prof. Alfred A. Berlin (1912–1978). It is my deepest belief that Alfred Berlin was one of the most outstanding chemists of the second half of this century. His contribution to oligomer science and polyconjugated systems has not been yet acknowledged by his contemporaries.

I am pleased to thank Prof. Yurii S. Lipatov, Member of the National Academy of Sciences of the Ukraine. During talks and discussions at his seminars in Kiev and Odessa some ideas that were later to become part of this book were first put into words.

It is appropriate to emphasize the fruitfulness of discussions with Profs. A. Tager, G. Korolev, V. Khozin, S. Baturin, V. Kuleznev, L. Manevich, A. Malkin, E. Oleinik, B. Rozenberg and, especially, V. Irzhak, as well as with Drs. B. Zadontsev and B. Zapadinskii.

I owe a special debt to my former students and associates: Dr. L. Abdrakhmanova, researchers Mrs. E. Vasil'chenko and L. Zhil'tsova, Drs. A. Kotova, S. Nadzharyan, T. Repina, M. Khotimskii, Sh. Shaginyan and S. Yaroshevskii, who participated in the studies summarized in this monograph.

I am also grateful to Profs. E. Yakhnin and G. Zaikov for their special role in making this book possible.

Special thanks are due to my wife Dr. M. Tokar', who assisted in preparing the manuscript and was the first to read it. It is her caring and support that, in the final analysis, made this book a reality.

The readership of this book will include primarily research people and process engineers at scientific centers of companies involved in development and production of materials based on oligomeric and polymeric systems. It may also be of interest to scientists working in the fields of physics, chemistry, and physical chemistry of oligomers and polymers. I hope the book may be of use to university teachers and graduate students.

INTRODUCTION

Pressing, molding, extrusion, vulcanization, and some other technological operations involved in fabrication of polymer articles are performed with the purpose of forming a material, which is thereby given a shape required for a particular application.

The task of a qualified process engineer is to predict possible structural transformations that take place in various stages of the process and to control the final structure and, hence, the performance of the article by simple methods (e.g., by varying composition, temperature, pressure, concentration of active additives, and so on). Accomplishment of this task encounters many difficulties. The development of a rational technology is thus reduced to solving a simply formulated but difficult problem: to obtain a final material or an article with the best (or at least satisfying the project specification) combination of properties at a minimum consumption of raw materials, energy, and time, and to avoid environmental pollution in all stages of the production cycle. Presently, this complex problem has not been solved on a uniform basis. Neither has any unified approach been developed to solve this problem.

One of the possible approaches to optimization of polymer processing can be formulated as follows [1]. In terms of chemical cybernetics, a technological process consists in that certain information is conferred to and recorded by the material: it is this information that determines the entire combination of properties of the final material. Here, the structure of the material serves as an information carrier. In the case of polymer technologies (thermoplastic and thermosetting), the structure formation involves a sequence of physical and chemical processes, such as softening, melting, solidification, vitrification, crystallization, (co)polymerization, (co)polycondensation, cross-linking, grafting, and so on. According to the general concepts of chemical cybernetics, for a closed technological cycle $I \cdot E = \text{const.}$ where I is the amount of information contained in the initial polymer (raw material) and E is the amount of energy consumed during the processing of the polymer to the final product. This fundamental relationship bears an important consequence: the most rational technology would correspond to $E \rightarrow 0$. This implies that the process must be organized so as to provide that the final product contains maximum information with minimum energy consumed during the processing. This can be achieved only if the initial materials are polymeric systems with the highest possible degree of structural organization (high initial information level). Thus, the greater the amount of information contained in the initial polymer, the smaller the amount of information that must be added during the technological cycle and the lower the amount of energy consumed in order to obtain the required combination of properties.

For a process engineer, development of a specific process is associated with the need to solve at least two distinct problems. The first one involves appropriate choice of objects (materials) that are to be subsequently processed. These materials must possess the highest possible (under the given conditions) degree of structural organization. In particular, this feature stipulates the natural tendency to use as raw materials the structurally regular oligomers rather than the random oligomers [2], or crystallizable polymers rather than the amorphous [3]. The second problem deals with the adjustment of curing regimes that would not interfere with the order that existed in the liquid phase prior to curing (liquid-crystalline structures, cybotaxes, associates, clusters, domains, elements of short-range order, and so on; the terminology has not yet been unified) but rather allow its conservation in the solid state [4].

Solution of the first task is inseparable from the achievements in the synthesis of compounds with controlled functionality and controlled interjunction spacing [5]. It is also largely related to the presently available knowledge of physico-chemical properties of compounds used to manufacture the materials. Solution of the second problem requires a deeper insight into the effects that kinetic and thermodynamic factors have on the development of the structure of a solid [4, 6, 7]; hence, it implies the need to acquire a deeper understanding of the mechanism of "liquid–solid polymer (article)" transition. These features also explain the importance, and even the necessity, of using the principles of physico-chemical mechanics [8] in the development of rational and highly effective processes for the production of composites [9].

Next we consider these principles in greater detail, with special emphasis on their implementation in the manufacture of general-purpose polymeric materials. We also examine some applications ensuing from this analysis and perform the analysis with materials based on oligomer mixtures. We chose oligomers for analysis first, because of their importance to modern polymer industry—indeed, more than 50% of the world's polymer wares production uses oligomers—and second, because the potential conserved in the structure of oligomers has not yet been realized in the production of polymers possessing a desired combination of properties. Finally, oligomers, especially the structurally regular ones, offer a convenient model for the analysis of physico-chemical regularities that control the liquid–solid transition. We begin with a description of the basic concepts and terminology used in this monograph and give modern classification of oligomers and their mixtures. This will help process engineers feel more at ease among the variety of objects used in industrial processes.

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CONTENTS

1 OLIGOMERS AND CHARACTERISTICS OF OLIGOMER BLENDS

1.1. OLIGOMERS: TERMINOLOGY AND CLASSIFICATION

The term "oligomer" (from Greek *oligos,* meaning several or a few, and *meros,* meaning a part or repetition) was originally introduced into scientific literature by I. Gelferich in 1930 to denote carbohydrates containing 3 to 6 monose residues. With time, the meaning of the term has considerably extended. At present, it is used to describe chemical substances occupying an intermediate position between monomers (low-molecular-mass compounds) and polymers (high-molecular-mass compounds).

The use of other terms sometimes encountered in periodic literature, such as pleinomer, synthetic resin, low-molecular-weight polymer, macromer, etc. produces terminological confusion and, what is more important, deprives oligomers of the strictly defined physical meaning as a condensed state of molecules with special properties. The special properties considered below account for the marked role that the oligomers play in many biological processes and in modern technology. For example, some cellular enzymes, polypeptide antibiotics, hormones, and other biologically active substances are in fact oligomeric compounds. The fundamental significance of oligomers as of a special condensed state of a substance is emphasized by the fact