

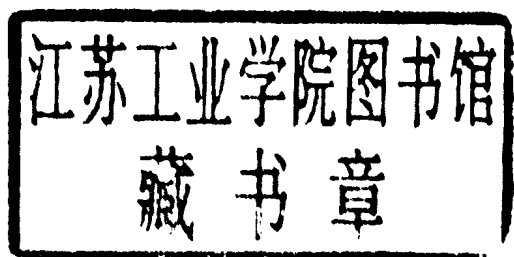
FAST POLYMERIZATION PROCESSES

Karl S. Minsker
and
Alexandre Al. Berlin

Polymer Science and Engineering Monographs
A State-of-the-Art Tutorial Series
Volume 1

Gordon and Breach Publishers

**FAST POLYMERIZATION
PROCESSES**



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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.

PREFACE

It is difficult to find a branch of chemical science that has never been studied. However, very fast chemical reactions in liquid phase, with reaction time lower than that of reagent mixing, represents a new field in chemistry and technology, both from the scientific and practical points of view. An example would be very fast isobutylene polymerization.

Essential new scientific propositions and methods have been discovered and introduced into practice, making it possible to consider fast chemical processes as an independent class of chemical reactions characterized by original regularities, specific control methods, technological fabrication of the process and the design of the main apparatus.

A great number of empirical methods of calculating chemical reactor designs exist. The main limitations of these methods are the introduction of many empirical parameters leading to difficulties in the scale conversion. However, methods of accurate calculation of the chemical reaction processes in various configurations—taking into account both chemical kinetics and mass- and heat transfer—recently have been developed. Such approaches were referred to by D. A. Frank-Kamenetsky as macrokinetics. This book gives examples of much analysis for fast chemical reaction occurring in reagent turbulent flows being mixed.

Due to the application of such approaches, we have managed to profoundly change the design of reactors for a number of fast chemical processes in “liquid-liquid” and “liquid-gas” systems such as isobutylene, α -olefin, piperilene oligomerization; ethylene, benzene and rubber chlorination; sulfuric acid alkylation; synthetic rubber production, and so on. The new reactors make it possible to considerably increase productivity, lower costs, power consumption and starting reagents, and to improve both product quality and ecological effects of the process.

This book will be of interest to researchers and engineers working in the chemical and petrochemical industries. It should prove useful for undergraduates specializing in chemical synthesis and technology.

The approaches and methods described in the book are still being developed and updated. Therefore, everything should not be taken as the “last” word. We hope that readers who become interested in these problems will watch the scientific papers appearing in this field of macrokinetics.

We are grateful to our late friend Academician Enikolopov/Enikolopyan/ N.S., as well as to the colleagues, co-workers, and

disciples whose names appear in the Reference section. Working with us for many years, they have devoted themselves to the fascinating and captivating search for new laws and new ways of solving many fundamental and technical problems.

We deeply appreciate the invaluable help of Farida Basirova, Svetiana Gantseva, and Sergei Minsker in preparing the manuscript.

INTRODUCTION

In chemistry and chemical engineering, especially the technology of the production of applied polymers, there are problems the solutions to which remain little studied or completely unknown. We are concerned with one of these: very fast polymerization in liquid-phase with the characteristic reaction times of the chemical reaction τ_{ch} less than 10^{-1} – 10^{-3} s. A typical example of a similar process is isobutylene polymerization [1, 2].

An understanding of the fundamental laws and the effects of spontaneous heating of the reaction mass on the rate and the direction of fast chemical reactions as well as on the main mass-molecular characteristics of the final products (in polymer production— \bar{M}_n and MWD) is of great significance. This is true both for controlling chemical processes in general and for selecting the design of the basic industrial equipment—polymerizers.

In order to obtain polymer products with the narrow, most probable inclusive MWD, to control the molecular characteristics, it is necessary to provide isothermal conditions of the reaction. This is usually achieved by removing the reaction heat evolved in exothermal processes and by the ideal mixing that provides a sufficiently uniform temperature field.

Theoretically, isothermal conditions in very fast reactions of polymerization can be created by using low concentrations of the monomer in the initial reaction mixture or by applying the catalyst for slower action. However, in these cases the reaction rate and the process productivity are considerably reduced. Besides, using great quantities of the solvent can seriously increase the power consumption and other expenses on the solvent regeneration. While the laboratory work can achieve well-known methods of obtaining isothermicity in polymerization, this is not true in the field. There, when working with very fast chemical processes, heat and mass transfer generally cannot be provided efficiently enough. Fast processes of liquid-phase polymerization are practically always characterized by high exothermicity of the reaction and low thermal conductivity of the reaction mixture. The result is local overheating of the reaction mass. Non-uniform time-spatial distributions of temperature, concentrations of the monomer and the catalyst and the degree of the reaction completion appear. As a result, very fast polymerization processes are hard to control and are characterized by a marked decrease of the total yield of the final product, poor quality, and

unjustified retention of the reaction mixture in reactors-polymerizers. In a number of cases, temperature fluctuations of polymerization lead to unpredictable results (thermal explosion, powerful hydro- and pneumoshocks etc.).

Nevertheless, in realizing fast polymerization in industry, traditional methods were used to compute the designs of basic reactors-polymerizers and to develop the procedure generally. *A priori*, it is considered that fast reactions proceed under isothermal conditions. This is basically incorrect, since in very fast liquid-phase polymerization in volumetric reactors it is impossible to provide efficient heat and mass transfer in time commensurate with that of the chemical reaction.

Meanwhile, both in this country and abroad, the state of technology in realizing very fast polymerization processes in liquid-phase is such that polymers (of isobutylene, in particular) are obtained in volumetric reactors of ideal displacement, with continuous action with the volume of 2–30 m³ at the intense mixing and heat removal.

The use of continuous action reactors of ideal displacement in liquid-phase fast polymerization is an even worse choice, as it results in still greater broadening of the MWD and the increase of the molecular mass of polymers formed in comparison to the results predicted by theoretical calculations for reactions proceeding under isothermal conditions. In practice, the isothermal process even for relatively slow chemical reactions cannot be realized in continuous action reactors of ideal displacement, since it is necessary to vary heat transfer along the reactor length according to the kinetics of heat evolution. The displacement reactors normally operate in adiabatic or intermediate, but far from isothermal, regimes (with outer heat removal excluded). Therefore, practically all reactors used in industry in fast chemical processes have essential shortcomings in design and, hence, as a rule, are inefficient in operation. Consequently, the quality of the products obtained is far from ideal, and processes in general are imperfect both in engineering and socio-economical aspects (that is, in terms of yield, quality, unrecovered waste, unjustified great power consumption, etc.).

Thus, realizing very fast chemical processes in real productions—in particular in that of liquid-phase electrophilic isobutylene polymerization—one should always bear in mind that the purely chemical aspect of the process is complicated by a number of physical processes starting with diffusion, mass and heat transfer, and hydrodynamic processes. The rate of fast chemical reactions, including polymerization, is controlled by the rate of the reagent coming to the reaction zone, i.e. the mixing rate (the diffusion rate) of the reacting substances. This fact makes the reaction rate and the reagent conversion depend on the

mass of the specimen, the thickness of the reaction zone layer and many other nonchemical factors.

Very fast chemical reactions proceed, as a rule, in the diffusion region and necessarily require the macrokinetic approach to the problem solution. We should note that the name of the science—macrokinetics—for studying the effect of physical processes and hydrodynamics on the chemical reaction run was suggested by Professor D. A. Frank-Kamenetsky [3]. It was most efficiently developed by specialists on burning [4].

Very fast liquid-phase polymerization reactions require the similar macrokinetic approach as well. For them a number of fundamental traditional concepts—for instance, isobutylene polymerization kinetics, and, as a consequence, technological procedure of the production of oligomers and polymers of isobutylene etc.—have to be reconsidered. In some cases, new theoretical and practical approaches must be developed. This fact has created great interest for many years in fundamental studies of liquid-phase electrophilic isobutylene polymerization as a model of very fast reaction. New data continue to create additional interest. For the last few years, it has been clear that the problems of the chemistry and technology of oligo- and polyisobutylene production, as well as of the other superfast chemical reactions and processes limited by mass and heat transfer, are not as simple as they may seem at first sight.

Instead of traditional problems such as process intensification and heat removal, extremely high rates of polymerization reactions give rise to the other and more complicated ones: modeling and controlling of superfast polymerization reactions with the creation of socially and economically beneficial technological procedures for production of polymers with the required characteristics. These characteristics are high specific process efficiency (the maximum output of the product per a unit of the reaction volume) with the minimum capital investment, efficient use of material and power, and control and maintenance of the process, as well as the production of polymers of definite molecular structure and chemical composition.

One should note that the new methodological and experimental approaches revealed on the suitable model of very fast chemical reactions—liquid-phase electrophilic (cationic) isobutylene polymerization—and the original results given later in the book are of general importance and are applicable to other fast liquid-phase polymerization processes—cation, anionic, free-radical ones. They also proved fruitful for many other processes, neither necessarily polymer nor chemical, where mass exchange is of great significance.

In part anticipating the results given later in the book, we should

point out that the combination of basically new results in fields of fundamental laws and engineering solutions in the realization of both purely scientific and applied discoveries in very fast liquid-phase processes means that these reactions should be referred to a separate class of chemical reactions, characterized by their own specificity and methodology of investigation. A separate class of oxidation reactions represents a similar example due to the characteristic and original macroscopic features of these reactions.

SYMBOLS

$[A^*]$	the catalyst concentration
D_T	the coefficient of the turbulent diffusion
k_i	the constant of the initiation rate
k_m	the constant of the chain transfer on monomer rate
k_p	the constant of the chain propagation
k_t	the constant of the termination chain rate
k_{tr}	the constant of the transfer chain rate
k_D	the constant of the diffusion rate
\bar{M}_n	the number-average molecular weight
\bar{M}_w	the weight-average molecular weight
\bar{M}_z	the z-average molecular weight
M_v	the viscosity-average molecular weight
MW	the molecular weight
MWD	the molecular weight distribution
$[M]$	the concentration of monomer
\bar{P}_n	the number average degree of polymerization
\bar{P}_w	the weight average degree of polymerization
\bar{P}_z	the z-average degree of polymerization
q	the heat effect of polymerization
τ_{ch}	the time of the chemical reaction
τ_{mix}	the average time of the component mixing
V	the linear speed of flow
α	the coefficient of heat transfer through the wall
λ_T	the coefficient of temperature conductivity
μ_T	the turbulent viscosity
ν	the kinematic viscosity
$\rho_n(j)$	the numerical function of the distribution on the degrees of polymerization
$\rho_w(j)$	the weight function of the distribution on the degrees of polymerization

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1 THE MACROKINETICS OF FAST POLYMERIZATION PROCESSES IN LIQUID-PHASE

1.1 THE PECULIARITIES OF VERY FAST POLYMERIZATION PROCESSES

In polymer chemistry there exist processes of very fast polymer synthesis, when the rates of chemical reactions are comparable with or higher than those of the reactant mixing. Such processes, in particular, include some solid-phase reactions in photo- or radiation initiation [5], explosive polymerization of the monomers under shift compression [6], some processes of cationic polymerization in the presence of sufficiently strong electrophilic catalysts (for instance, the polymerization of styrene, vinyl alkyl ethers, isobutylene etc. in the presence of BF_3 , AlCl_3 , SnCl_4 etc.) [1, 2, 7], some reactions of anionic polymerization of vinyl monomers [8], the ionic polymerization of formaldehyde and acetaldehyde [9], the free radical polymerization of ethylene at high pressures [10], complex radical polymerization [11], a number of processes of non-equilibrium polycondensation [12] etc. The constants of chain propagation rates for some of them are given in Table 1.

Among very fast polymerization reactions, one of the most studied in terms of macrokinetics theory, due to general theoretical lucidity and greater practical value, is the electrophilic liquid-phase cationic polymerization of isobutylene [1, 2], which may be taken for the classical model of a fast reaction.

Table 1. The constants of chain propagation rates in fast polymerization based on different mechanisms

Monomer	Solvent	Reaction conditions	k_p , 1/mol·s	E_p , kJ/mol	$1g A_p$, l/mol·s	Ref.
The anionic polymerization						
styrene (polymerization in free poly-styrene anions)	tetrahydrofuran	counterion Na ⁺ , 298 K	950	5.9	9.05	[13, 14]
	dimethoxyethane	counterion Na ⁺ , 298 K	4000	~ 5	8.3	[15]
	tetrahydropyran	counterion Li ⁺ , 296 K	6600	5.1	6.8	[11, 14]
2-vinyl pyridine	tetrahydrofuran	counterion Na ⁺ , 298 K	7300	—	—	[16]
4-vinyl pyridine	tetrahydrofuran	counterion Na ⁺ , 298 K	3500	—	—	[16]
The cationic polymerization						
isobutylvinyl ether	dichloromethane	catalyst (C ₆ H ₅) ₃ CSbCl ₆	4000	—	—	[17]
		C ₇ H ₇ SbCl ₆	6800	—	—	[17]
isobutylene	—	ZnO, 273 K	1.5·10 ⁸	—	—	[18]
		γ-radiation, 133–193 K	3.0·10 ⁶	—	—	[19]
		AlCl ₃ , 243 K	1.0·10 ⁶	—	—	[20, 21]

The common way to obtain oligo- and polyisobutylene (PIB) with the molecular mass (MW) 112–50,000 in industry is the cationic polymerization of isobutylene (IB) in the presence of AlCl₃ in hydrocarbon medium (butane etc.) at the temperature interval of 173–353 K in complex design reactors-mixers with the volume of 1.5–30 m³ [2, 22].

The application of the PIB depends on the MW, and the polymer product quality in most cases is also dependent on the MWD. This requires strict observation of the technological parameters in obtaining PIB and making the reaction thermostatic.

To provide heat removal and the required output according to thermal and material balances, the reactors have well-developed inner and outer heat-exchanging surfaces (up to 130 m² and more) with liquid ethylene or ammonia, highly intensive mixing facilities, capable of linear rates of reaction mass flow of 1–10 m/s and great value of heat exchange in the reactor at an average time interval up to 1.8–36·10³ s. The