

Key Elements in POLYMERS for ENGINEERS and CHEMISTS

From Data to Applications

Editors

Alexandr A. Berlin, DSc
Viktor F. Kablov, DSc
Andrey A. Pimerzin, DSc
Simon S. Zlotsky, PhD



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Gennady E. Zaikov, DSc, and A. K. Haghi, PhD

Reviewers and Advisory Board Members



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ABOUT THE EDITORS

Alexandr A. Berlin, DSc

Professor Alexandr A. Berlin, DSc, is Director of the N. N. Semenov Institute of Chemical Physics at the Russian Academy of Sciences, Moscow, Russia. He is a member of the Russian Academy of Sciences and many national and international associations. Dr. Berlin is world-renowned scientist in the field of chemical kinetics (combustion and flame), chemical physics (thermodynamics), chemistry and physics of oligomers, polymers, and composites and nanocomposites. He is the contributor of 100 books and volumes and 1000 original papers and reviews.

Viktor F. Kablov, DSc

Viktor F. Kablov, DSc, was appointed Director of Volzhsky Polytechnical Institute (branch) of VSTU–VPI (branch) of VSTU in 2000, and in 2002, he was elected Head of the Department of Polymer Chemical Technology and Industrial Ecology at the Institute. Professor Kablov has organized new training courses in modeling, computer-assisted methods and information systems in polymer engineering, engineering creativity methods, polymer chemistry and physics, and biotechnology. In 2010, he opened a Master's degree program in elastomer processing technology. He has also authored over 150 inventions, more than 300 research publications, 6 textbooks and 3 monographs.

Prof. Kablov's area of research relates to developing a scientific basis for obtaining elastomer materials operating in extreme conditions (heat-, fire-, and corrosion-resistant materials, antifriction composite materials); developing nano- and microheterogenic processes; modifying and operational additives to improve adhesive; thermal oxidation; and processing properties of polymer materials, as well as increasing the fire resistance of materials; developing materials for medical applications and fundamentally new hybrid polymers based on biopolymers and synthetic polymers; obtaining high selectivity sorbents based on template synthesis; developing waste bio recycling methods, as well as research in other areas of technology.

Andrey Pimerzin, DSc

Andrey Pimerzin, DSc, was appointed Vice Rector of the Samara State Technical University, Samara, Russia, in 2007. He was also elected as Head of the Department of Chemical Technology Oil Gas Refining at the same university in 2001. In 2009, Professor Pimerzin was invited as a researcher at the Thermodynamics

Research Center NIST in the USA, and in 2011, he was one of the organizers of the international conference RCCT-2011. Under Andrey Pimerzin's supervision, eight PhD and one Doctor of Science theses have been defended. He is the author of more than 250 science publications, including 11 textbooks and 9 patents. His research interests include chemical and statistical thermodynamics of organic compounds, thermochemistry, kinetics, heterogeneous catalysis, and refining technology.

Simon S. Zlotsky, PhD

Professor Simon Solomonovich Zlotsky received his BS in chemistry from Chemistry and Technological Department of Ufa Petroleum Institute in 1968. From 1970 to 1973 he studied and gained his PhD from the Moscow Institute of the Petrochemical and Gas Industry. Dr. Zlotsky worked as a research fellow at the Ufa State Petroleum Technological University (1973–77) and researched his doctoral thesis on chemistry of cyclic acetals. From 1982 to 2010 he was a Professor in the Department of General Chemistry in the Ufa State Petroleum Technological University, and he has headed the department since 2010.

REVIEWERS AND ADVISORY BOARD MEMBERS

Gennady E. Zaikov, DSc

Gennady E. Zaikov, DSc, is Head of the Polymer Division at the N. M. Emanuel Institute of Biochemical Physics, Russian Academy of Sciences, Moscow, Russia, and Professor at Moscow State Academy of Fine Chemical Technology, Russia, as well as Professor at Kazan National Research Technological University, Kazan, Russia. He is also a prolific author, researcher, and lecturer. He has received several awards for his work, including the Russian Federation Scholarship for Outstanding Scientists. He has been a member of many professional organizations and on the editorial boards of many international science journals.

A. K. Haghi, PhD

A. K. Haghi, PhD, holds a BSc in urban and environmental engineering from University of North Carolina (USA); a MSc in mechanical engineering from North Carolina A&T State University (USA); a DEA in applied mechanics, acoustics and materials from Université de Technologie de Compiègne (France); and a PhD in engineering sciences from Université de Franche-Comté (France). He is the author and editor of 65 books as well as 1000 published papers in various journals and conference proceedings. Dr. Haghi has received several grants, consulted for a number of major corporations, and is a frequent speaker to national and international audiences. Since 1983, he served as a professor at several universities. He is currently Editor-in-Chief of the *International Journal of Chemoinformatics and Chemical Engineering* and *Polymers Research Journal* and on the editorial boards of many international journals. He is also a member of the Canadian Research and Development Center of Sciences and Cultures (CRDCSC), Montreal, Quebec, Canada.

CONTENTS

<i>List of Contributors</i>	<i>xi</i>
<i>List of Abbreviations</i>	<i>xv</i>
<i>Preface</i>	<i>xvii</i>
1. RAFT-Polymerization of Styrene—Kinetics and Mechanism	1
Nikolai V. Ulitin, Aleksey V. Oparkin, Rustam Ya. Deberdeev, Evgenii B. Shirokih, and Gennady E. Zaikov	
2. A Detailed Review on Pore Structure Analysis of Electrospun Porous Membranes	29
Bentolhoda Hadavi Moghadam, Vahid Mottaghitalab, Mahdi Hasanzadeh, and Akbar Khodaparast Haghi	
3. Experimental Techniques for Application of Recycled Polymers in Construction Industries.....	51
O. Emamgholipour and A. K. Haghi	
4. Nanocomposites Polyethylene/Organoclay on Suprasegmental Level	107
G. V. Kozlov, K. S. Dibirova, G. M. Magomedov, and G. E. Zaikov	
5. Quantum and Wave Characteristics of Spatial-Energy Interactions	115
G. A. Korablev, and G. E. Zaikov	
6. Key Elements on Nanopolymers—From Nanotubes to Nanofibers ...	129
A. K. Haghi and G. E. Zaikov	
7. Polyacetylene	251
V. A. Babkin, G. E. Zaikov, M. Hasanzadeh, and A. K. Haghi	
8. Features of Macromolecule Formation by RAFT-Polymerization of Styrene in the Presence of Trithiocarbonates	313
Nikolai V. Ulitin, Timur R. Deberdeev, Aleksey V. Oparkin, and Gennady E. Zaikov	

9. A Study on Physical Properties of Composites Based on Epoxy Resin	333
J. Aneli, O. Mukbaniani, E. Markarashvili, G. E. Zaikov, and E. Klodzinska	
10. Synthesis, Structural Properties, Development and Applications of Metal-Organic Frameworks in Textile	343
M. Hasanzadeh and B. Hadavi Moghadam	
11. Thermal Behavior and Ionic Conductivity of the PEO/PAc and PEO/PAc Blends	359
Amirah Hashifudin, Sim Lai Har, Chan Chin Han, Hans Werner Kammer, and Siti Nor Hafiza Mohd Yusoff	
12. Correlation Between the Storage Time of the NRL and the Efficiency of PMMA Grafting to NR.....	371
Yoga Sugama Salim, Nur Aziemah Zainudin, Chin Han Chan, and Kai Weng Chan	
13. A Study on Composite Polymer Electrolyte	385
Tan Winie, N.H.A. Rosli, M.R. Ahmad, R.H.Y. Subban, and C.H. Chan	
14. A Study on Solid Polymer Electrolytes	399
Siti Nor Hafiza Mohd Yusoff, Sim Lai Har, Chan Chin Han, Amirah Hashifudin, and Hans–Werner Kammer	
15. Modification of PC-PHBH Blend Monolith.....	411
Yuanrong Xin and Hiroshi Uyama	
<i>Index.....</i>	<i>423</i>

LIST OF CONTRIBUTORS

M. R. Ahmad

Faculty of Applied Sciences, Universiti Teknologi MARA, 40450 Shah Alam, Malaysia

J. Aneli

R. Dvali Institute of Machine Mechanis, email: JimAneli@yahoo.com

V. A. Babkin

Volgograd State Architect-build University, Sebykov Department, Russia

C. H. Chan

Faculty of Applied Sciences, Universiti Teknologi MARA, 40450 Shah Alam, Malaysia

Rustam Ya. Deberdeev

Kazan National Research Technological University, 68 Karl Marx Street, 420015 Kazan, Republic of Tatarstan, Russian Federation, Fax: +7 (843) 231-41-56; E-mail: n.v.ulitin@mail.ru

K. S Dibirova

Dagestan State Pedagogical University, Makhachkala 367003, Yaragskii st., 57, Russian Federation

O. Emamgholipour

University of Guilan, Iran

Akbar Khodaparast Haghi

Department of Textile Engineering, University of Guilan, Rasht, Iran, E-mail: Haghi@Guilan.ac.ir

Sim Lai Har

Centre of Foundation Studies, Universiti Teknologi MARA, 42300 Puncak Alam, Selangor.Malaysia

Mahdi Hasanzadeh

Department of Textile Engineering, University of Guilan, Rasht, Iran, Email: m_hasanzadeh@aut.ac.ir, Tel.: +98-21-33516875; fax: +98-182-3228375

Amirah Hashifudin

Faculty of Applied Sciences, Universiti Teknologi MARA, 40450 Shah Alam, Selangor. Malaysia

E. Markarashvili

Javakhishvili Tbilisi State University Faculty of Exact and Natural Sciences, Department of Macromolecular Chemistry, I. Chavchavadze Ave., 3, Tbilisi 0128, Republic of Georgia

O. Mukbaniani

Javakhishvili Tbilisi State University Faculty of Exact and Natural Sciences, Department of Macromolecular Chemistry, I. Chavchavadze Ave., 3, Tbilisi 0128, Republic of Georgia, email: OmariMui@yahoo.com

Hans-Werner Kammer

University of Halle, Mansfelder Str. 28, D-01309 Dresden, Germany

E. Klodzinska

Institute for Engineering of Polymer Materials and Dyes, 55 M. Skłodowskiej-Curie str., 87-100 Torun, Poland, E-mail: S.Kubica@impib.pl

G. A. Korablev

¹Izhevsk State Agricultural Academy, Basic Research and Educational Center of Chemical Physics and Mesoscopy, Udmurt Scientific Center, Ural Division, Russian Academy of Science, Russia, Izhevsk, 426000, e-mail: korablev@udm.net, biakaa@mail.ru

G. V. Kozlov

Dagestan State Pedagogical University, Makhachkala 367003, Yaragskii st., 57, Russian Federation

G. M. Magomedov

Dagestan State Pedagogical University, Makhachkala 367003, Yaragskii st., 57, Russian Federation

Bentolhoda Hadavi Moghadam

Department of Textile Engineering, University of Guilan, Rasht, Iran, E-mail address: motaghitalab@guilan.ac.ir

Siti Nor Hafiza Mohd Yusoff

Faculty of Applied Sciences, Universiti Teknologi MARA, 40450 Shah Alam, Selangor. Malaysia

Vahid Mottaghitalab

Department of Textile Engineering, University of Guilan, Rasht, Iran, E-mail address: motaghitalab@guilan.ac.ir

V Nikolai

Kazan National Research Technological University, 68 Karl Marx Street, 420015 Kazan, Republic of Tatarstan, Russian Federation, Fax: +7 (843) 231-41-56, E-mail: n.v.ulitin@mail.ru

Aleksey V. Oparkin

Kazan National Research Technological University, 68 Karl Marx Street, 420015 Kazan, Republic of Tatarstan, Russian Federation Fax: +7 (843) 231-41-56; E-mail: n.v.ulitin@mail.ru

N. H. A. Rosli

Faculty of Applied Sciences, Universiti Teknologi MARA, 40450 Shah Alam, Malaysia

Yoga Sugama Salim

Department of Chemistry, University of Malaya, 50603 Kuala Lumpur, Malaysia

Evgenii B. Shirokih

Kazan National Research Technological University, 68 Karl Marx Street, 420015 Kazan, Republic of Tatarstan, Russian Federation, Fax: +7 (843) 231-41-56; E-mail: n.v.ulitin@mail.ru

R. H. Y. Subban

Faculty of Applied Sciences, Universiti Teknologi MARA, 40450 Shah Alam, Malaysia

Ulitin, Timur

Kazan National Research Technological University, 68 Karl Marx Street, 420015 Kazan, Republic of Tatarstan, Russian Federation, Fax: +7 (843) 231-41-56; E-mail: n.v.ulitin@mail.ru

Nikolai V. Ulitin

Kazan National Research Technological University, 68 Karl Marx Street, 420015 Kazan, Republic of Tatarstan, Russian Federation Fax: +7 (843) 231-41-56; E-mail: n.v.ulitin@mail.ru

Hiroshi Uyama

Department of Applied Chemistry, Graduate School of Engineering, Osaka University, Suita, Osaka 565-0871, Japan

Kai Weng Chan

Synthomer (M) Sdn. Bhd., 86000 Kluang, Malaysia

Tan Winie

Faculty of Applied Sciences, Universiti Teknologi MARA, 40450 Shah Alam, Malaysia*. Tel.: +60-3-55435738; fax: +60-3-55444562, E-mail address: tanwinie@salam.uitm.edu.my

Yuanrong Xin

Department of Applied Chemistry, Graduate School of Engineering, Osaka University, Suita, Osaka 565-0871, Japan

Siti Nor Hafiza Mohd Yusoff

Faculty of Applied Sciences, Universiti Teknologi MARA, 40450 Shah Alam, Selangor, Malaysia

Gennady E. Zaikov

N. M. Emanuel Institute of Biochemical Physics, Russian Academy of Sciences, 4 Kosygina st., Moscow, Russian Federation, 119334, Fax: +7(499)137-41-01; E-mail: chembio@sky.chph.ras.ru

Nur Aziemah Zainudin

Faculty of Applied Sciences, Universiti Teknologi MARA, 40500 Shah Alam, Malaysia
Chin Han Chan Faculty of Applied Sciences, Universiti Teknologi MARA, 40500 Shah Alam, Malaysia

LIST OF ABBREVIATIONS

AFM	atomic force microscopy
AIBN	azobisisobutyronitrile
ATR	attenuated total reflection
CPE	composite polymer electrolyte
CTMP	chemithermomechanical pulp
DBTC	dibenzyltritiocarbonate
DCAA	dichloroacetic acid
DPNR	deproteinized natural rubber
DSC	differential scanning calorimetry
ENR	epoxidized natural rubber
eV	electron-volts
IS	impedance spectroscopy
ITS	indirect tensile strength
LB	Lattice–Boltzmann
LLDPE	linear low density polyethylene
M&S	modeling and simulation
MDD	maximum dry density
MEMS	microelectromechanical systems
MMA	methyl methacrylate
MMD	molecular-mass distribution
MMD	molecular-mass distribution
MMT	montmorillonite
MNR	modified natural rubber
MOFs	metal-organic frameworks
MWNT	multi-walled nanotubes
NIPS	non-solvent induced phase separation
NR	natural rubber
MST	mechanical stability time
NRL	natural rubber latex
ODE's	ordinary differential equations
OSA	objective-based simulated Annealing
OWC	optimum water content
Pac	polyacrylate
PAN	polyacrylonitrile
PANi	polyaniline

PC	polycarbonate
PD	polydispersity
PEI	polyethylenimine
PEO	poly ethylene oxide
PPy	polypyrrole
PSM	post-synthetic modification
PSW	plastic solid waste
RAFT	reversible addition-fragmentation chain transfer
RDP	radial density profile
RH	rice husk ash
RVP	radial velocity profile
SBU _s	secondary building units
SC	clayey sand
SEM	scanning electron microscopy
SEP	spatial-energy parameter
SF	silica fume
SPE	solid polymer electrolyte
SRNF	resistant nanofiltration
SWNT	single-wall nanotubes
TEM	transmission electron microscopy
TEOS	tetraethoxysilane
TEPA	tetraethylenepentamine
THF	tetrahydrofuran
TMTD	thiuramdisulphide
TSC	total solid content

PREFACE

Polymers have played a significant part in the existence of humans. They have a role in every aspect of modern life, including health care, food, information technology, transportation, energy industries, etc. The speed of developments within the polymer sector is phenomenal and, at the same, time, crucial to meet demands of today's and future life. Specific applications for polymers range from using them in adhesives, coatings, painting, foams, and packaging to structural materials, composites, textiles, electronic and optical devices, biomaterials and many other uses in industries and daily life. Polymers are the basis of natural and synthetic materials. They are macromolecules, and in nature are the raw material for proteins and nucleic acids, which are essential for human bodies.

Cellulose, wool, natural rubber and synthetic rubber, plastics are well-known examples of natural and synthetic types. Natural and synthetic polymers play a massive role in everyday life, and a life without polymers really does not exist. A correct understanding of polymers did not exist until 1920s. In 1922, Staudinger published his idea that polymers were long chain molecules with normal chemical bonds holding them together. But for nearly 10 years this idea did not attract much attention. Around this period other researchers like Carothers who tended towards Staudinger's idea, discovered a type of synthetic material, which could be produced by its constituent monomers. Later on it was shown that as well as addition reaction, polymers could be prepared through condensation mechanism.

Previously it was believed that polymers could only be prepared through addition polymerization. The mechanism of the addition reaction was also unknown and hence there was no sound basis of proposing a structure for the polymers. This lack of information was the main controversy existed between Staudinger and his critics. The studies by Carothers and other researchers resulted in theorizing the condensation polymerization. It became clear that difunctional molecules like dihydric alcohols and dicarboxylic acids could react repeatedly with the release of water to form polyesters of high molecular mass. This mechanism became well understood and the structure of the resultant polyester could be specified with greater confidence.

In 1941/42 the world witnessed the infancy of polyethylene terephthalate or better known as the polyester. A decade later for the first time polyester/cotton blends introduced. In those days Terylene and Dacron (commercial names for polyester fibers) were miracle fibers but still overshadowed by nylon. Not many would have predicted those decades later, polyester would have become the

world's inexpensive, general purpose fibers as well as becoming a premium fiber for special functions in engineering textiles, fashion and many other technical end-uses. From the time nylon and polyester were first used there have been an amazing technological advances which have made them so cheap to manufacture and widely available.

These developments have made the polymers such as polyesters to contribute enormously in today's modern life. One of the most important applications is the furnishing sector (home, office, cars, aviation industry, etc.), which benefits hugely from the advances in technology. There are a number of requirements for a fabric to function in its chosen end use, for example, resistance to pilling and abrasion, as well as, dimensional stability. Polyester is now an important part of the upholstery fabrics. The shortcomings attributed to the fiber in its early days have mostly been overcome. Now it plays a significant part in improving the life span of a fabric, as well as its dimensional stability, which is due to its heat-setting properties.

About half century has passed since synthetic leather a composite material completely different from conventional ones came to the market. Synthetic leather was originally developed for end-uses such as, the upper of shoes. Gradually other uses like clothing steadily increased the production of synthetic leather and suede. Synthetic leathers and suede have a continuous ultrafine porous structure comprising a three-dimensional entangled nonwoven fabric and an elastic material principally made of polyurethane. Polymeric materials consisting of the synthetic leathers are polyamide and polyethylene terephthalate for the fiber and polyurethanes with various soft segments, such as aliphatic polyesters, polyethers and polycarbonates for the matrix.

The introduction of plastics is associated with the twentieth century but the first plastic material, celluloid, were made in 1865. During the 1970s, clothes of polyester became fashionable but by the 1980s synthetics lost the popularity in favor of natural materials. Although people were less enthusiastic about synthetic fabrics for everyday wear, Gore-Tex and other synthetics became popular for outdoors and workout clothing. At the same time as the use of synthetic materials in clothing declined, alternative uses were found. One great example is the use of polyester for making beverage bottles where it replaced glass with its shatterproof properties as a significant property.

In general it can be said that plastics enhance and even preserve life. Kevlar, for instance, when it is used in making canoes for recreation or when used to make a bulletproof vest. Polyester enhances life, when this highly nonreactive material is used to make replacement human blood vessels or even replacement skin for burn victims. With all the benefits attributed to plastics, they have their negative side. A genuine environmental problem exists due to the fact that the synthetic polymers do not break down easily compared with the natural polymers. Hence the need not only to develop biodegradable plastics, but also to work on more

effective means of recycling. A lot of research needed to study the methods of degradation and stabilization of polymers in order to design polymers according to the end-use.

Among the most important and versatile of the hundreds of commercial plastics is polyethylene. Polyethylene is used in a wide variety of applications because it can be produced in many different forms. The first type to be commercially exploited was called low-density polyethylene (LDPE). This polymer is characterized by a large degree of branching, forcing the molecules to pack together rather than loosely forming a low-density material. LDPE is soft and pliable and has applications ranging from plastic bags, containers, textiles, and electrical insulation, to coatings for packaging materials.

Another form of polyethylene differing from LDPE in structure is high-density polyethylene (HDPE). HDPE demonstrates little or no branching, resulting in the molecules to be tightly packed. HDPE is much more rigid than LDPE and is used in applications where rigidity is important. Major uses of HDPE are plastic tubing, bottles, and bottle caps. Other variations of polyethylene include high and ultra-high molecular mass ones. These types are used in applications where extremely tough and resilient materials are needed.

Natural polymers unlike the synthetic ones do possess very complex structure. Natural polymers such as cellulose, wool, and natural rubber are used in many products in large proportions. Cellulose derivatives are one of the most versatile groups of regenerated materials with various fields of application. Cellulose is found in nature in all forms of plant life, particularly in wood and cotton. The purest form of cellulose is obtained from the seed hairs of the cotton plant, which contain up to 95% cellulose. The first cellulose derivatives came to stage around 1845 when the nitration of starch and paper led to discovery of cellulose nitrate. In 1865 for the first time a moldable thermoplastic made of cellulose nitrate and castor oil.

In 1865 the first acetylation of cellulose was carried out but the first acetylation process for use in industry was announced in 1894. In 1905 an acetylation process was introduced which yielded a cellulose acetate soluble in the cheap solvent, acetone. It was during the First World War when cellulose acetate dope found importance for weather proofing and stiffening the fabric of aircraft wings. There was a large surplus production capacity after the war, which led to civilian end uses such as the production of cellulose acetate fibers by 1920's. Cellulose acetate became the main thermoplastic molding material when the first modern injection molding machines were designed. Among the cellulose derivatives, cellulose acetates are produced in the largest volume. Cellulose acetate can be made into fibers, transparent films and the less substituted derivatives are true thermoplastics. Cellulose acetates are moldable and can be fabricated by the conventional processes. They have toughness, good appearance, capable of many color variations including white transparency.

New applications are being developed for polymers at a very fast rate all over the world at various research centers. Examples of these include electro active polymers, nanoproducts, robotics, etc. Electro active polymers are special types of materials, which can be used for example as artificial muscles and facial parts of robots or even in nanorobots. These polymers change their shape when activated by electricity or even by chemicals. They are lightweight but can bear a large force, which is very useful when being utilized for artificial muscles. Electro active polymers together with nanotubes can produce very strong actuators. Currently research works are carried out to combine various types of electro active polymers with carbon nanotubes to make the optimal actuator. Carbon nanotubes are very strong, elastic, and conduct electricity. When they are used as an actuator, in combination with an electro active polymer the contractions of the artificial muscle can be controlled by electricity. Already works are under way to use electro active polymers in space. Various space agencies are investigating the possibility of using these polymers in space. This technology has a lot to offer for the future, and with the ever-increasing work on nanotechnology, electro active materials will play very important part in modern life.

— **Alexandr A. Berlin, DSc, Viktor F. Kablov, DSc,
Andrey A. Pimerzin, DSc, and Simon S. Zlotsky, PhD**

CHAPTER 1

RAFT-POLYMERIZATION OF STYRENE—KINETICS AND MECHANISM

NIKOLAI V. ULITIN, ALEKSEY V. OPARKIN,
RUSTAM YA. DEBERDEEV, EVGENII B. SHIROKIH,
and GENNADY E. ZAIKOV

CONTENTS

1.1	Introduction.....	2
1.2	Experimental Part	2
1.2.1	Mathematical Modeling of Polymerization Process.....	3
1.2.2	Rate Constants	9
1.2.3	Model's Adequacy	18
1.2.4	Numerical approach.....	21
1.3	Conclusion	26
	Keywords.....	27
	References.....	27

1.1 INTRODUCTION

The kinetic modeling of styrene controlled radical polymerization, initiated by 2,2'-asobis(isobutirnitrite) and proceeding by a reversible chain transfer mechanism was carried out and accompanied by "addition-fragmentation" in the presence dibenzyltritiocarbonate. An inverse problem of determination of the unknown temperature dependences of single elementary reaction rate constants of kinetic scheme was solved. The adequacy of the model was revealed by comparison of theoretical and experimental values of polystyrene molecular-mass properties. The influence of process controlling factors on polystyrene molecular-mass properties was studied using the model

The controlled radical polymerization is one of the most developing synthesis methods of narrowly dispersed polymers nowadays [1–3]. Most considerations were given to researches on controlled radical polymerization, proceeding by a reversible chain transfer mechanism and accompanied by "addition-fragmentation" (RAFT – reversible addition-fragmentation chain transfer) [3]. It should be noted that for classical RAFT-polymerization (proceeding in the presence of sulphur-containing compounds, which formula is $Z-C(=S)-S-R'$, where Z – stabilizing group, R' – outgoing group), valuable progress was obtained in the field of synthesis of new controlling agents (RAFT-agents), as well as in the field of research of kinetics and mathematical modeling; and for RAFT-polymerization in symmetrical RAFT-agents' presence, particularly, tritiocarbonates of formula $R'-S-C(=S)-S-R'$, it came to naught in practice: kinetics was studied in extremely general form [4] and mathematical modeling of process hasn't been carried out at all. Thus, the aim of this research is the kinetic modeling of polystyrene controlled radical polymerization initiated by 2,2'-asobis(isobutirnitrite) (AIBN), proceeding by reversible chain transfer mechanism and accompanied by "addition-fragmentation" in the presence of dibenzyltritiocarbonate (DBTC), and also the research of influence of the controlling factors (temperature, initial concentrations of monomer, AIBN and DBTC) on molecular-mass properties of polymer.

1.2 EXPERIMENTAL PART

Prior using of styrene (Aldrich, 99%), it was purified of aldehydes and inhibitors at triple cleaning in a separatory funnel by 10%-th (mass) solution of NaOH (styrene to solution ratio is 1:1), then it was scoured by distilled water to neutral reaction and after that it was dehumidified over $CaCl_2$ and rectified in vacuo.

AIBN (Aldrich, 99%) was purified of methanol by re-crystallization.

DBTC was obtained by the method presented in research [4]. Masses of initial substances are the same as in Ref. [4]. Emission of DBTC was 81%. NMR ^{13}C (CCl_3D) δ , ppm: 41.37, 127.60, 128.52, 129.08, 134.75, and 222.35.

Examples of polymerization were obtained by dissolution of estimated quantity of AIBN and DBTC in monomer. Solutions were filled in tubes, 100 mm

long, and having internal diameter of 3 mm, and after degassing in the mode of “freezing-defrosting” to residual pressure 0.01-mmHg column, the tubes were unsoldered. Polymerization was carried out at 60°C.

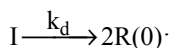
Research of polymerization’s kinetics was made with application of the calorimetric method on Calvet type differential automatic microcalorimeter DAK-1-1 in the mode of immediate record of heat emission rate in isothermal conditions at 60°C. Kinetic parameters of polymerization were calculated basing on the calorimetric data as in the work [5]. The value of polymerization enthalpy $\Delta H = -73.8 \text{ kJ} \times \text{mol}^{-1}$ [5] was applied in processing of the data in the calculations.

Molecular-mass properties of polymeric samples were determined by gel-penetrating chromatography in tetrahydrofuran at 35°C on chromatograph GPCV 2000 “Waters”. Dissection was performed on two successive banisters PLgel MIXED-C 300×7.5 mm, filled by stir gel with 5 μm vesicles. Elution rate – 0.1 $\text{mL} \times \text{min}^{-1}$. Chromatograms were processed in programme “Empower Pro” with use of calibration by polystyrene standards.

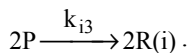
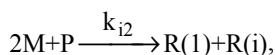
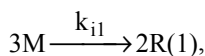
1.2.1 MATHEMATICAL MODELING OF POLYMERIZATION PROCESS

Kinetic scheme, introduced for description of styrene controlled radical polymerization process in the presence of trithiocarbonates, includes the following phases.

1. Real initiation

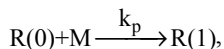


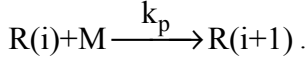
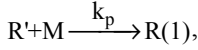
2. Thermal initiation [6]. It should be noted that polymer participation in thermal initiation reactions must reduce the influence thereof on molecular-mass distribution (MMD). However, since final mechanism of these reactions has not been ascertained in recording of balance differential equations for polymeric products so far, we will ignore this fact.



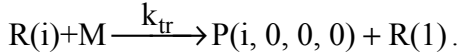
In these three reactions summary concentration of polymer is recorded as P.

3. Chain growth

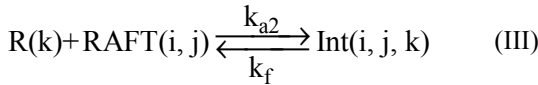
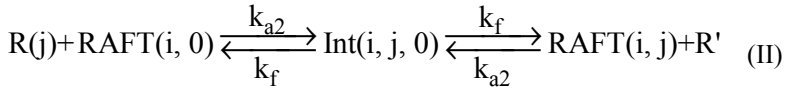
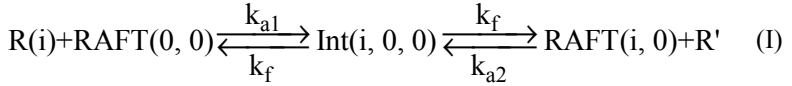




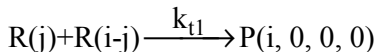
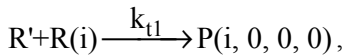
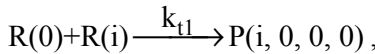
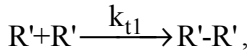
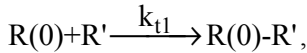
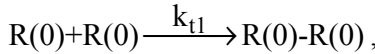
4. Chain transfer to monomer



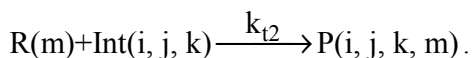
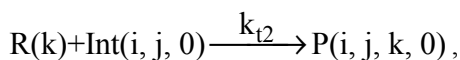
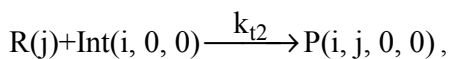
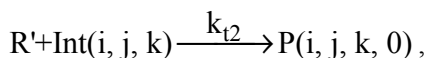
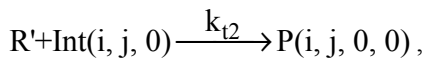
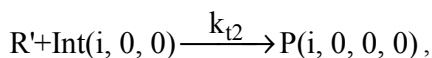
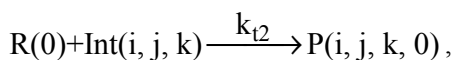
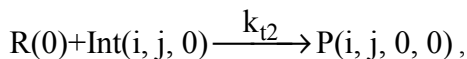
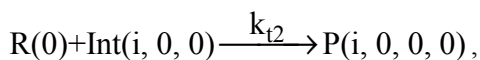
5. Reversible chain transfer [4]. As a broadly used assumption lately, we shall take that intermediates fragmentation rate constant doesn't depend on leaving radical's length [7].



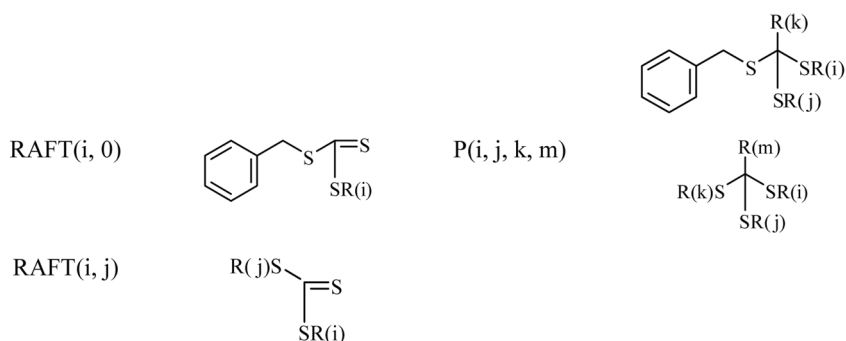
6. Chain termination [4]. For styrene's RAFT-polymerization in the trithio-carbonates presence, besides reactions of radicals quadratic termination



are character reactions of radicals and intermediates cross termination.



In the introduced kinetic scheme: I , $R(0)$, $R(i)$, R' , M , $RAFT(i, j)$, $Int(i, j, k)$, $P(i, j, k, m)$ – reaction system's components (refer to Table 1); i, j, k, m – a number of monomer links in the chain; k_d – a real rate constant of the initiation reaction; k_{i1} , k_{i2} , k_{i3} , – thermal rate constants of the initiation reaction's; k_p , k_{tr} , k_{a1} , k_{a2} , k_f , k_{t1} , k_{t2} are the values of chain growth, chain transfer to monomer, radicals addition to low-molecular RAFT-agent, radicals addition to macromolecular RAFT-agent, intermediates fragmentation, radicals quadratic termination and radicals and intermediates cross termination reaction rate constants, respectively.



The differential equations system describing this kinetic scheme, is as follows:

$$d[I] / dt = -k_d[I];$$

$$d[R(0)]/dt = 2fk_d[I] - [R(0)](k_p[M] + k_{t1}(2[R(0)] + [R'] + [R]) + k_{t2}(\sum_{i=1}^{\infty} [Int(i, 0, 0)] +$$

$$+ \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} [Int(i, j, 0)] + \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} \sum_{k=1}^{\infty} [Int(i, j, k)]));$$

$$d[M] / dt = -(k_p([R(0)] + [R'] + [R]) + k_{tr}[R])[M] - 3k_{i1}[M]^3 - 2k_{i2}[M]^2([M]_0 - [M]);$$

$$d[R']/dt = -k_p[R'][M] + 2k_f \sum_{i=1}^{\infty} [Int(i, 0, 0)] - k_{a2}[R'] \sum_{i=1}^{\infty} [RAFT(i, 0)] +$$

$$+ k_f \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} [Int(i, j, 0)] - k_{a2}[R'] \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} [RAFT(i, j)] - [R'](k_{t1}([R(0)] + 2[R'] + [R]) +$$

$$+ k_{i2}(\sum_{i=1}^{\infty} [Int(i, 0, 0)] + \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} [Int(i, j, 0)] + \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} \sum_{k=1}^{\infty} [Int(i, j, k)]));$$

$$d[RAFT(0,0)] / dt = -k_{a1}[RAFT(0,0)][R] + k_f \sum_{i=1}^{\infty} [Int(i, 0, 0)];$$

$$\begin{aligned}
& d[R(1)]/dt = 2k_{i1}[M]^3 + 2k_{i2}[M]^2([M]_0 - [M]) + 2k_{i3}([M]_0 - [M])^3 + k_p[M]([R(0)] + [R'] - \\
& \quad - [R(1)]) + k_{tr}[R(i)][M] - k_{a1}[R(1)][RAFT(0,0)] + k_f[Int(1, 0, 0)] - \\
& \quad - k_{a2}[R(1)] \sum_{i=1}^{\infty} [RAFT(i, 0)] + 2k_f[Int(1, 1, 0)] - k_{a2}[R(1)] \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} [RAFT(i, j)] + \\
& \quad + 3k_f[Int(1, 1, 1)] - [R(1)](k_{t1}([R(0)] + [R'] + [R]) + k_{t2}(\sum_{i=1}^{\infty} [Int(i, 0, 0)] + \\
& \quad + \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} [Int(i, j, 0)] + \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} \sum_{k=1}^{\infty} [Int(i, j, k)])), i = 2, \dots; \\
& d[R(i)]/dt = k_p[M]([R(i-1)] - [R(i)]) - k_{tr}[R(i)][M] - k_{a1}[R(i)][RAFT(0,0)] + k_f[Int(i, 0, 0)] - \\
& \quad - k_{a2}[R(i)] \sum_{i=1}^{\infty} [RAFT(i, 0)] + 2k_f[Int(i, j, 0)] - k_{a2}[R(i)] \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} [RAFT(i, j)] + 3k_f[Int(i, j, k)] - \\
& \quad - [R(i)](k_{t1}([R(0)] + [R'] + [R]) + k_{t2}(\sum_{i=1}^{\infty} [Int(i, 0, 0)] + \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} [Int(i, j, 0)] + \\
& \quad + \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} \sum_{k=1}^{\infty} [Int(i, j, k)])), i = 2, \dots; \\
& d[Int(i, 0, 0)]/dt = k_{a1}[RAFT(0,0)][R(i)] - 3k_f[Int(i, 0, 0)] + k_{a2}[R'] [RAFT(i, 0)] - \\
& \quad - k_{t2}[Int(i, 0, 0)]([R(0)] + [R'] + [R]); \\
& d[Int(i, j, 0)]/dt = k_{a2}[RAFT(i, 0)][R(j)] - 3k_f[Int(i, j, 0)] + k_{a2}[R'] [RAFT(i, j)] - \\
& \quad - k_{t2}[Int(i, j, 0)]([R(0)] + [R'] + [R]); \\
& d[Int(i, j, k)]/dt = k_{a2}[RAFT(i, j)][R(k)] - 3k_f[Int(i, j, k)] - k_{t2}[Int(i, j, k)]([R(0)] + [R'] + [R]);
\end{aligned}$$

$$d[\text{RAFT}(i, 0)]/dt = 2k_f[\text{Int}(i, 0, 0)] - k_{a2}[\text{R}'][\text{RAFT}(i, 0)] - k_{a2}[\text{RAFT}(i, 0)][\text{R}] + 2k_f[\text{Int}(i, j, 0)];$$

$$d[\text{RAFT}(i, j)]/dt = k_f[\text{Int}(i, j, 0)] - k_{a2}[\text{R}'][\text{RAFT}(i, j)] - k_{a2}[\text{RAFT}(i, j)][\text{R}] + 3k_f[\text{Int}(i, j, k)];$$

$$d[P(i, 0, 0, 0)]/dt = [R(i)](k_{t1}([R(0)] + [R']) + k_{tr}[M]) + \frac{k_{t1}}{2} \sum_{j=1}^{i-1} [R(j)][R(i-j)] + \\ + k_{t2}[\text{Int}(i, 0, 0)]([R(0)] + [R']);$$

$$d[P(i, j, 0, 0)]/dt = k_{t2}([\text{Int}(i, j, 0)]([R(0)] + [R']) + \sum_{i+j=2}^{\infty} [R(j)][\text{Int}(i, 0, 0)]);$$

$$d[P(i, j, k, 0)]/dt = k_{t2}([\text{Int}(i, j, k)]([R(0)] + [R']) + \sum_{i+j+k=3}^{\infty} [R(k)][\text{Int}(i, j, 0)]);$$

$$d[P(i, j, k, m)]/dt = k_{t2} \sum_{i+j+k+m=4}^{\infty} [R(m)][\text{Int}(i, j, k)].$$

where f – initiator's efficiency; $[R] = \sum_{i=1}^{\infty} [R(i)]$ – summary concentration of macro-radicals; t – time.

A method of generating functions was used for transition from this equation system to the equation system related to the unknown MMD moments [8].

Number-average molecular mass (M_n), polydispersity index (PD) and weight-average molecular mass (M_w) are linked to MMD moments by the following expressions:

$$M_n = (\sum \mu_1 / \sum \mu_0) M_{ST}, \quad PD = \sum \mu_2 \sum \mu_0 / (\sum \mu_1)^2, \quad M_w = PD \cdot M_n,$$

where $\sum \mu_0$, $\sum \mu_1$, $\sum \mu_2$ – sums of all zero, first and second MMD moments; $M_{ST} = 104$ g/mol – styrene's molecular mass.

1.2.2 RATE CONSTANTS

1.2.2.1 REAL AND THERMAL INITIATION

The efficiency of initiation and temperature dependence of polymerization real initiation reaction rate constant by AIBN initiator are determined basing on the data in this research, which have established a good reputation for mathematical modeling of leaving in mass styrene radical polymerization [6]:

$$f = 0.5, \quad k_d = 1.58 \cdot 10^{15} e^{-15501/T}, \quad s^{-1},$$

where T – temperature, K.

As it was established in the research, thermal initiation reactions' rates constants depend on the chain growth reactions rate constants, the radicals' quadratic termination and the monomer initial concentration:

$$\begin{aligned}
 k_{i1} &= 1.95 \cdot 10^{13} \frac{k_{t1}}{k_p^2 M_0^3} e^{-20293/T}, \text{ L}^2 \cdot \text{mol}^{-2} \cdot \text{s}^{-1}; \\
 k_{i2} &= 4.30 \cdot 10^{17} \frac{k_{t1}}{k_p^2 M_0^3} e^{-23878/T}, \text{ L}^2 \cdot \text{mol}^{-2} \cdot \text{s}^{-1}; \\
 k_{i3} &= 1.02 \cdot 10^8 \frac{k_{t1}}{k_p^2 M_0^2} e^{-14807/T}, \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}.
 \end{aligned} \tag{6}$$

1.2.2.2 CHAIN TRANSFER TO MONOMER REACTION'S RATE CONSTANT

On the basis of the data in research [6]:

$$k_{tr} = 2.31 \cdot 10^6 e^{-6376/T}, \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}.$$

1.2.2.3 RATE CONSTANTS FOR THE ADDITION OF RADICALS TO LOW-MOLECULAR AND MACROMOLECULAR RAFT-AGENTS

In research [9], it was shown by the example of dithiobenzoates at first that chain transfer to low- and macromolecular RAFT-agents of rate constants are functions of respective elementary constants. Let us demonstrate this for our process. For this record, the change of concentrations $[\text{Int}(i, 0, 0)]$, $[\text{Int}(i, j, 0)]$, $[\text{RAFT}(0,0)]$ and $[\text{RAFT}(i, 0)]$ in quasistationary approximation for the initial phase of polymerization is as follows:

$$d[\text{Int}(i, 0, 0)]/dt = k_{a1}[\text{RAFT}(0,0)][R] - 3k_f[\text{Int}(i, 0, 0)] \approx 0, \tag{1}$$

$$d[\text{Int}(i, j, 0)]/dt = k_{a2}[\text{RAFT}(i, 0)][R] - 3k_f[\text{Int}(i, j, 0)] \approx 0, \tag{2}$$

$$d[\text{RAFT}(0,0)] / dt = -k_{a1}[\text{RAFT}(0,0)][R] + k_f[\text{Int}(i, 0, 0)], \quad (3)$$

$$d[\text{RAFT}(i, 0)]/dt = 2k_f[\text{Int}(i, 0, 0)] - k_{a2}[\text{RAFT}(i, 0)][R] + 2k_f[\text{Int}(i, j, 0)]. \quad (4)$$

The Eq. (1) expresses the following concentration $[\text{Int}(i, 0, 0)]$:

$$[\text{Int}(i, 0, 0)] = \frac{k_{a1}}{3k_f}[\text{RAFT}(0,0)][R].$$

Substituting the expansion gives the following $[\text{Int}(i, 0, 0)]$ expression to Eq. (3):

$$d[\text{RAFT}(0,0)] / dt = -k_{a1}[\text{RAFT}(0,0)][R] + k_f \frac{k_{a1}}{3k_f}[\text{RAFT}(0,0)][R].$$

After transformation of the last equation, we have:

$$\frac{d[\text{RAFT}(0,0)]}{[\text{RAFT}(0,0)]} = -\frac{2}{3}k_{a1}[R]dt.$$

Solving this equation (initial conditions: $t = 0$, $[R] = [R]_0 = 0$, $[\text{RAFT}(0,0)] = [\text{RAFT}(0,0)]_0$), we obtain:

$$\ln \frac{[\text{RAFT}(0,0)]}{[\text{RAFT}(0,0)]_0} = -\frac{2}{3}k_{a1}[R]t. \quad (5)$$

To transfer from time t , being a part of Eq. (5), to conversion of monomer C_M , we put down a balance differential equation for monomer concentration, assuming that at the initial phase of polymerization, thermal initiation and chain transfer to monomer are not of importance:

$$d[M] / dt = -k_p[R][M]. \quad (6)$$

Transforming the Eq. (6) with its consequent solution at initial conditions $t = 0$, $[R] = [R]_0 = 0$, $[M] = [M]_0$:

$$d[M] / [M] = -k_p[R]dt,$$

$$\ln \frac{[M]}{[M]_0} = -k_p [R] t. \quad (7)$$

Link rate $[M]/[M]_0$ with monomer conversion (C_M) in an obvious form like this:

$$C_M = \frac{[M]_0 - [M]}{[M]_0} = 1 - \frac{[M]}{[M]_0},$$

$$\frac{[M]}{[M]_0} = 1 - C_M.$$

We substitute the last ratio to Eq. (7) and express time t :

$$t = \frac{-\ln(1 - C_M)}{k_p [R]}. \quad (8)$$

After substitution of the expression (8) by the Eq. (5), we obtain the next equation:

$$\ln \frac{[\text{RAFT}(0,0)]}{[\text{RAFT}(0,0)]_0} = \frac{2}{3} \frac{k_{a1}}{k_p} \ln(1 - C_M). \quad (9)$$

By analogy with introduced $[M]/[M]_0$ to monomer conversion, reduce ratio $[\text{RAFT}(0,0)] / [\text{RAFT}(0,0)]_0$ to conversion of low-molecular RAFT-agent – $C_{\text{RAFT}(0,0)}$. As a result, we obtain:

$$\frac{[\text{RAFT}(0,0)]}{[\text{RAFT}(0,0)]_0} = 1 - C_{\text{RAFT}(0,0)}. \quad (10)$$

Substitute the derived expression for $[\text{RAFT}(0,0)] / [\text{RAFT}(0,0)]_0$ from Eq. (10) to Eq. (9):

$$\ln(1 - C_{\text{RAFT}(0,0)}) = \frac{2}{3} \frac{k_{a1}}{k_p} \ln(1 - C_M). \quad (11)$$

In the research [9], the next dependence of chain transfer to low-molecular RAFT-agent constant C_{tr1} is obtained on the monomer and low-molecular RAFT-agent conversions:

$$C_{\text{tr1}} = \frac{\ln(1 - C_{\text{RAFT}(0,0)})}{\ln(1 - C_M)}. \quad (12)$$

Comparing Eqs. (12) and (11), we obtain dependence of chain transfer to low-molecular RAFT-agent constant C_{tr1} on the constant of radicals' addition to macromolecular RAFT-agent and chain growth reaction rate constant:

$$C_{\text{tr1}} = \frac{2}{3} \frac{k_{a1}}{k_p}. \quad (13)$$

From Eq. (13), we derive an expression for constant k_{a1} , which will be based on the following calculation:

$$k_{a1} = 1.5 C_{\text{tr1}} k_p, \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$$

As a numerical value for C_{tr1} , we assume value 53, derived in research [4] on the base of Eq. (12), at immediate experimental measurement of monomer and low-molecular RAFT-agent conversions. Since chain transfer reaction in RAFT-polymerization is usually characterized by low value of activation energy, compared to activation energy of chain growth, it is supposed that constant C_{tr1} doesn't depend or slightly depends on temperature. We will propose as an assumption that C_{tr1} doesn't depend on temperature [10].

By analogy with k_{a1} , we deduce equation for constant k_{a2} . From Eq. (2) we express such concentration $[\text{Int}(i, j, 0)]$:

$$[\text{Int}(i, j, 0)] = \frac{k_{a2}}{3k_f} [\text{RAFT}(i, 0)][R].$$

Substitute expressions, derived for $[\text{Int}(i, 0, 0)]$ and $[\text{Int}(i, j, 0)]$ in Eq. (4):

$$d[\text{RAFT}(i, 0)]/dt = \frac{2}{3} k_{a1} [\text{RAFT}(0,0)][R] - \frac{1}{3} k_{a2} [\text{RAFT}(i, 0)][R]. \quad (14)$$

Since in the end it was found that constant of chain transfer to low-molecular RAFT-agent C_{tr1} is equal to divided to constant k_p coefficient before expression $[RAFT(0,0)][R]$ in the balance differential equation for $[RAFT(0,0)]$, from Eq. (14) for constant of chain transfer to macromolecular RAFT-agent, we obtain the next expression:

$$C_{tr2} = \frac{1}{3} \frac{k_{a2}}{k_p}.$$

From the last equation we obtain an expression for constant k_{a2} , which based on the following calculation:

$$k_{a2} = 3C_{tr2}k_p, \text{ L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}. \quad (15)$$

In research [4] on the base of styrene and DBTK, macromolecular RAFT-agent was synthesized, thereafter with a view to experimentally determine constant C_{tr2} , polymerization of styrene was performed with the use of the latter. In the course of experiment, it may be supposed that constant C_{tr2} depends on monomer and macromolecular RAFT-agent conversions by analogy with Eq. (12). As a result directly from the experimentally measured monomer and macromolecular RAFT-agent conversions, value C_{tr2} was derived, equal to 1,000. On the ground of the same considerations as for that of C_{tr1} , we assume independence of constant C_{tr2} on temperature.

1.2.2.4 RATE CONSTANTS OF INTERMEDIATES FRAGMENTATION, TERMINATION BETWEEN RADICALS AND TERMINATION BETWEEN RADICALS AND INTERMEDIATES

In research [4] it was shown, that RAFT-polymerization rate is determined by this equation:

$$(W_0 / W)^2 = 1 + \frac{k_{t2}}{k_{t1}} K [RAFT(0,0)]_0 + \frac{k_{t3}}{k_{t1}} K^2 [RAFT(0,0)]_0^2,$$

where W_0 and W – polymerization rate in the absence and presence of RAFT-agent, respectively, s^{-1} ; K – constant of equilibrium (III), $L\cdot\text{mol}^{-1}$; k_{t3} – constant of termination between two intermediates reaction rate, $L\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$ [11].

For initiated AIBN styrene polymerization in DBTC's presence at 80°C, it was shown that intermediates quadratic termination wouldn't be implemented and RAFT-polymerization rate was determined by equation [4]:

$$(W_0 / W)^2 = 1 + 8[\text{RAFT}(0,0)]_0.$$

Since $\frac{k_{t2}}{k_{t1}} \approx 1$, then at 80°C $K = 8 \text{ L} \cdot \text{mol}^{-1}$ [4]. In order to find dependence of constant K on temperature, we made research of polymerization kinetics at 60°C. It was found, (Fig. 1), that the results of kinetic measurements well rectify in coordinates $(W_0 / W)^2 = f([\text{RAFT}(0,0)]_0)$. At 60°C, $K = 345 \text{ L} \cdot \text{mol}^{-1}$ was obtained. Finally dependence of equilibrium constant on temperature has been determined in the form of Vant-Goff's equation:

$$K = 4.85 \cdot 10^{-27} e^{22123/T}, \text{ L} \cdot \text{mol}^{-1}. \quad (16)$$

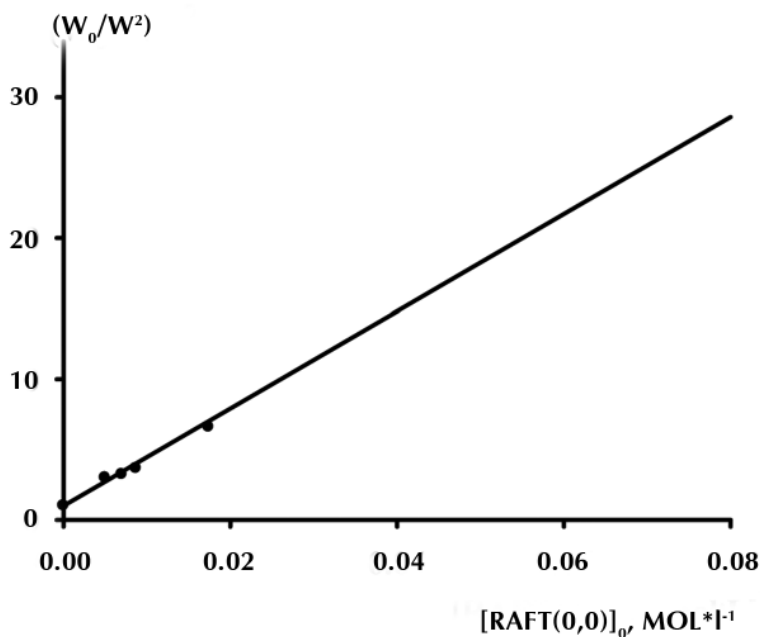


FIGURE 1 Dependence $(W_0 / W)^2$ on DBTC concentration at 60°C.

In compliance with the equilibrium (III), the constant is equal to

$$K = \frac{k_{a2}}{3k_f}, \text{ L} \cdot \text{mol}^{-1}.$$

Hence, reactions of intermediates fragmentation rate constant will be as such:

$$k_f = \frac{k_{a2}}{3K}, \text{ s}^{-1}. \quad (17)$$

The reactions of intermediates fragmentation rate constant was built into the model in the form of dependence (17) considering Eqs. (15) and (16).

As it has been noted above, ratio k_{t2} / k_{t1} equals approximately to one, therefore it will taken, that $k_{t2} \approx k_{t1}$ [4]. For description of gel-effect, dependence as a function of monomer conversion c_M and temperature T (K) [12] was applied:

$$k_{t2} \approx k_{t1} \approx 1.255 \cdot 10^9 e^{-844/T} e^{-2(A_1 C_M + A_2 C_M^2 + A_3 C_M^3)}, \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1},$$

where $A_1 = 2.57 - 5.05 \cdot 10^{-3} T$; $A_2 = 9.56 - 1.76 \cdot 10^{-2} T$; $A_3 = -3.03 + 7.85 \cdot 10^{-3} T$.

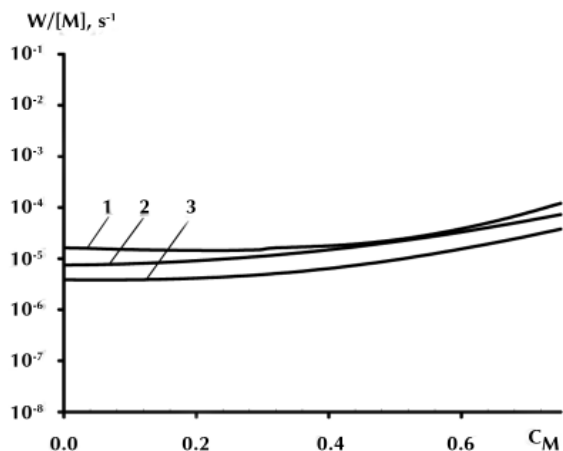
1.2.2.5 RATE CONSTANT FOR CHAIN GROWTH

The method of polymerization, being initiated by pulse laser radiation [13] is used for determination of rate constant for chain growth k_p lately. It is anticipated that such an estimation method is more correct, than the traditionally used revolving sector method [12]. We made our choice on temperature dependence of the rate constant for chain growth that was derived on the ground of method of polymerization, being initiated by pulse laser radiation:

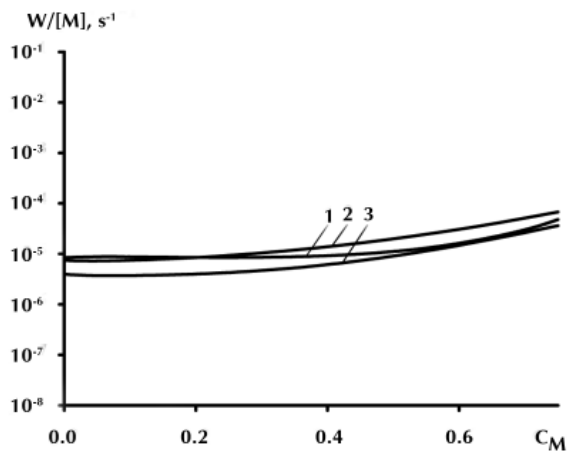
$$k_p = 4.27 \cdot 10^7 e^{-3910/T}, \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}, \quad (18)$$

since this dependence is more adequately describes the change of polymerization reduced rate with monomer conversion in the network of the developed mathematical model (Fig. 2), than temperature dependence, which is derived by revolving sector method [12]:

$$k_p = 1.057 \cdot 10^7 e^{-3667/T}, \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}. \quad (19)$$



(a)

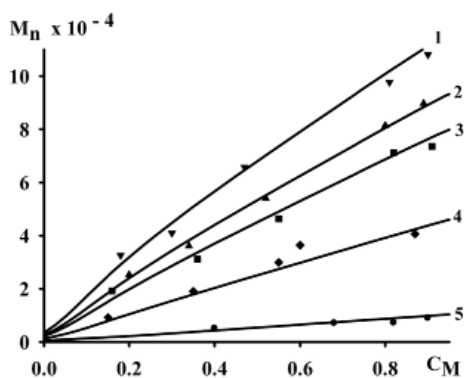


(b)

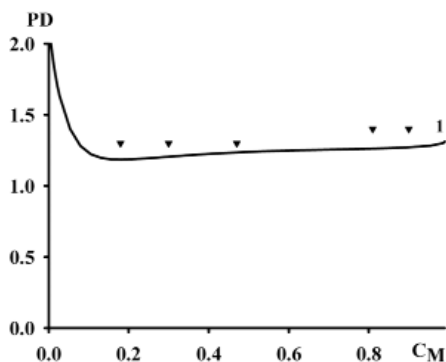
FIGURE 2 Dependence of initiated AIBN ($[I]_0=0.01 \text{ mol}\cdot\text{L}^{-1}$) styrene polymerization reduced rate on monomer conversion at 60°C (1 – experiment; 2 – estimation by introduced in this research mathematical model with temperature dependence of k_p (18); 3 – estimation by introduced in this research mathematical model with temperature dependence of k_p (19): $[\text{RAFT}(0,0)]_0 = 0 \text{ mol}\cdot\text{L}^{-1}$ (a), 0.007 (b).

1.2.3 MODEL'S ADEQUACY

The results of polystyrene molecular-mass properties calculations by the introduced mathematical model are presented in Figs. 3 and 4. Mathematical model of styrene RAFT-polymerization in the presence of trithiocarbonates, taking into account the radicals and intermediates cross termination, adequately describes the experimental data that prove the process mechanism, built in the model. The essential proof of the mechanism correctness is that in case of conceding the absence of radicals and intermediates cross termination – the experimental data wouldn't substantiate theoretical calculation by the mathematical model, introduced in this assumption (Fig. 5).

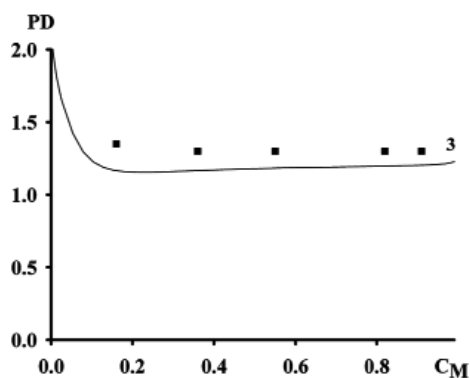


(a)

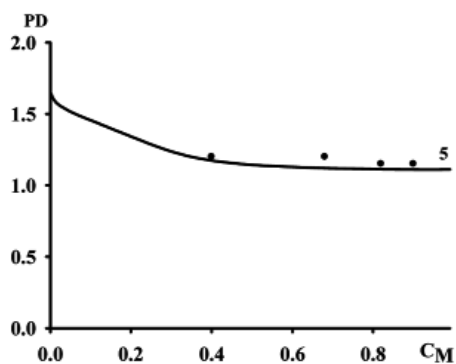


(b)

FIGURE 3 (Continued)

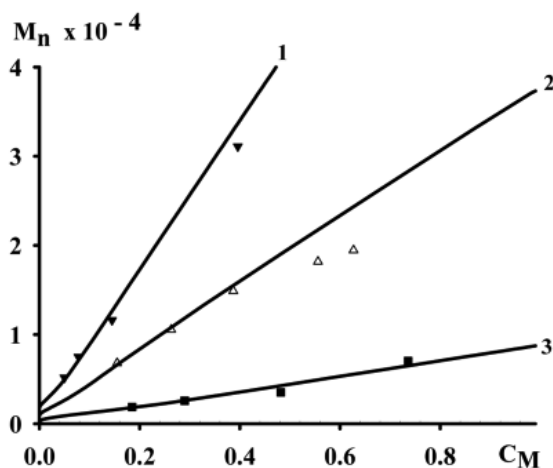


(c)

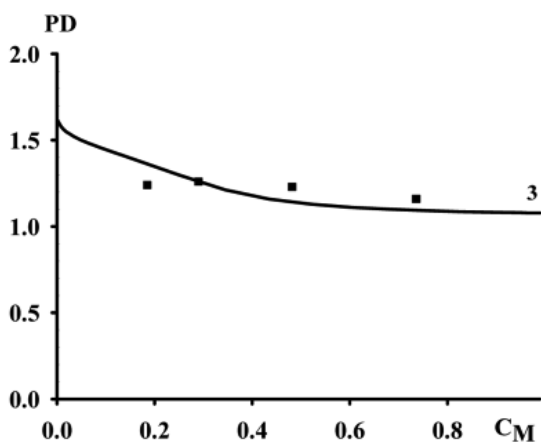


(d)

FIGURE 3 Dependence of number-average molecular mass (a) and polydispersity index (b)–(d) on monomer conversion for being initiated by AIBN ($[I]_0 = 0.01 \text{ mol}\cdot\text{L}^{-1}$) styrene bulk RAFT-polymerization at 60°C in the presence of DBTC (lines – estimation by model; points – experiment): $[\text{RAFT}(0,0)]_0 = 0.005 \text{ mol}\cdot\text{L}^{-1}$ (1), 0.007 (2), 0.0087 (3), 0.0174 (4), 0.087 (5).



(a)



(b)

FIGURE 4 Dependence of number-average molecular mass (a) and polydispersity index (b) on monomer conversion for being initiated by AIBN ($[I]_0 = 0.01 \text{ mol} \cdot \text{L}^{-1}$) styrene bulk RAFT-polymerization at 80°C in DBTC presence (lines – estimation by model; points – experiment): $[\text{RAFT}(0,0)]_0 = 0.01 \text{ mol} \cdot \text{L}^{-1}$ (1), 0.02 (2), 0.1 (3) [4].

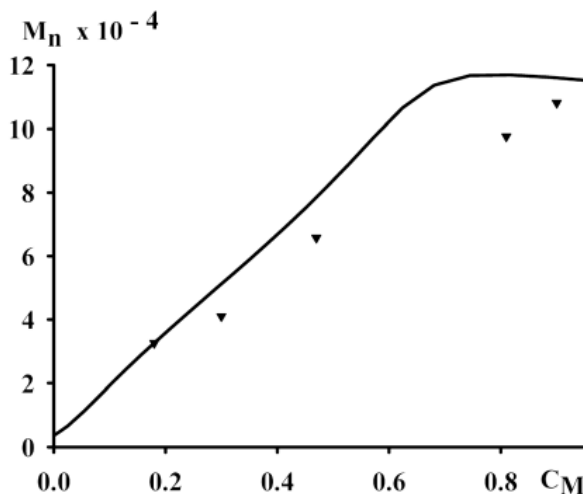


FIGURE 5 Dependence of number-average molecular mass on monomer conversion for initiated AIBN ($[I]_0 = 0.01 \text{ mol}\cdot\text{L}^{-1}$) styrene bulk RAFT-polymerization at 60°C in DBTC presence $[\text{RAFT}(0,0)]_0 = 0.005 \text{ mol}\cdot\text{L}^{-1}$ (lines – estimation by model assuming that radicals and intermediates cross termination are absent; points – experiment).

Due to adequacy of the model realization at numerical experiment it became possible to determine the influence of process controlling factors on polystyrene molecular-mass properties.

1.2.4 NUMERICAL APPROACH

Research of influence of the process controlling factors on molecular-mass properties of polystyrene, synthesized by RAFT-polymerization method in the presence of AIBN and DBTC, was made in the range of initial concentrations of: initiator – $0\text{--}0.1 \text{ mol}\cdot\text{L}^{-1}$, monomer – $4.35\text{--}8.7 \text{ mol}\cdot\text{L}^{-1}$, DBTC – $0.001\text{--}0.1 \text{ mol}\cdot\text{L}^{-1}$; and at temperatures – $60\text{--}120^\circ\text{C}$.

1.2.4.1 THE INFLUENCE OF AIBN INITIAL CONCENTRATION BY NUMERICAL APPROACH

It was set forth that generally in the same other conditions, with increase of AIBN initial concentration number-average, the molecular mass of polystyrene decreases (Fig. 6). At all used RAFT-agent initial concentrations, there is a linear or close to linear growth of number-average molecular mass of polystyrene with monomer conversion. This means that even the lowest RAFT-agent initial concentrations affect the process of radical polymerization. It should be noted that at high RAFT-agent initial concentrations (Fig. 7) the change of AIBN initial concentra-

tion practically doesn't have any influence on number-average molecular mass of polystyrene. But at increased temperatures (Fig. 8), in case of high AIBN initial concentration, it is comparable to high RAFT-agent initial concentration; polystyrene molecular mass would be slightly decreased due to thermal initiation.

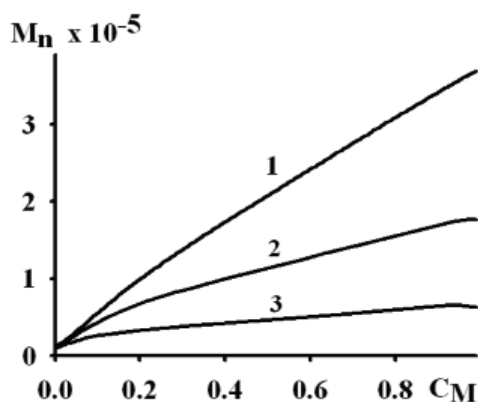


FIGURE 6 Dependence of number-average molecular mass M_n on monomer conversion C_M (60°C) $[M]_0 = 6.1 \text{ mol}\cdot\text{L}^{-1}$, $[\text{RAFT}(0, 0)]_0 = 0.001 \text{ mol}\cdot\text{L}^{-1}$, $[I]_0 = 0.001 \text{ mol}\cdot\text{L}^{-1}$ (1), 0.01 (2), 0.1 (3).

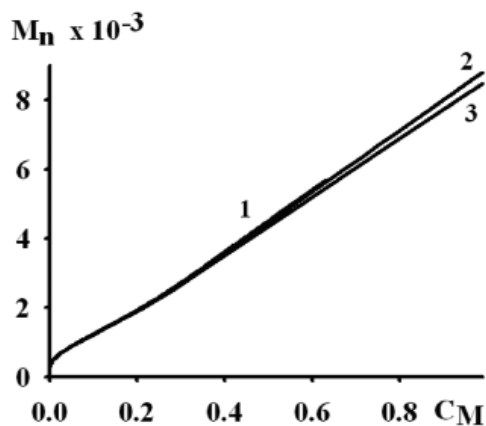


FIGURE 7 Dependence of number-average molecular mass M_n on monomer conversion C_M (60°C) $[M]_0 = 8.7 \text{ mol}\cdot\text{L}^{-1}$, $[\text{RAFT}(0, 0)]_0 = 0.1 \text{ mol}\cdot\text{L}^{-1}$, $[I]_0 = 0.001 \text{ mol}\cdot\text{L}^{-1}$ (1), 0.01 (2), 0.1 (3).

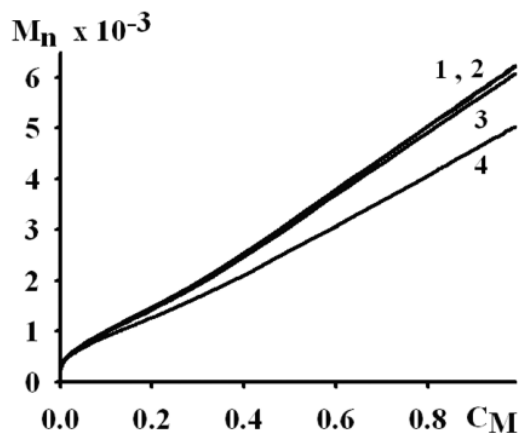


FIGURE 8 Dependence of number-average molecular mass M_n on monomer conversion C_M (120°C) $[M]_0 = 6.1 \text{ mol} \cdot \text{L}^{-1}$, $[\text{RAFT}(0, 0)]_0 = 0.1 \text{ mol} \cdot \text{L}^{-1}$, $[I]_0 = \text{mol} \cdot \text{L}^{-1}$ (1), 0.001 (2), 0.01 (3), 0.1 (4).

Since the main product of styrene RAFT-polymerization process, proceeding in the presence of trithiocarbonates, is a narrow-dispersed high-molecular RAFT-agent (marked in kinetic scheme as $\text{RAFT}(i, j)$), which is formed as a result of reversible chain transfer, and widely-dispersed (minimal polydispersity – 1.5) polymer, forming by the radicals quadratic termination, so common polydispersity index of synthesizing product is their ratio. In a broad sense, with increase of AIBN initial concentration, the part of widely-dispersed polymer, which is formed as a result of the radicals quadratic termination, increase in mixture, thereafter general polydispersity index of synthesizing product increases.

However, at high temperatures this regularity can be discontinued – at low RAFT-agent initial concentrations the increase of AIBN initial concentration leads to a decrease of polydispersity index (Fig. 9, curves 3 and 4). This can be related only thereto that at high temperatures thermal initiation and elementary reactions rate constants play an important role, depending on temperature, chain growth and radicals quadratic termination reaction rate constants, monomer initial concentration in a complicated way [6]. Such complicated dependence makes it difficult to analyze the influence of thermal initiation role in process kinetics, therefore the expected width of MMD of polymer, which is expected to be synthesized at high temperatures, can be estimated in every specific case in the frame of the developed theoretical regularities.

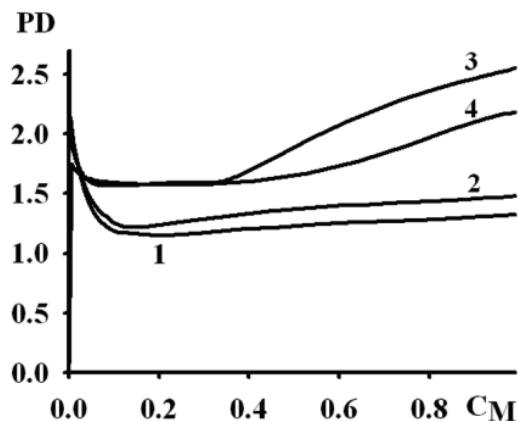


FIGURE 9 Dependence of polydispersity index PD on monomer conversion C_M (120°C) $[M]_0 = 8.7 \text{ mol}\cdot\text{L}^{-1}$, $[\text{RAFT}(0, 0)]_0 = 0.001 \text{ mol}\cdot\text{L}^{-1}$, $[I]_0 = 0 \text{ mol}\cdot\text{L}^{-1}$ (1), 0.001 (2), 0.01 (3), 0.1 (4).

Special attention shall be drawn to the fact that for practical objectives, realization of RAFT-polymerization process without an initiator is of great concern. In all cases at high temperatures as the result of styrene RAFT-polymerization implementation in the presence of RAFT-agent without AIBN, more high-molecular (Fig. 10) and more narrow-dispersed polymer (Fig. 9, curve 1) is built-up than in the presence of AIBN (Fig. 9, curves 2–4).

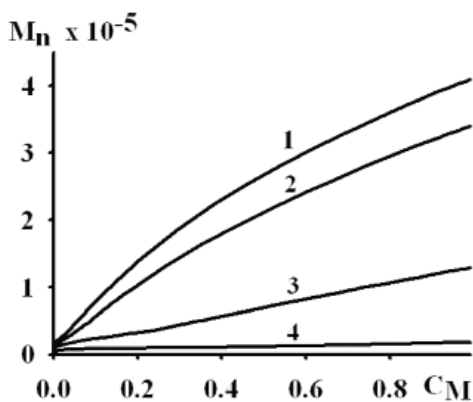


FIGURE 10 Dependence of number-average molecular mass M_n on monomer conversion C_M (120°C) $[M]_0 = 8.7 \text{ mol}\cdot\text{L}^{-1}$, $[\text{RAFT}(0, 0)]_0 = 0.001 \text{ mol}\cdot\text{L}^{-1}$, $[I]_0 = 0 \text{ mol}\cdot\text{L}^{-1}$ (1), 0.001 (2), 0.01 (3), 0.1 (4).