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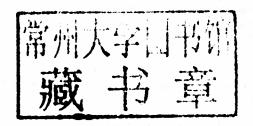
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# THE FRACTAL PHYSICS OF POLYMER SYNTHESIS

# ABOUT THE AUTHORS

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A. K. Mikitaev, DSc, is Professor and Head of the Chair of organic chemistry and high-molecular compounds at Kabardino-Balkarian State University in Nal'chik, Russia during 1971–1990 and from 2004 until now. He set up the Scientific-Educational Center "Polymer and Composites" in 2008. He developed and worked in industry on the production technology of poly(butylenes terephtalate) and nanocomposite materials and its basis, including nanocomposite thermoelastoplastics. His scientific interest in synthesis of polymers includes developing strategies for manufacture of polymers of different classes. He is the author of more than 1000 scientific works, including 14 books, and he has received 160 author's certificates and patents.


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# LIST OF ABBREVIATIONS

| | |
|---|---|
| CATA | Chloroanhydride of terephtalic acid |
| DDM | Diaminodiphenylmethane |
| DLA | Diffusion limited aggregation |
| DMDAACh | Dimethyldiallylammoniumchloride |
| EAEA | Ethylallylethylacrylate |
| IGC | Inversed gas chromatography |
| MWD | Molecular weight distribution |
| PC | Polycarbonate |
| PMMA | Poly(methyl methacrylate) |
| PPQX | Polyphenylquinoxalines |
| PPX | Polyphenylxalines |
| PPX | Polyphenylxalines |
| PSA | Ammonium persulphate |
| PSF | Polysulfone |
| PVC | Poly(vinyl chloride) |
| SANS | Small angle neutron scattering |

# LIST OF SYMBOLS

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$\dot{\gamma}$ = Shear rate

$t_g^T$ = Theoretical magnitude

$\overline{D}_f$ = Fractal dimension

$\Sigma\sigma$ = Gammet's constant

$\vec{\delta}$ = Solubility parameter

$T_{g_1}$ and $T_{g_2}$ = Homopolymers glass transition temperatures

$M_n^*$ and $M_{n+1}^*$ = Threshold masses of atoms

Df = Macromolecular coil fractal dimension.

K$\eta$ = Constant

m0 = Monomer link

Q = Conversion degree

Rg = Gyration radius

Su = Specific surface of nanofiller particles

T  Temperature

Z$\infty$ = Parameter limiting value

## GREEK SYMBOLS

$\alpha$ = Macromolecular coil swelling coefficient

$\beta$e = Fraction of macromolecular coil

$\delta$ = Feigenbaum's constant

$\delta$f = absolute value of components

$\eta$ = intrinsic viscosity

$\eta$red = reduced viscosity

$\nu$ = flory exponent

$\rho$Euc = Euclidean object

$\rho$p = polymer density

$\varphi^*$ = threshold value of concentration

$\chi$s = empirical parameter

# PREFACE

One of the principal objects of theoretical research in any field of knowledge is to find the point of view from which the subject appears in its greatest simplicity.

In spite of the enormous number of papers dealing with the influence of the medium on the rate of chemical reactions (including synthesis of polymers), no strict quantitative theory capable of "universal" application has been put forward up to now. And so it is possible to describe the relationship between the reaction rate constants and the equilibrium constants with the nature of the medium in which the reactions take place by means of a single equation.

The absence of general theory of the influence of the environment on the kinetics of chemical reactions can be explained by the fact that the change of solvent (or transition from liquid to solid phase) cannot only influence the process rate but also frequently results in complication of the reaction mechanism. The calculation of the individual contributions made by each factor is thus, in most cases, rather complicated and requires a deep and comprehensive study of the properties of the medium and of the reacting particles. This is because of a quantitative evaluation of all types of interactions between the reacting particles with medium can occur only by arriving ones on the basis of full knowledge of these properties.

Aristotle asserted that "among the unknown in the nature surrounding us, the most unknown thing is time, because nobody knows what time is and how it can be controlled". Since then definite positive changes have happened in this field. Particularly, the branch of science named chemical kinetics was established, which gave people the opportunity to predict the behavior of chemical reagents with time, and disclose the inner mechanism of the interaction between particles (molecular, ions, radicals and atoms) in various chemical processes.

The main aspects of the fractal analysis application for the description of the behavior of macromolecular coils in the diluted solution are also considered to emphasize the intercommunication of the classical and fractal (structural) characteristics of macromolecular coils. Developed in the physical chemistry of polymer solutions, the basic ideas are the basis of our understanding of the peculiar properties of polymers. Such an approach allows one to receive the direct correlations "structure-properties", which is the main task of any physical domain including the physical chemistry of polymer solutions and polymers synthesis.

Hence, the fractal analysis, that is a purely physical (structural) conception, and the irreversible aggregation models, closely connected with it, provide a simple quantitative description of both environment and time, whereas a reaction mechanism change also influences the reaction course of high-molecular systems. This is possible just owing to introduction of the polymer structure in its different states.

**— G. V. Kozlov, DSc, A. K. Mikitaev, DSc, and Gennady E. Zaikov, DSc**

# ABSTRACT

In the present monograph the description of the main reactions of high-molecular substances (polycondensation, radical polymerization, branched polymers synthesis, curing of cross-linked polymers, synthesis of polymer nanocomposites *in situ*, catalyzed reactions) is proposed within the frameworks of the fractal analysis and an irreversible aggregation models. The synergetics and percolation theory were also used. The notion of the polymer structure in solution (macromolecular coil) and its condensed state is introduced, and their intercommunication is established. This allows predicting the solid-state polymer characteristics that are already at the stage of synthesis. The influence of both environment and reaction duration and also of aggregation (synthesis) mechanism change effect can be taken into account within the frameworks of the mentioned conceptions. The polymers synthesis in a melt is also considered. It is significant that the fractal analysis, being purely physical conception, gives an exact and simple quantitative description of both indicated above reactions kinetics and their final (limiting) characteristics.

# INTRODUCTION

In spite of the enormous number of papers dealing with the influence of the medium on the rate of chemical reactions (including synthesis of polymers), no strict quantitative theory capable of "universal" application has been put forward up to now. It is now possible to describe the relationship between the reaction rate constants and the equilibrium constants with the nature of the medium in which the reactions take place by means of a single equation.

This important book, for the first time, gives structural and physical grounds of polymers synthesis and curing, and the fractal analysis is used for this purpose. This book presents important aspects on fractal physics of polymer synthesis such as polycondensation, radical polymerization, the branched polymers synthesis, and the curing of cross-linked polymers. The fractal analysis is used for this purpose. The book covers the theoretical fundamentals of macromolecules fractal analysis and then goes on to discuss the fractal physics of polymer synthesis and the fractal analysis and synergetics of catalytic systems. The fractal physics of polymer synthesis presents descriptions of the main reactions of high-molecular substances within the frameworks of fractal analysis and an irreversible aggregation models. Synergetics and percolation theory were also used.

The fractal physics of polymer synthesis is a new topic in the research field of polymer synthesis, which has attracted increasing interest due to its potential applications in the real world, such as modeling of polymeric materials. In this part, basic theory for fractional differential equations and numerical simulations for these equations will be introduced and discussed for polymers of different classes and polymers solutions. In the infinite dimensional dynamics part, we emphasize numerical calculation and theoretical analysis, including constructing various numerical methods and computing the corresponding limit sets, etc. In this book, we show interest in network dynamics and fractal dynamics together with numerical simulations as well as their applications. For each topic the theoretical concepts are carefully explained using examples and applications within the framework of fractal approximations taking into account the hydro-dynamical interactions.

The book covers the theoretical fundamentals of macromolecules fractal analysisand then goes on to discuss the fractal physics of polymer solutions.

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# CHAPTER 1

# POLYCONDENSATION

## CONTENTS

## 1.1 THE SOLVENT NATURE INFLUENCE ON STRUCTURE AND FORMATION MECHANISM OF POLYCONDENSATION POLYMERS

As it is known [1], the following relationship is one from the fractal definitions in reference to a macromolecular coil:

$$R_g \sim N^{1/D_f} \tag{1}$$

where Rg is macromolecular coil gyration radius, N is polymerization degree, Df is macromolecular coil fractal dimension.

The comparison of the Eq. (1) and the known Flory equation [2]:

$$R_g \sim N^\nu, \tag{2}$$

where $\nu$ is Flory exponent, shows that between parameters Df and $\nu$ the intercommunication exists Eq. (3):

$$D_f = \frac{1}{\nu} . \tag{3}$$

Nevertheless, the Eqs. (1) and (2) are valid for different objects. If Flory equation is correct for arbitrary coils, then the fractal Eq. (1) — for only semi-similar ones (by the fractal definition [3]).

The fractal analysis main rules in reference to polymer solutions description can be found in the reviews [4, 5]. The common remark should be made in respect to the Eq. (1). The fractal dimension Df characterizes macromolecular coil structure, defining its elements distribution in space. The increase of Df means Rg decreasing at N = const, i.e., a coil compactness enhancement.

Since the introduction in analysis of macromolecular coil structure, characterized by its fractal dimension Df, is the key moment of polycondensation process fractal physics, then the value Df determination methods are necessary for practical application of polycondensation fractal analysis for solutions. This parameter for macromolecular coil in solution is defined by two groups of interactions: interactions polymer-solvent and interactions of coil elements among them [6]. At

present several methods of the first from the indicated groups interactions exist and all of them can be used to a certain extent for Df calculation [5].

The simplest experimental method of Df calculation is the equation [7]:

$$D_f = \frac{3}{1+a_\eta},\tag{4}$$

where $a_\eta$ is the exponent in Mark–Kuhn–Houwink equation, connecting intrinsic viscosity and molecular weight of a polymer.

From the Eq. (4) it follows, that the exponent $a_\eta$, earlier assumed purely empirical characteristic, has a clear structural interpretation. One from the calculated methods of Df determination uses the known Huggins equation, which gives the dependence of reduced viscosity $\eta$red on concentration c for diluted polymer solutions [8]:

$$\eta_{red} = [\eta] + k_H [\eta]^2 c + ...,\tag{5}$$

where $[\eta]$ is intrinsic viscosity, kH is Huggins constant, which characterizes polymer-solvent interactions level.

Besides, the relation between specific viscosity $\eta$sp, c and $[\eta]$ can be obtained, using Shultz–Blashke equation [9]:

$$[\eta] = \frac{\eta_{sp}/c}{1+K_\eta \eta_{sp}},\tag{6}$$

where $K\eta$ is the constant, accepting in the first approximation equal to 0.28.

The Eqs. (5) and (6) at the condition c=const (the value c is accepted further equal to 0.5 mass. %) allows to obtain the simple expression for kH estimation [10]:

$$k_H = \frac{0.14}{1-0.14[\eta]}\tag{7}$$

For kH calculation the authors [10] supposed that all the used in work polymers (polyarylates (PAr), poly(vinyl chloride) (PVC), poly(methyl methacrylate) (PMMA), polysulfone (PSF) and polycarbonate (PC)) had the same molecular weight MM = 5 × 105.

Such value MM was chosen because its smaller values give close values kH that increase an estimations error. The values [η], corresponding to the indicated MM magnitude, were calculated according to Mark–Kuhn–Houwink equation [11–13].

In paper [10], the dependence of Df, obtained according to the Eq. (4), on parameter $k_H^{-2}$ is adduced (such form of the dependence was chosen with the purpose of its linearization). A good linear correlation was obtained for 30 different polymer-solvent pairs (correlation coefficient is equal to 0.930 [10]), allowing to predict simply enough the value Df. It is expected that for other MM values the correlation Df $(k_H^{-2})$ will have a similar form, but another slope. The mentioned dependence Df $(k_H^{-2})$ allows to make a conclusions number. First, an impression is created that this correlation gives the dependence Df on the polymer-solvent interactions only, characterized by Huggins parameter kH and does not take into account interactions of coil elements among them. However, this correlation linearity itself supposes, that it takes into consideration the second group factors, as well which was mentioned above. For example, it is well known [11], that chain rigidity enhancement results to exponent aη increase in Mark–Kuhn–Houwink equation and, hence, to Df reduction (the Eq. (4)). Simultaneously chain rigidity enhancement results to [η] growth at other equal conditions. Thus, both the chain rigidity increase and the improvement of the solvent theormodynamical quality in respect to polymer give the same effect — [η] increase and, correspondingly, kH growth according to the Eq. (7). This, in its turn, results to $k_H^{-2}$ decrease and Df reduction that is expected. This supposition is confirmed experimentally — in paper [14] the increase of Kuhn statistical segment length A, characterizing the chain thermodynamical rigidity, at the improvement of the solvent thermodynamical quality for two polyarylates, is shown.

Secondly, as it follows from the Eq. (7), the minimum value kH = 0.14 (or maximum value $k_H^{-2} \approx 51$) is reached at [η] = 0. From the plot Df $(k_H^{-2})$ it follows that Df ≈2.25 corresponds to this value kH. As it is known [6], the screening of the exluded volume interactions results to Df increase and at complete screening (the compensation of the mentioned effects) $D_f^c$ value corresponds to the so-called compensated state. Within the frameworks of Flory's theory, when the compensation is realized by the interactions with other coils, $D_f^c$ =2.5 (for three-dimensional Euclidean space). Another method for the decrease of repulsive interactions among coil elements is the introduction of the attractive interactions.