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Synthesis of polymers and modification of polymeric materials in electromagnetic fields

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Data on the effect of electromagnetic fields on polymerization processes are analyzed and integrated. The results of investigation of the response of polymeric systems including polymerization mixtures, polymer solutions, melts and gels to external electromagnetic fields are discussed. Mechanisms of changes in the kinetic parameters of cationic polymerization of certain monomers are considered. They are based on ideas of spatial redistribution of growing macroions and counterions depending on the degree of dissociation of the active sites, which can lead to an increase in the polymerization rate, stabilize it or slow down the process. It is shown that these mechanisms are universal for other ionic systems. Almost all types of polymerization processes are discussed to reveal potential fields of their application in additive manufacturing technologies. High demand for further studies of the effect of electromagnetic fields on polymeric objects is pointed out in connection with the need to solve problems in the design of novel materials and functional structures.
The bibliography includes 214 references.

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1. Introduction

Modern science of polymers and polymeric materials science as key branches of the science of chemistry have developed as allied sciences accumulating important information. It is Academician A.L.Buchachenko who contributed largely to the field in question and justly noted [1, 2] that 'in the 20th century chemistry became an exact science; many quantitative regularities and precise laws (including the 'electron periodicity' of the Mendeleev law) were established; a very high metrological level of determination of atomic, molecular, thermodynamic and kinetic constants, characterizing both substances and chemical processes, was attained'.

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Emphasize that improved metrological level of research is to a great extent related to the discovery of various physical effects [3] observed under the action of various fields of different intensity. An example is provided by P.Bridgman's 1914 studies † that led to the discovery of irreversible transition of yellow phosphorus to black phosphorus at a pressure of 12 kbar and a temperature of ~200 °C (the latter allotrope of phosphorus is significantly different from the former). At present, it is justly considered that P.Bridgman found a new physical method for creation of materials.[4] In the 1970–80s, researchers from the scientific school headed by Academician N.S.Enikolopov at the Institute of Chemical Physics, USSR Academy of Sciences, successfully utilized a Bridgman pressure apparatus to polymerize a number of organic compounds that do not form polymers under ambient conditions.[4] More recently, the results obtained were used to design highly efficient reactors that produce high pressure and shear similarly to the Bridgman pressure apparatus.

Creation of new sources of other physical fields has been accompanied by establishment of mechanisms of chemical reactions and determination of stability of various materials under the action of such fields. Polymerization processes and finished polymers are convenient objects for studying the consequences of the action of various types of factors since polymers possess the largest number of variable characteristics among all chemical substances.[5]

Emphasize that among physical methods of investigation of polymers, copolymers and many other materials, methods utilizing nondestructive electric, magnetic and electromagnetic fields are most widely used owing to great importance of information on the structure and properties of these materials. The methods in question first of all include NMR and EPR spectroscopies, as well as electrophysical, optoelectric and electrokinetic, magnetoelectric, tenso- and barometric and other methods.

At present, this multidisciplinary endeavour with a deep history is at the next step of development. Indeed, initial studies of the response to the action of electromagnetic fields, aimed at detecting certain effects, were accompanied by accumulation of experimental data, followed by development of relevant concepts and led to practical use of the effects of electromagnetic fields in scientific research, industry and technology. Nearly 30 monographs published in the last 15–20 years concern the effects of electromagnetic fields on chemical compounds; however, no review articles are available as yet.

The syntheses of polymers and copolymers begin with nucleation of active sites that can be accomplished in different ways. Most widely used is chemical initiation involving initiators of radical, cationic, anionic or ionic coordination polymerization.[6] Other methods are also developed, in particular, those utilizing electromagnetic fields, such as photopolymerization, electrochemical and radiation-induced polymerization, generation of active species under the action of high-frequency or ultrahigh-frequency electric field, and initiation of polymerization using low-temperature high-frequency plasma or low-frequency discharge.

† See 'Recent Works in the Field of High Pressures' by P.Bridgman [*Rev. Modern Physics*, **18** (1), 1 (1946)]

Electromagnetic field effects are mainly used for the following purposes:

— to generate active sites and to carry out subsequent polymerization, as well as to gain additional information on the nature of the active sites since these data cannot always be obtained by direct methods; and

— to synthesize new polymers and to extend methods for controlling their properties.

Some of the methods listed above are used not only in polymerization processes, but also in, *e.g.*, medicine for sterilization and for polymer recycling. The field of application of these methods extends continuously. It covers such areas of physical chemistry of polymers and polymer-based composite materials, as studies on relaxation processes in polymer solutions, gels and solids (electric polarization of ferroelectric polymers and polymeric materials with non-centrosymmetrical inclusions) and modification of composite materials containing ferro- and ferrimagnetic elements in magnetic fields.[7]

In almost all cases listed above the structure and properties of polymers and copolymers are modified using electric or magnetic and electromagnetic fields in a wide frequency (ν) range. Electromagnetic radiation is classified by frequencies into certain ranges (Table 1) and characterized by different equivalent energies since the oscillator energy is proportional to frequency. In particular, γ-radiation corresponds to the frequency range $\nu > 3 \times 10^{19}$ Hz and energies > 124 keV. For the UV range, the frequencies of 790 and 30 000 THz correspond to energies of 3.27 and 124 eV, respectively. Therefore, the lower the electromagnetic field frequencey the lower the energy supplied to the system under study provided the same irradiation time. Note that this is only a trend rather than a rule because the actual amount of absorbed energy depends on the type of the medium. We will not dwell on this situation and address the reader to references to corresponding Sections (see, in particular, a monograph [8]).

Polymer synthesis, or polymerization, is one of the most complicated areas in chemistry since it involves of many competing reactions including polymer chain propagation, chain termination or transfer, disproportionation, *etc.* Starting from different reaction compositions and polymerization conditions, one gets polymers with specified properties, the molecular mass, molecular mass distribution and structure being the most important. Besides, there has been considerable activity aimed at controlling these and other parameters using synthetic approaches and physical methods. The behaviour of polymeric materials and structures based on them under the action of external electric, mag-

Table 1. Electromagnetic waves.[8]

Range	ν /Hz	Photon energy /eV
Microwave and UHF	$10^9 - 3 \times 10^{11}$	$4 \times 10^{-7} - 10^{-3}$
Infrared	$3 \times 10^{11} - 3.9 \times 10^{14}$	$1.2 \times 10^{-3} - 1.6$
Visible	$3.9 \times 10^{14} - 7.7 \times 10^{14}$	1.6–3.2
Ultraviolet	$7.7 \times 10^{14} - 3 \times 10^{16}$	$3.2 - 1.2 \times 10^2$
X-ray	$3 \times 10^{16} - 3 \times 10^{19}$	$1.2 \times 10^2 - 1.2 \times 10^5$
γ-Radiation	$3 \times 10^{19} - 3 \times 10^{22}$	$1.2 \times 10^5 - 1.2 \times 10^8$

netic and electromagnetic fields is intimately related to their chemical composition and physical properties through a variety of parameters, first of all, the field magnitude — weak (or measuring), moderate, and strong, the frequency and temperature ranges and other external conditions. The response and possible irreversible changes in the properties of the systems under study, especially in moderate and strong fields, can occur both in the course of polymerization and fabrication of composite materials and during operation. On the other hand, polymeric materials can act as dielectrics, semiconductors or conductors in fields of certain strength. The electrophysical properties of polymers have found application in various fields. Of course, it is of great importance to distinguish between critical and non-critical external electromagnetic fields acting on polymeric materials, to determine how the properties of materials change and whether these changes can be used to modify the materials in order to attain next-level structural changes and corresponding properties.

This review mainly addresses the studies reported in the last 15–17 years; in some cases, for the completeness purposes we present the key results of earlier studies that are still relevant. As far as we know, no reviews that include an analysis of the entire spectrum of electromagnetic field actions on polymeric systems are available in scientific literature while the results obtained are scattered over different-type publications. We first of all analyze original studies and the results of R&D in the field of synthesis and modification of polymeric systems that, to one extent or another, involve application of d.c. or a.c. electric, magnetic as well as electromagnetic fields. We will dwell on studies of polymerization and the influence of electromagnetic field on polymeric systems in a wide frequency range. We determined and summarized key factors responsible for initiation of polymerization under the action of electromagnetic field and for the effects related to spatial redistribution and orientation of the component molecules in conventional polymerization systems and in finished polymers. Finally, we will consider the state of the art in and prospects for application of electrophysical methods and accumulated results.

2. Electric polarization of polymers and electromagnetic field effects

Polarization is the displacement of bound charges or orientation of dipole moments under the action of electric field. Polarization in polymers has been considered in detail in a monograph.[9] Additional information and examples can be found in the literature. However, there is a lack of comprehensive publications devoted to polarization and its influence on the polymerization kinetics in the Russian literature. In connection with specific features of polymeric state, mention should be made of certain general considerations as applied to the electrical properties of polymers.

Polarization of polymeric and other systems and their response to the electric field applied are most often studied using a parallel-plate capacitor with the substance under study sandwiched between electrodes separated by the distance d. Having applied a potential difference V across the plates, the electric field (F) between them is given by $F = V/d$.

The degree of polarization of a substance is determined by the relative dielectric constant. Application of an electric field causes redistribution of charges (electrons and protons) in the material, *viz*., positive charges attract to the negative electrode, while negative charges attract to the positive electrode. The effect of electric field applied to isotropic materials causes the appearance in each elementary volume of a small dipole moment aligned with the field. Polarization is defined as the vector characterizing the magnitude and direction of the electric moment induced by the external field in the material.

An analysis on the molecular or microscopic level should take account of molecular polarization that can be divided into electronic, atomic and orientation components.

Electron polarization. Under the action of external electric field electrons in atom are displaced relative to the positively charged nucleus. These displacements are small because the effect of external field is usually much weaker than the effect of atomic nucleus. Indeed, with a proton charge of 1.6×10^{-19} C and a typical atomic radius of 10^{-10} m the electric field strength at the electron site is 10^{11} V m^{-1}.

Atomic polarization. External electric field can lead to displacements of atomic nuclei in a molecule or crystal lattice. Heavy atomic nuclei are more inert than electrons; therefore, atomic polarization should occur at lower frequencies compared to electron polarization and it is indeed observed at frequencies corresponding to at most the IR range. The atomic polarization is typically one tenth of the electron polarization.

Orientation polarization. In an external field, molecules having nonzero intrinsic permanent dipole moments are aligned with the field and thus become polarized along the field direction. The dipole orientation rate depends strongly on intermolecular interactions. It is of great importance to take account of the fact that orientation of molecular dipoles in polymers can occur rather slowly and contribute largely to the overall polarization of materials in external field.

Polymers are divided into two large groups, namely, polar and nonpolar ones. The molar polarization of nonpolar substances, *e.g*., polyethylene, is almost constant in accordance with the Clausius–Mossotti relation. For polar polymers, two situations are possible, where (i) the polymer chain bearing side groups adopts a fixed rigid conformation or (ii) a flexible backbone bears freely rotating side groups. Both types of polymers are of considerable interest. In electronic industry, polymers are mainly used as insulators (materials with low dielectric constant) and integrated circuit substrates. Foaming of nonpolar polymers is one of the best methods for producing insulators. Polyimides are the most appropriate insulating materials for modern microelectronics.

The molar polarization of polymers with high dielectric constant decreases with increasing temperature. This property of polymers is used in studies of molecular motions by thermally stimulated depolarization technique.[10,11]

An analysis of recently published data on the properties of polymers revealed an important role of chemical design of polymer structures. Chemists with good reason replace a proportion of hydrogen atoms by fluorine ones. In particular, the polarizability of C–F bonds is lower than that of C–H bonds and, therefore, fluoropolymers have low dielectric constants and are characterized by low dielectric loss in a wide frequency range.

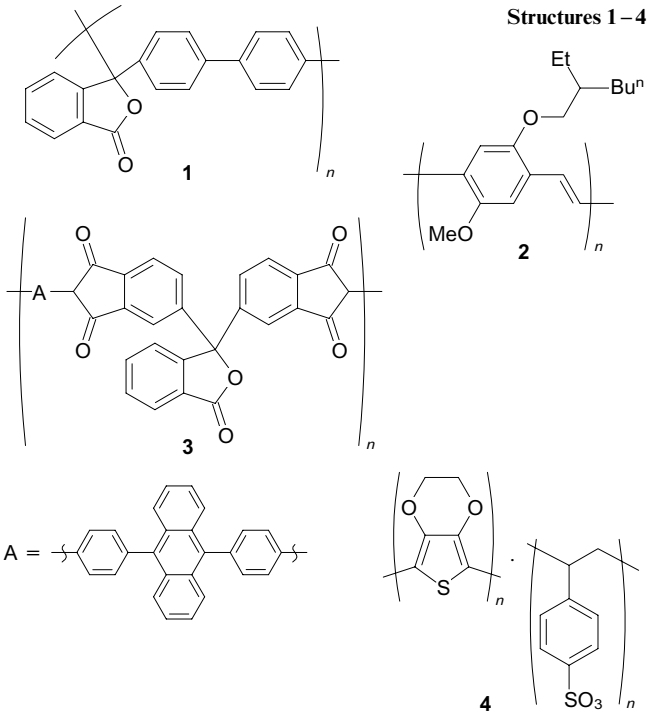
Polarization of polymers is used for the preparation of micro- and nanofilaments by electrospinning technique, which is utilized for, *e.g.*, the formation of mats using electroflocculation technology and for electrostatic separation of milled polymer wastes to prepare them for recycling (see below).

2.1. Switching polymer films to high-conductivity state revisited

Recently, there has been considerable research activity concerning the mechanism of switching polymer films to high-conductivity state under the action of external electric field. Interest in this effect is due to the development of nonvolatile memory devices based on polymer films.

Systematic studies on switching dielectric thin polymer films to high-conductivity state began in the 1980s. The event history can be found in the literature (see, *e.g.*, Refs 12 and 13). The switching effect was observed in various polymer films including those formed by polypropylene,[14] poly(diphenylene phthalide) (**1**),[12] poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene)] (**2**),[15,16] polyimide (**3**), poly(vinyl carbazole),[17] a complex of poly(3,4-ethylenedioxythiophene) and polystyrene sulfonic acid (**4**),[18] and poly(*o*-anthranilic acid-*co*-*o*-nitroaniline).[19]

Structures 1–4



To gain a better insight into physical processes accompanying switching of polymer films to the high-conductivity state, transport of charge carriers in poly(diphenylene phthalide) films was studied.[19,20] In particular, the dependence of the drift mobility of electrons and holes on the pressure applied to films of different thickness was determined and the character of current flow and the type of the main charge carriers in the pre-threshold region were investigated.

Taking poly(diphenylene phthalide) as an example, it was shown that the switching effect is related to the nature of the polymer rather than oxidation of the electrode or metallic filamentation originating from the metallic electrodes.[21] In the experiments with layered samples (so-called sandwich structures 'electrode/polymer/electrode') the electrodes were made of indium tin oxide (ITO) on glass plates. One plate was spin coated with a polymer film. The other plate with ITO electrodes was pressed to the surface of the polymer film. Usually, ITO is treated as degenerate semiconductor with sufficiently high intrinsic conductivity;[22] the switching effect in the ITO film or metallic filamentation are unknown. The observed switching in the polymer samples with the ITO electrodes confirms that switching in the experiments in question is due to electronic processes in the polymer film. Various mechanisms were proposed to explain switching of the polymer to the high-conductivity state (see a review [12] and original publications [16,23,24]).

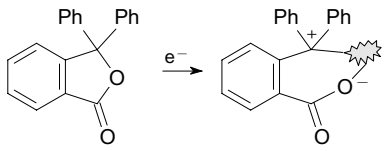
In the case of sandwich structuresá transition of the polymer to the high-conductivity state should be distinguished from transition of the entire sample.[16] The latter can be triggered by the change from one-carrier injection to double injection, which leads to efficient bimolecular recombination of charge carriers. Usually, injection of charge carriers from one electrode of the sample occurs more readily that from the other electrode. As the applied voltage or uniaxial-compression pressure increases, the height and width of the potential barrier to charge carriers at the electrodes decreases. This leads to charge carrier injection from the opposite electrode, the injection being tunnelling in character. The transition of the sample from insulating to the conducting state is called the surface effect, while the transition of the polymer *per se* to the conducting state is called the bulk effect. After the transition the sample spends some time in the conducting state. In the case of the surface effect this behaviour is due to the presence of a large number of charge carrier traps near the electrode/polymer interface. The bulk charge of the trapped charge carriers can change the injection properties of the contact, so the sample remains in the conducting state for some time.

In the case of the bulk effect the transition to the conducting state is accompanied by the formation of high-conductivity channels 10–50 nm in diameter, which penetrate the polymer film from one electrode to the other.[12] These channels can degrade if corresponding triggers are eliminated under the action of temperature or other factors. Often, the sample remains in the conducting state for a long time. The onset of the high-conductivity state was associated [25] with externally induced change of the sp^3- to sp^2-hybridization for a part of the backbone carbons followed by the formation of rather long π–π-conjugated regions. The propagation of the conducting pulse along the polymer chain is described by a soliton mechanism. However, this mechanism is inapplicable to many wide-gap polymers in which switching from the dielectric to the conducting state occurs under the action of external perturbation factors.[12]

In our opinion, an important role in the switching to the high-conductivity state can be played by a charge-carrying fragment of the polymer film, *e.g.*, a phthalide moiety containing an unstable C–O bond between the central (quaternary) carbon atom and oxygen atom in polymers **1** and **3**.[26] Calculations [27] predicted the existence of a stable configuration of molecular anions with a broken C–O bond, which is formed upon the interaction with free thermal electrons (Scheme 1).

Summing up, mention may be made that in spite of considerable research activity, opinions are different as to

Scheme 1



the mechanism of polymer switching to the high-conductivity state and the state of the art requires the development of new experimental methods to gain a better insight into the effects observed.

2.2. On superconductivity in polymers

Pioneering studies on the search for conditions for the synthesis of polymers with superconducting properties and transition of entire polymer samples or their parts to the superconducting state date back to the 1980s.[28] The case in point is to answer the question whether an UV-irradiated polymer can go to the local or bulk superconducting state. At that time, few authors paid attention to the fact that measurements were performed using conventional metallic electrodes and the superconducting state was detected using instrumental zero. The problem was debated for long. We believe that a comprehensive answer to the question mentioned above is presented in a thesis[29] whose author generalized the results obtained by researchers from the Ioffe Institute, Russian Academy of Sciences, and by their colleagues from other institutes. That study, as well as relevant publications and communications presented at specialist conferences made it clear that high metallic conductivity in metal/polymer/metal structures can be achieved in the preconduction region of electric field strength at certain polymer film thickness values typical of each material and the onset of superconducting current in superconductor – polymer – superconductor (S – P – S) structures is feasible.

The critical thicknesses of polymer films sandwiched between electrodes are presented in Table 2.[29] If the film thickness is less than the critical value, the film is in the conducting state. The superconducting transition temperatures (T_c) of the polymer films correlate with T_c of the electrode materials. For instance, an S – P – S structure with a polyamidine film as P and tin electrodes (T_c = 3.72 K) has $T_c = \sim 3$ K, while a related system with neodymium electrodes (T_c = 9.2 K) has T_c below 3 K. It was shown[30] that superconducting current flowing across the polymer in the S – P – S structure is due to resonant tunnelling of Cooper pairs between the highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO, respectively) of adjacent macromolecules and that the critical current density and polymer film thickness depend on the coherence length of a Cooper pair in the superconductor brought in contact with the polymer.

Table 2. Critical thickness (d) of polymer films corresponding to transition of polymers to conducting state.[29]

Polymer	d/μm
Polyetherquinoline	⩽0.2
Polyamide	0.7
Poly(siloxane imide) PSI-2	0.8
Poly(siloxane imide) PSI-10	1.0
Polyamidine	1.0
Poly(siloxane imide) PSI-20	1.3
Polyazomethine	1.5

The results obtained are of considerable importance for both basis research and practice since the S – P – S structures exhibit the Josephson effect, can be used as sensors for weak magnetic field, in production of voltage maintenance standard and act as sources of microwave radiation.

2.3. Effects in static electric and magnetic fields

From the standpoint of physical chemistry of polymers the most important effects observed under the action of electromagnetic fields are as follows:[31]

— desorption of impurities from the surface of metals and other solids used as fillers for polymers; this is crucial to additive manufacturing technologies in order to improve adhesion to the filler and to obtain monolithic products/items;

— deformation of solid dielectrics (electrostriction);

— breakup of liquid or melt droplets (electrospinning).

One should take into account changes in the following parameters under the action of electromagnetic fields:

— dielectric constant of polar polymers or polymeric ferroelectrics;

— light reflection from transparent film (electroreflectance);

— refractive index of crystalline polymers (Pockels-1 effect);

— light polarization in polymer crystals (Pockels-2 effect);

— transparency of nematic liquid crystals (Fréedericksz transition);

— transparency of Kerr electrooptical cells (Kerr effect);

— transparency of electrochromic film (electrochromic effect);

— adhesive force between semiconductors (dielectrics) and substrates (electroadhesive effect);

— shape of a liquid metal or polymer melt droplet;

— frequency of light scattered by suspensions;

— magnetization of magnets (magnetoelectric effect);

— adhesive contact break force owing to Coulomb interaction between charges;

— motion of charged particles (electrophoresis);

— polarization plane rotation of light propagating through crystals (linear electrogyration);

— rotation angle of conductors in electrically conducting liquids.

The most important effects observed in static electric fields are as follows:

— strong decrease in scattering of light reflected by cholesteric liquid crystals;

— decrease in resistivity of dielectrics (Poole – Frenkel effect);

— onset of a momentum of force acting on elongated dielectric pieces;

— onset of potential difference in anisotropic semiconductors (Sasaki – Shibuya effect);

— onset of attractive force between solid conductors and dielectrics (Coulomb force);

— increase in viscosity of liquid dielectrics (viscoelectric effect), in viscosity of electrorheological liquid, in magnetic permeability of magnetic semiconductor exposed to light (photomagnetic effect), in resistance of semiconductor nanostructures, in heat transfer from solids in gases, and in resistivity of semiconductors (violation of Ohm law);

— decrease in resistivity of crystals (Esaki effect);

— increase in adsorption of the surface of adsorbents (field adsorption), enhancement of luminescent afterglow of phosphors (Gudden-Pohl effect);

— acceleration and retardation of ionic polymerization;

— appearance of polarization which ensures fabrication of materials for second harmonic generation; static fields are necessary for electrostatic levitation, dielectrophoresis and other electrokinetic phenomena.

Magnetic field accelerates radical polymerization and causes the molecular mass of polymers to increase. Strong and, especially, nonuniform, magnetic fields $>10-15$ T allow one to observe magnetic levitation; the polymerization rate and molecular mass of polymers are also changd under these conditions. Magnetic field applied to liquid-crystalline polymers causes orientation of domains and formation of anisotropic structures in polymers containing magnetic particles. Polymer blends containing magnetic particles are used for fabrication of nanofilaments by magnetospinning technique.

2.4. Effects in electromagnetic fields

A feature of the microwave field (1–30 GHz) consists in heating reaction mixtures with high dielectric loss in this frequency range through dipole orientation polarization; this is typical of materials containing polar liquids. In most cases, there is a lack of non-thermal contribution to the observed changes.

It is noteworthy that at present, a conceptual framework for additive manufacturing technologies is developed. In this connection, selection of effects emerging under the action of external fields is topical. We believe that in the future many electromagnetic field effects will find wide application in additive manufacturing technologies on the nano-, micro- and macroscopic level.[31, 32]

3. Electrochemical polymerization

Electrochemical polymerization is a noncatalytic method for the synthesis of polymers. In this respect it is similar to glow discharge polymerization, photopolymerization and radiation-induced polymerization. The method involves generation of active sites (ions, radical ions, *etc.*) during the electrochemical oxidation or reduction of molecules of any component (*e.g.*, a monomer or an additive) instead of conventional chemical initiation and results in the formation of reactive compounds with unsaturated valence. Electrochemical polymerization is of limited use for the synthesis of saturated insulating polymers since an insulating layer is rapidly formed at the electrode and thus precludes the formation of active sites. As a consequence, the process ceases in a relatively short time. This does not occur in the synthesis of high-conducting polyconjugated polymers, which makes it possible to fabricate rather thick films. Currently, *e.g.*, polyaniline is synthesized in the presence of sulfonic acids. The process involves the formation of monomer radicals that add to the growing chain or form oligomers to be oxidized and connected to one another to give longer chains. Often, monomers contain several reactive bonds, so products can have branched or cross-linked rather that linear structures.

Electrochemical polymerization offers the following advantages:[33]

— simple equipment including an electrochemical cell, a working electrode, a counterelectrode and a reference electrode;

— carrying out the process at constant electric current or at constant potential (from 15 to 50 V);

— the possibility to obtain polymers as films at a certain electrode; and

— ready control of the reaction conditions by varying the electrode potential, electric current as well as the solvent and other components of the reaction mixture.

Polyconjugated polymers are synthesized in the presence of polymeric acids. They retain the main properties intrinsic to the polymer (*e.g.*, polyaniline, PANI) obtained in inorganic acids and acquire new properties, such as solubility in water.[34, 35] Additional advantages of this method over conventional PANI synthesis include a higher rate of the process at lower reactant concentrations and higher stability at elevated temperatures, in media with pH >7 and on long-term storage. When polymeric acids are used in electrochemical synthesis, the PANI–polymeric acid complex being formed also has some benefits over PANI synthesized in the presence of inorganic acids, namely, the possibility of formation of continuous uniform film, good adhesion of the film to the substrate and a faster redox reaction that remains reversible up to pH ~ 9.

Detailed information on the early stage of the studies on electrochemical polymerization can be found in original publications[36, 37] and in a monograph.[38] The state of the art in this field is presented in a multi-author book.[39] Mention should also be made of a handbook[40] where many aspects of electrochemistry, syntheses, properties and prospects for applications of polymers have been thoroughly considered. As to interfacial phenomena and electroanalytical chemistry of polymers and other materials, the reader is referred to Ref. 41.

A hypothetical scheme of electrochemical polymerization of pyrrole (Scheme 2) shows that its oxidation results in the formation of a radical cation at anode. This species serves as active site of subsequent stepwise polymerization. At the same time, the mechanism of electrochemical synthesis of polypyrrole is still debatable and there is incessant research activity in this field.[42]

Currently, not only polyconjugated polymers (*e.g.*, polyacetylene, polypyrrole, *etc.*), but also polyazines have found various applications. Polyazines are a new class of electroactive polymers that simultaneously possess electronic and ionic conductivity. Using them, one can synthesize polymers with 'molecular fingerprints'. The process involves the following stages:

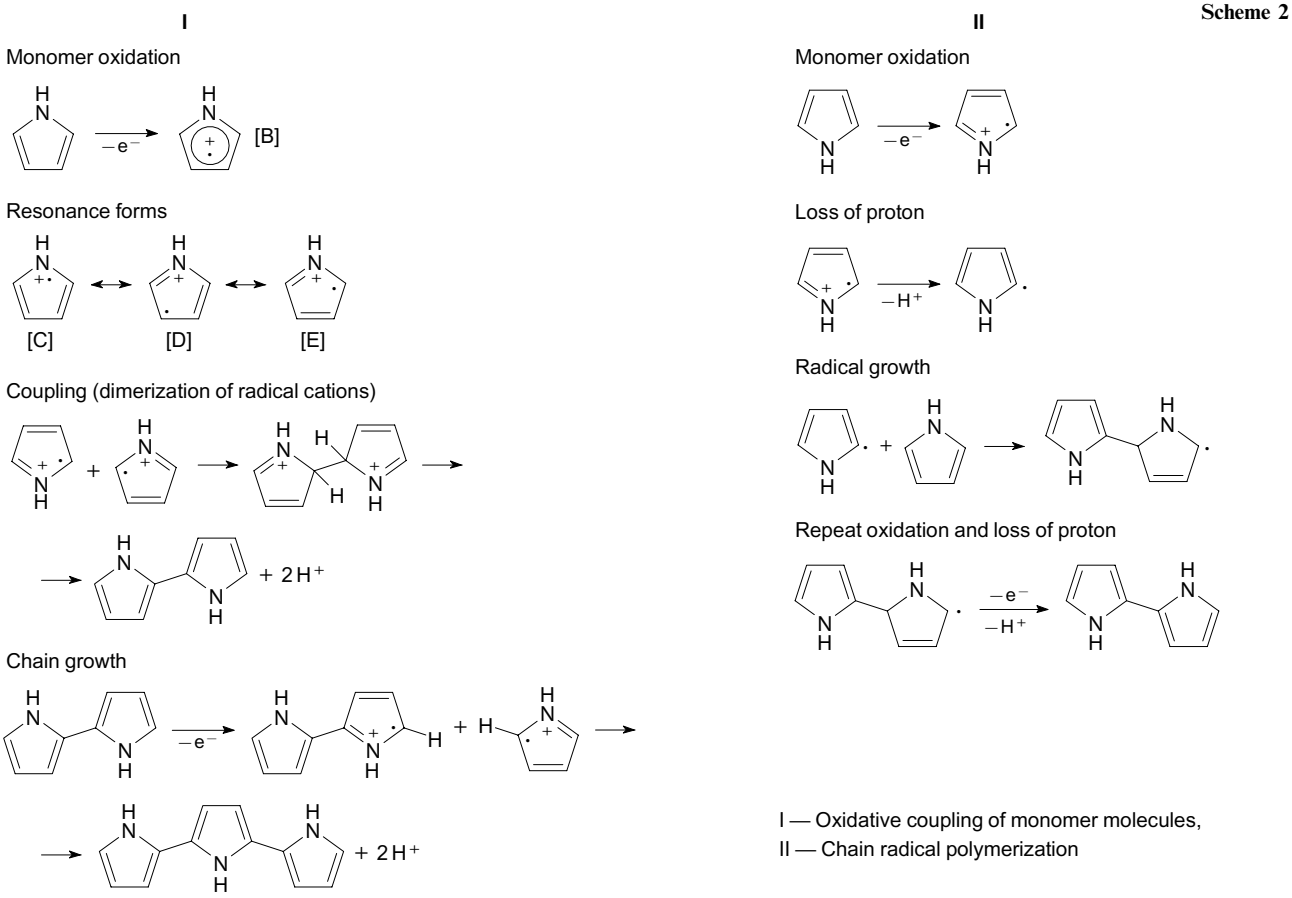
— formation of a complex between functional groups of monomers (oligomers, polymers) and appropriate template (compound to be matched by the polymer);

— stabilization of the complex upon formation of 3D structure of the polymer through intermolecular cross-links; and

— removal of the template.

'Molecular fingerprints' thus formed are identical to the template molecule in shape, size and inter-charge separa-

Scheme 2



tions and can re-bind and 'recognize' the template among a variety of other molecules.[43]

Concluding this Section, we will dwell on important results obtained in studies on electro- and photochemical control of radical polymerization, efficient techniques for controlling the kinetics, molecular mass and microstructure of polymer chains. In addition to electrochemical polymerization, electrochemically mediated atom transfer radical polymerization is also used.[44] In this case, application of an electric potential allows one to exactly specify the amount of catalyst. This facilitates control of the kinetics of conventional radical polymerization.

Thus, key characteristics of polymers can be controlled electrochemically.[45]

4. Ionic polymerization in electric field

A large number of studies on the electric field effect on polymerization, mainly anionic and cationic, in media with different dielectric constants in the presence of various catalysts are available.[46–49] The effects observed are explained using certain models, while experimental data are often hard to compare since there is no detailed information on experimental methods and conditions.

Electric field effects were studied[49] using two types of cells, namely, dilatometric cells with parallel-plate Rogowski-profile electrodes to produce a highly uniform electric field and cells with coaxial electrodes that make it possible to create nonuniform fields (Fig. 1). An original design of the former allowed one to apply the electric field to the entire reaction volume. At an applied voltage of 1 kV, the electric field strength in the cells was 1 and 0.7–14 kV cm^{-1}, respectively. Cationic polymerization systems were studied using 1,3-dioxolane (DO), styrene and α-methylstyrene as monomers and tin tetrachloride, boron trifluoride etherate and triphenylmethylhexafluoroantimony as catalysts. Polymerization was conducted in bulk or in solvents (1,2-dichloroethane, nitrobenzene, methylene chloride) at 25 and 40 °C in high vacuum using thoroughly purified reactants.

Ionic polymerization is most often described using a two-particle model with the following equation for the polymerization rate (W):

$$W = (k'C + k''p)M \quad (1)$$

where k' and k'' are the rate constants for chain propagation for ion pairs and free ions, respectively; C and p are the concentrations of ion pairs and free ions, respectively, and M is the monomer concentration (is it commonly accepted that $k' > k''$).

Earlier, acceleration of polymerization in uniform electric field ($E \approx 1-3$ kV cm^{-1}) was treated as a consequence of an increase in the dissociation constant of active species of an ion-pair type (so-called second Wien effect),‡ which

‡ The discovery of the electric field effect on ionic polymerization was a pleasant surprise. Professor M.Szwarc, who discovered living ionic polymerization, included a Section 'The Wien effect in ionic polymerization' in his fundamental monograph 'Anionic polymerization'[46] and thus attracted the attention of researchers to this area of research.

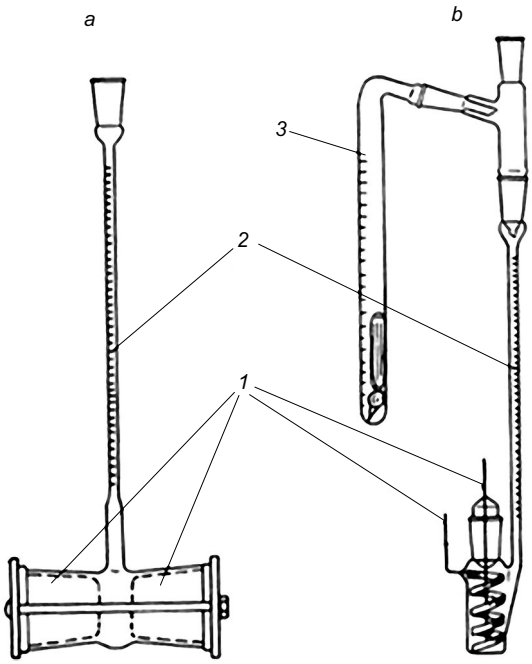


Figure 1. Cells to produce uniform (*a*) and nonuniform electric field (*b*).[49]
Shown are electrodes (*1*), dilatometers for visual monitoring the course of polymerization (*2*) and a volumetric tube (*3*).

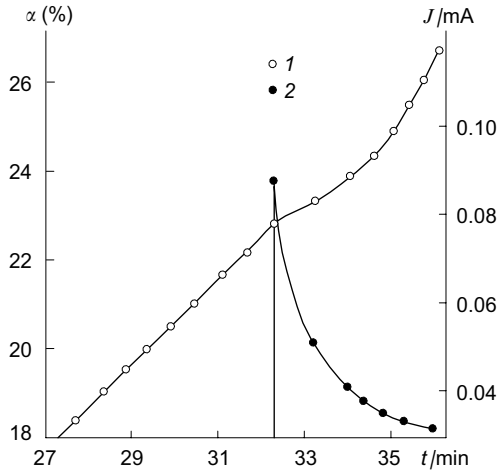


Figure 2. Monomer conversion α (*1*) and current J (*2*) in the transient period after switching on voltage during bulk polymerization of 1,3-dioxolane (DO) in the presence of $SnCl_4$.[49]
Conditions: [DO] = 13.4 mol litre^{-1}, [$SnCl_4$] = 1.4×10^{-2} mol litre^{-1}; T = 40 °C, V = 1 kV.

was expected to increase the concentration of free ions.[48] It should be noted that the second Wien effect was discovered and analyzed [50] as conductometric, characteristic of weak electrolytes; however, no attempts to relate it to active sites of polymerization were reported. Theoretical calculations and experiments showed that realization of this effect in polymeric systems requires much higher electric field strength of the order of 50–100 kV cm^{-1}. Thorough experiments and calculations revealed that acceleration of polymerization reaction cannot be explained by heating of the reaction mixture by Joule heat, desolvation of ions moving in electric field, *etc*. An analysis of published data showed that studies of the electric field effect on ionic polymerization require taking account of nonuniform concentration of ions in the reaction volume between electrodes owing to spatial charge redistribution due to electrophoresis of charged particles.

A model [49] describing the effect of external electric field is as follows: due to a large size difference between macroions and counterions [51] the mobility of the growing polymer ion (μ_p) is much lower than that of the counterion (μ_n), *i.e.* $\mu_p \ll \mu_n$. Therefore, switching on the electric field will cause negatively charged counterions to move faster towards the electrode, and the equilibrium ion pair $\rightleftarrows$ free ions will shift towards growing free ions. Since $k' > k''$ (see above), the polymerization rate should increase.

A preliminary (approximate) estimate of the degree of dissociation of active sites in equilibrium polymerization of 1,3-dioxolane was made using the results of conductivity measurements of solutions of catalysts with monomer additives (no polymerization occurs at monomer concentrations lower than the limiting value) and in the initial stage of polymerization. It was found that polymerization of DO in the presence of $SnCl_4$ with voltage switched on proceeds faster than the process with voltage switched off. A transient period was observed clearly. During this period, the polymerization rate gradually increased (Fig. 2). The duration of the transient period (3–6 min) was independent of the initial electric current and matched the duration of the current decrease period (current varied from 0.08 to 0.5 mA). This means that the increase in the temperature of the reaction mixture (at most 0.5 °C) was not responsible for the observed acceleration.

It was found that the effect depends on the voltage polarity, namely, a change in this parameter causes the polymerization rate to increase to a greater extent if the positive potential is applied to the central electrode (electric field strength at the central electrode was $\sim$7 kV cm^{-1} *vs.* $\sim$0.5 kV cm^{-1} at the external electrode). Switching on the voltage in different steps of polymerization (at different conversions) in the system DO–EtO·BF_3 caused no changes in the reaction rate, although a space charge was accumulated in the reaction volume, as was indicated by nonzero discharge current upon switching off the voltage. The lack of electric field effect on this system seems to be due to low degree of dissociation of active sites (this was confirmed by conductivity measurements) and to small $k'' : k'$ ratio, as follows from the theory of electric field effect on the polymerization kinetics.

The electric field effect on the system DO–Ph_3CSbF_6 depends on the catalyst concentration, *i.e.*, on the rate of polymerization before switching on the voltage (Fig. 3). At higher concentration (curves *1*, *2*), the polymerization rate remains unchanged under the action of electric field, whereas at lower concentrations, the process ceases 10 to 15 min after switching on the voltage and the limiting conversion decreases considerably (curves *4*, *5*). The polymerization retardation time is independent of voltage polarity; the earlier the time instant the voltage is applied the shorter this time. The charge current fades out within $\sim$1 min irrespective of the polymerization rate. Probably, a decrease in the charge current is due to migration of counterions, whereas low-mobile macroions move much more slowly, and their discharge at the electrode or accu-

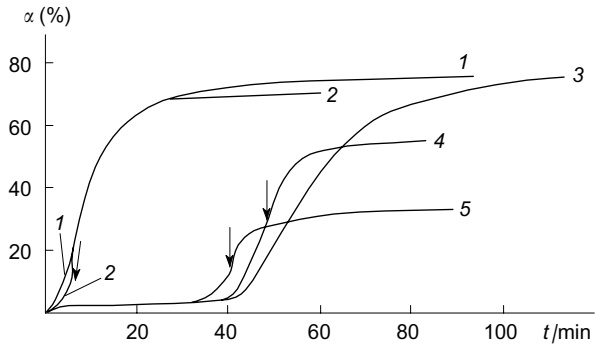


Figure 3. Polymerization kinetics of 1,3-dioxolane (DO) in dichloroethane in the presence of Ph_3CSbF_6 at $T = 25$ °C and $V = 1$ kV.[49]
Conditions: [DO] = 5.08 mol litre^{-1} and [Ph_3CSbF_6] = 10^{-5} mol litre^{-1} (*1*, *2*) and [DO] = 6 mol litre^{-1}, [Ph_3CSbF_6] = 2.8×10^{-5} mol litre^{-1} (*3*–*5*). Arrows denote the high voltage application instants.

mulation in the volume containing no monomer leads to retardation of the polymerization process. According to a known model,[31] this situation should be observed if the degree of dissociation of active sites equals unity (this is also implied from conductivity data for mixtures of catalyst with small amounts of the monomer). At a higher polymerization rate, no retardation occurs since the reaction goes to completion before the redistribution of macroions under the action of electric field occurs. Indeed, in this case the time needed to complete polymerization is close to the retardation time at lower catalyst concentrations.

An important contribution of spatial redistribution of ions is also indicated by inhomogeneity of the molecular mass of polydioxolane (PDO) in the reaction volume.[49] The characteristic viscosity of PDO in the anode region ($[\eta]^+$) was higher than in the remaining bulk ($[\eta]_0$). The volume of the polymer in the anode region was 8% – 10% of the total polymer volume. In the system DO – $SnCl_4$, the $[\eta]^+ : [\eta]_0$ ratio was equal to 1.4, being independent of the degree of conversion. The polymerization rate of DO in the presence of $Et_2O \cdot BF_3$ remained constant under the action of electric field and the characteristic viscosity $[\eta]^+$ of this system showed no increase. The $[\eta]^+ : [\eta]_0$ ratio at conversions between 25% and 40% was constant and equal to 1.1.

The inhomogeneity of the molecular mass of PDO is most pronounced in the system DO – Ph_3CSbF_6. In particular, at low catalyst concentrations corresponding to retardation of polymerization process, one had $[\eta]^+ : [\eta]_0 = 5$ and this ratio decreased in deeper reaction stages. At higher catalyst concentrations, where the DO polymerization rate remains unchanged upon switching on the voltage, the characteristic viscosity of PDO in the anode region was lower than in the remaining bulk ($[\eta]^+ : [\eta]_0 = 0.7$; this ratio approached unity with increasing conversion). Probably, an increase in the molecular mass of the polymer in the anode region is due to lower concentration of macroions in this space region. Clearly, the mechanisms of the regularities observed can be refined during the studies of changes in the molecular mass distribution of the polymers under the action of electric field.

Equations derived within the framework of the model for redistribution of ions in the bulk were used to calculate a number of kinetic constants of the polymerization systems studied. Since no electric field effect is observed in the system DO – $Et_2O \cdot BF_3$, quantitative data were not obtained and only the degree of dissociation of active sites was estimated as $\sim 5 \times 10^{-4}$. A study on the kinetics of transient period in the system DO – Ph_3CSbF_6 gave the following results: $k'' = 390$ litre mol^{-1} s^{-1} and the mobility of macroions was 3×10^{-6} cm^2 V^{-1} s^{-1}. The k'' value agrees with the published data. The rate constants for chain propagation in the system DO – $SnCl_4$ were estimated at $k'' = 0.12$ litre mol^{-1} s^{-1} and $k'' : k' = 12$.

A communication[52] concerning radical polymerization of methyl methacrylate to obtain a polymeric electret seems to be a pioneering study on polymerization in electric field. The authors reported some retardation of the polymerization process and formation of conventional electret; however, these effects were not thoroughly studied, probably since no electrets with specific properties were obtained.

Key results of the studies on electric field effects on cationic polymerization in electric fields are as follows:

— there exists a critical degree of dissociation of active sites; depending on the value of this parameter, polymerization can accelerate, proceed at constant rate or decelerate;

— the increase in the molecular mass of PDO in the anode region by a factor of ~ 1.5 depends on the ratio of the intrinsic viscosities in the anode region and in the remaining bulk; the intrinsic viscosity gradient at constant polymerization rate is low (~ 1.1); the intrinsic viscosity gradient at retardation of polymerization depends on monomer conversion and is about 1.6, 2.8 and 3.3 at a conversion of 32%, 37% and 51%, respectively;

— calculations were performed and dependences based on the concept of changes in the degree of dissociation of active sites due to spatial redistribution of growing cations and counterions were proposed; these dependences are valid for both cationic and anionic processes.

Experimentss[49] revealed an important contribution of electrophoresis and electroosmosis to ionic polymerization.[51] These electrokinetic phenomena are related to the motion of one phase relative to the other phase. They were discovered by Professor F.F.Reuss at Imperial Moscow University in 1809. The motion of charged particles in conditional inter-chain channels after application of voltage to the cell electrodes is illustrated in Fig. 4.[53, 54]

An analysis of published data on the electric field effects on various systems showed[55, 56] that studies of polymerization in electric field should be carried out taking into

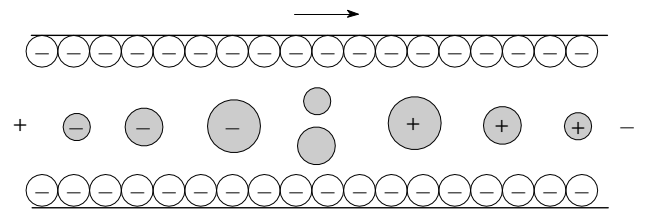


Figure 4. A schematic of electrophoresis of polymer particles, which illustrates a possible ion migration mechanism involving separation in electric field.[53]
The arrow specifies the direction of electroosmotic flow in hypothetical capillary. Electrically neutral particles are in the central part of the capillary.

account the possibility for dielectrophoresis to occur and induce electrostatic levitation in the reaction volume; this is of particular importance in those cases where the polymer being formed is insoluble in the reaction medium. Dielectrophoresis can also have an effect in the case of radical polymerization since it depends on the polarity of the medium and on the magnitude and nonuniformity of the electric field applied.[52–57] The direction of dielectrophoresis depends on the polarity of dipole, which is in turn determined by the polarization and conductivity of the environment. Both calculations and experimental data confirm that the effect is observed only in nonuniform fields. Qualitative reasoning can be as follows. A growing active site can be treated as polar particle. Placing such a particle in nonuniform electric field causes its polarization and the appearance of induced dipole moment, like for all dielectrics. The modulus of the dipole moment vector depends on the particle size, on the applied electric field and, of course, on the polarizability difference between the particle and the medium. A more complicated situation occurs if the synthesis is accompanied by precipitation of polymer as, *e.g.*, in heterophase equilibrium polymerization of trioxane in electric field. In this case, electrocrystallization can occur, that is, the formation and growth of crystals in the bulk of the reaction mixture and deposition at a certain electrode. Electrocrystallization is a first-order phase transition and has much in common with vapour-phase and solution crystallization. However, unlike the last-named process, electrocrystallization is accompanied by charge transfer to nucleation sites.[58–62] One should distinguish between homogeneous and heterogeneous electronucleation that accompanies the formation of colloidal particles in the bulk and ion deposition at electrodes, respectively. Heterogeneous electronucleation can be preceded by the formation of polymer films, which influences the nucleation rate of the new phase.

Electrocrystallization is a method of investigation of the mechanisms of nucleation and crystal growth (since it allows one to vary the supersaturation over a wide range by applying a voltage)[62] and serves as basis for many electrochemical technologies including electrolysis and electroplating. It is unclear whether electrocrystallization in polymer syntheses is feasible, although answer to this question is of considerable importance.

Kinetic studies showed[31] that in the case of heterophase equilibrium polymerization of trioxane at monomer concentrations between 1.5 and 4.2 mol litre^{-1}, the limiting concentration of trioxane in polymerization blend decreases from 1.5 mol litre^{-1} in ambient conditions to 0.14 mol litre^{-1} in electric field probably due to acceleration of polymer crystallization. The results obtained in ambient conditions in the absence of electric field agree with published data.[63] Numerous examples of phase transitions under the action of external fields are presented in a monograph,[62] so the argument formulated above can be considered justified.

The effect of record-high uniform electric fields (field strength up to 110 kV cm^{-1}) on the structural parameters of poly(vinyl acetate) (PVA) and poly(methyl methacrylate) (PMMA) obtained by radiation-induced polymerization was studied.[64] (see§) It was found that the structural parameters of PVA remain unchanged, whereas the structure of PMMA changes noticeably. Also, the proportion of syndiotactic units increases with increasing the field strength and reaches a maximum value at 30 kV cm^{-1} and the stereo structure varies to some extent, namely, a little-pronounced trend towards alternation of iso- and syndiotactic units was observed.

These results agree with those reported in a study[65] aimed at controlling the polymer structure, *viz.*, at changing the ratio between isotactic and syndiotactic PMMA structures in electric fields of strength 10 to 100 kV cm^{-1} in the presence of benzoyl peroxide. It was established that the proportion of syndiotactic structure increases with increasing field strength during bulk polymerization,[64, 65] but the effect weakens appreciably in the case of solution polymerization in toluene. Although communications[64, 65] were not followed by other publications of those authors, the results obtained are of paramount importance because of high level of scientific research. In principle, they are consistent with theoretical conclusions drawn in the more recent studies[66, 67] of the possibility of manifestation of such effects in electric fields of strength $\sim$1 V Å^{-1}.

5. Magnetic field effects and radical polymerization processes

The key event in chemistry is the 'birth' of a molecule.[1] As applied to polymer chemistry, this is nucleation of an active site and its growth to a specified size. According to a scheme and concept of 'new isotopism' developed by Academician A.L.Buchachenko and to his classification of controlling factors, these are energy and Coulomb interaction for 'old isotopism' and the angular momentum and magnetic interaction for 'new isotopism'.[2] Correspondingly, the isotope effects include a classical, mass-dependent effect for 'old' isotopism and a magnetic (spin-dependent) effect for 'new' isotopism. The aforesaid makes it possible to answer an important question as to when one can expect the response of polymerization mixture to the magnetic field effects since the magnetic isotope effect acts as indicator of the reaction mechanism. The magnetic field strength ($\boldsymbol{H}$) is a vector quantity, a quantitative measure that is independent of the magnetic properties of the medium. In practice, the determination of the module of the vector $\boldsymbol{H}$ in ferromagnetic media is based on the fact that its tangential component remains unchanged on going from one medium to another. Having a uniformly magnetized body, the magnetic field strength measured at its surface, aligned with the magnetization direction, matches that inside the body. Polymerization in magnetic fields was intensively studied in the mid-20th century. In these experiments an important role is played by the equipment and proper experimental design. Many experiments with magnetic fields of different strength as well as the results of studies on polymers in strong constant magnetic fields were considered in a monograph.[68] Although published three decades ago, it still remains relevant.

A number of publications are devoted to the effect of constant external magnetic field (up to 7 T) on radical polymerization (see, *e.g.*, Refs 69–74). The magnetic field effect manifests itself as a change in the polymerization rate and (in some cases) as an increase in the molecular mass of the polymer being formed. In most cases the effects observed were explained by the fact that the stages of radical formation (initiation) and recombination depend

§ This study carried out at the Physics Department, Leipzig University (Germany) involved high-resolution NMR experiments.

on the spin state of unpaired electron, which changes in external magnetic field. The spin polarization and magnetic field effects in free-radical reactions are coupled phenomena having common physical mechanisms. They are determined by the stage of interaction between two radicals constituting a radical pair. Within the lifetime of the radical pair, the magnetic spin effects due to singlet–triplet (S–T) conversions are realized. This requires that the time of S–T conversion be comparable with the lifetime of the radical pair. In this case, the effect of external magnetic field on S–T conversions will make the rate of the reaction involving the growing free radicals and the molecular mass of the polymer magnetic field dependent.

An unexpected assumption was made[75] regarding the reasons for significant acceleration of radical polymerization in weak magnetic fields. Based on analysis of experimental data, the authors[75] concluded that in constant magnetic fields (10^{-4}–10^{-3} T) the rate of radical recombination reactions is at most 10% at a characteristic lifetime of the radical pair of 10^{-9} s; therefore, this mechanism is inappropriate to explain much more pronounced effects. They suggested a possible strong heating of photochemically excited polymerization system by weak magnetic fields; however, no temperature measurements were performed.

It should be noted that at present, magnetic field effects on dielectrics and materials containing magnetic particles are studied in connection with the development of smart functional structures.[76]

6. Microwave-assisted polymerization and modification of polymers

In the electromagnetic spectrum, microwaves span a range from 300 MHz to 300 GHz (between UHF and far IR) on the frequency scale. The microwave range corresponds to wavelengths from 100 cm to 1 mm. The wavelengths of microwave radiation are intermediate between those of visible light and radio waves; therefore, microwave radiation exhibits certain properties of light and radio waves. Unlike electric fields, microwave radiation is supplied to objects under study using waveguides rather than electrodes, so there is no point in considering interfacial polarization in this case.[77] Like light, microwave radiation is propagated in straight lines and absorbed by many substances including liquids that are used as loads for microwave transmission lines and as media for polymerization (*e.g.*, water). Potentially, all polar liquid dielectrics with high dielectric loss in the microwave range are suitable to this end. Such media act as sources of heat for polymerization mixtures (through nonuniform orientation polarization), so they can be used as components of highly efficient absorbing structures.[78] It should be noted that the development of studies on microwave heating of polar liquids is due to attempts to elucidate the structure of liquids and the mechanism of formation of associates of compounds of different polarity. Progress in this field became possible as klystrons and magnetrons (generators of microwave radiation) and devices for high-precision measurements of electrical characteristics in this range were developed in the 1940s.

Among studies on polymerization in microwave fields, a prominent place is occupied by those devoted to polymerization and copolymerization of water-soluble polymers including *N*-vinylpyrrolidone and acrylamide, methyl methacrylate and styrene.[78–80] Optimum polymerization conditions and the composition of products were established, and the possibility was demonstrated to carry out controlled polymerization and copolymerization the rate of which increases with increasing dielectric constant of the medium. It was shown with certainty that polymerization in microwave fields along with photo- and radiation-induced polymerization may appear to be an integral part of additive manufacturing technologies.[81–83]

Microwave radiation is used to initiate polymerization (mainly radical polymerization) and to heat reaction mixtures through dipole orientation loss provided the presence of polar components or by the magnetic loss mechanism if the medium contains, *e.g.*, ferromagnets. This is achieved using generators operating in the frequency range from 300 MHz to 300 GHz, which corresponds to wavelengths from 1 m to 1 mm; the frequency range from 0.915 to 2.45 GHz is most appropriate for bulk heating.

An important question is as to whether there is nonthermal contribution to polymerization. Information on the subject is contradictory since high-precision temperature¶ measurement under microwave radiation is complicated, while experimentalists in most cases dwell on benefits attained. A prevailing view[84] is that microwave heating through dipole orientation polarization ensures heating of polar components present in the medium. At the same time, dielectric and magnetic materials absorb 2.45 GHz microwave radiation in different manner, so corresponding heating kinetics are different; consequently, the kinetic regularities observed in certain studies can also be different.

Publications[86–90] are devoted to consequences of the action of microwave radiation on polymerization mixtures. For instance, the styrene polymerization time decreased by a factor of 70 while the molecular mass of the polymer increased by a factor of 1.2 under the action of microwave radiation compared to conventional heating.[86] Bulk polymerization of vinyl acetate, styrene, methyl methacrylate and acrylonitrile under the action of low-power microwave radiation led to considerable increase in the molecular mass of the polymer.[86] It is believed[88] that in spite of high rate of the microwave-assisted reaction, the polymerization conditions are comparable with the conditions in the case of conventional heating. The rates of polymerization of 2,5-dibutoxy-1,4-phenylenevinylene in the presence of homogeneous catalyst under microwave heating and on conventional heating in an oil bath were compared.[89] In the former case, the average molecular mass of the polymer after 1 h was higher, while in the latter case the reaction rate was three times faster. Interesting results were obtained in the synthesis of polymers from poorly polymerizable fumarate monomers.[90] It was found that these monomers differ in reactivity. For instance, diisopropyl fumarate and di-

¶ Since the reliability of experimental results obtained under the action of microwave radiation can be improved by, *e.g.*, high-precision measurement of reaction temperature,[84,85] we recommend the monograph *Chemistry under Extreme or Non-Classical Conditions*. (Eds R.van Eldic, C.D.Hubbard). (Wiley, New-York; Berlin, 1997), which concerns a number of original methods of temperature measurements. In particular, xylene is recommended as thermometric liquid because of small loss in the microwave region; therefore, the temperature readings will be undistorted. However, this requires calibration of the thermometer.

cyclohexyl fumarate were more reactive than di(2-ethylhexyl) fumarate and di(2-phenylethyl) fumarate. This manifested itself in lower conversions of the last two monomers under moderate microwave heating, whereas the average molecular mass and polydispersity were only slightly different from those achieved on conventional heating.

It has been accepted for long that the application of thyratrons and magnetrons is limited to radio detection and ranging. However, since the discovery of microwave heating effect and subsequent design of modern ovens the application field of these devices considerably extended to household appliances, experimental equipment and industry. However, the problem of shielding from microwave radiation posed because of negative effect on electronic equipment and living organisms. On the other hand, since radio detection and ranging using microwave radiation proved to be highly efficient, the Stealth Programme [91, 92] was initiated to sovle problems related to reduction of the radar signature of military equipment. This required considerable research efforts and consumption of material resources. The design of radar camouflage absorbers was aimed to attain prescribed reflection coefficients and weight-size parameters; the goal was successfully achieved. This activity was accompanied by improvement of thyratron and magnetrons technologies and invention of microwave ovens for home use. Research and development in the field of radar-absorbing compositions and shielding materials for civil applications including safe workplace and protection of microelectrons devices in premises where heavy-duty microwave ovens are used.[93, 94] It should be noted that liquid polar dielectrics [95] can be used as microwave radiation absorbers (for details, see a monograph [96]).

Nonthermal effects of microwave fields are studied by researchers who work in different areas of natural sciences. Radical pairs and biradicals are increasingly prevalent intermediates of many organic photochemical and certain thermal reactions.[96, 97]

It is commonly accepted that a singlet intermediate state is formed from the singlet excited state in the reactions occurring with conservation of the spin angular momentum; correspondingly, the triplet intermediate state is formed from the triplet excited state. Radical pairs in solution coherently fluctuate between singlet and triplet electronic states, while recombination reactions are often controlled by electron–nuclear hyperfine interactions on the nanosecond time scale.[98] The authors [98] believe that only a pair of singlet neutral radicals recombines. A triplet pair intersystem is transformed to a singlet pair, or radicals escape from the solvent cage and enter into reaction independently in a later reaction stage.[99] An increasing efficiency of triplet–singlet intersystem crossing (mixing of states) leads to faster recombination. It was established that static magnetic field can induce intersystem crossing in biradicals; this magnetic field effect was successfully interpreted from the standpoint of the mechanism of formation of radical pairs.[100, 101]

The concept [100, 101] provided an explanation for nuclear and electron spin polarization during chemical reactions, in particular, chemically induced dynamic nuclear polarization or reaction yield detected magnetic resonance. Since external magnetic field is stronger than hyperfine interactions, it slows down the singlet–triplet intersystem crossing due to Zeeman splitting and the probability of radical recombination for a triplet pair decreases, whereas microwave field with energy equal to the energy difference between triplet levels (T_{+1} or T_{-1} and T_0) returns the excess population from the T_{+1} or T_{-1} states back to the mixed state. Switching on strong magnetic field for a singlet pair increases the probability of recombination that can also be controlled by varying the characteristics of microwave radition.[101]

Microwave-induced spin dynamics should be treated as a prototype of nonthermal microwave field effect. Indeed, since a radical pair (biradical) is often created photochemically, this undoubtedly deserves attention and treatment within the framework of photochemistry. It was reported that, *e.g.*, the duration of photosynthetic charge separation can be controlled with microwave radiation.[102] Moreover, Okazaki and co-workers [103] reported the possibility of controlling chemical reactions by inducing an EPR transition of the intermediate radical pair during photoreduction of anthraquinone in micellar solution under external magnetic field and simultaneous microwave irradiation. A similar study using bifunctional molecules is available.[104] Research in this field has been well documented.[100, 101, 105, 106]

Static magnetic fields weaker than typical hyperfine interactions can also influence the yield of recombination reactions of radical pairs.[107, 108] This effect is opposite to the strong field effect.[109, 110] A few publications concerning the effect of time-dependent magnetic fields on chemical and physical processes in the absence of strong static field are available. This effect was described [111–113] as the influence of alternating magnetic field (frequency range of 1–80 MHz) on fluorescence of a complex formed in the photochemical reaction of anthracene with 1,3-dicyanobenzene. Hoff and Cornelissen [114] substantiated the assumption that the kinetics of the triplet state can be affected by a pulse of resonant microwaves rather than static field. Rodgers [115] reviewed theoretical and experimental aspects of research into magnetic field effects in chemical systems and presented a historical overview of investigations in this field.

Thus, the aforesaid show that generally the role of nonthermal contribution of microwave radiation to the kinetics of chemical reactions including polymerization should be studied separately in each particular case.

7. Plasmolysis in physical chemistry of polymers

A plasma † is a partially or fully ionized gas in which the density of positive charges almost exactly matches that of negative charges.[116, 117] Plasma is formed in electric discharge in a gas and during combustion and explosion. Matter heated to hundreds of thousands or millions degrees cannot consist of neutral atoms. The average kinetic energies of particles in plasma can be different; therefore, generally a plasma is characterized by a set of temperature values including the electron (T_e), ion (T_i) and atom (T_a) temperatures. A low-temperature plasma corresponds to $T_i < 10^5$ K, while a high-temperature plasma corresponds to $T_i > 10^6$ K. Low-temperature plasma is used in gas-discharge light sources and gas lasers.

The degree of ionization of a plasma is given by the ratio of the number of ionized particles to the total number of

† The term 'plasma' was proposed in 1929 by American researchers I.Langmuir and L.Tonks.

particles. Typical of low-temperature plasma are low degrees of ionization ($< 1\%$); this is the case for so-called technological plasma which is most often created using electric fields to accelerate electrons that ionize atoms. Typical applications of low-temperature plasma include plasma-assisted modification of surface properties and surface etching (in semiconductor industry), cleaning of gases and liquids (ozonation of water and combustion of soot particles in diesel engines). A hot plasma is almost always fully ionized (degree of ionization is about 100%); usually, it is hot plasma that is often called the fourth state of matter. An example is provided by solar plasma. Critically important to the existence of plasma is its temperature. The plasma density, *i.e.*, the number of free electrons per unit volume, also is an important parameter.

Yet another characteristic of plasma is the density of neutral atoms (n_0). Hot plasma is characterized by small n_0 values; nevertheless, this parameter can play a significant role in physics of processes occurring in plasma. Since plasma is a very good conductor, its electric properties are of particular importance. The plasma potential is the average electric potential at a given point. If a body is immersed into plasma, its potential is generally lower than the plasma potential owing to the formation of a Debye layer. This is the so-called floating potential. Being a good conductor, plasma 'tends' to shield all electric fields, which leads to a quasi-neutral state where the density of negative charges almost exactly matches that of positive charges. Owing to the same property of plasma, separation of positive and negative charges is impossible at distances exceeding the Debye length and at times longer than the period of plasma oscillations. A good example of non-quasi-neutral plasma is an electron beam; however, the density of non-neutral plasma should be very low; otherwise, it will rapidly decay through Coulomb repulsion. In some cases, it is used to shield electromagnetic radiation. Transformation of gas into plasma requires at least partial ionization of neutral atoms. There are various methods of ionization in nature and technology.[118]

The most widely used ionization techniques are as follows: thermal ionization, ion electric discharge ionization,[119] ionization under the action of pressure and ionization by laser radiation. Plasma is most widely used in lighting engineering (in gas-discharge lamps) and electric welding. Any substance heated to a sufficiently high temperature goes to a plasma state. This can be most easily done using alkali metal (sodium, potassium, caesium) vapours. A flame is characterized by some thermal conductivity; it is a slightly ionized system, *i.e.*, a kind of plasma. Thermal conductivity of flames is due to admixture of sodium that can be identified from yellow colour. Full ionization of a gas requires temperatures of the order of tens of thousand degrees. Besides, plasma is used in various gas discharge devices including a.c./d.c. converters, voltage stabilizers, plasma amplifiers, microwave generators and cosmic ray counters. All so-called gas lasers (He-Ne, Kr, CO_2, *etc.*) are actually plasma lasers since gas mixtures in them are ionized using electric discharge. Conduction electrons in metals (ions occupying fixed positions in the crystal lattice neutralize their charges) as well as free electrons and mobile 'holes' (vacancies) in semiconductors also exhibit the properties of plasma and are therefore called solid-state plasma.

Electric arc-based plasma guns[116, 117] that generate low-temperature plasma allow one to heat almost all gases to 7000 – 10 000 K within a few centi- or milliseconds. The invention of plasma guns was followed by emergence of a new branch of science called plasma chemistry; many chemical reactions accelerate or occur only in plasma jet. Plasma guns are used in mining industry and for plasma arc cutting. Plasma engines and magnetohydrodynamic power plants are also available. Various designs of plasma accelerators are developed. The problem of controlled thermonuclear fusion is central to plasma physics.

Plasma-assisted coating of films involves polymerization of organic molecules in plasma and deposition of the polymer on a substrate.[120, 121] Plasma-assisted polymerization is initiated by breaking bonds in monomer molecules; polymerization of saturated compounds in plasma is also possible. A feature of plasma-assisted polymerization consists in the formation of less regular molecular structures with higher density of cross-links compared to analogues prepared using, *e.g.*, liquid-phase processes. Nevertheless, coating of polymer films found various applications; in particular, barrier, hydrophilic, hydrophobic, *etc.* coatings are widely used. In cold plasma, atoms are ionized while molecules become split.[121]

Only electrons can be accelerated and heated under the action of high-frequency electromagnetic radiation in vacuum. All other particles (ions, atoms) remain cold; therefore, the plasma temperature increases by 40 – 50 degrees only. Plasma chemists use the fact that gas-phase or surface reactions involving particles excited in gas discharge can occur at low temperatures. Plasma technology became indispensable in solving many engineering problems in various industries. In particular, it is used for surface modification of materials including polymers in order to reduce or increase the surface tension, defatting of metallic surfaces, polymerization and coating of thin films with specified properties, and for reduction of the friction coefficient.[121]

Plasma methods are widely used in polymer chemistry.[119, 122 – 126] Low-pressure plasma is most appropriate for processing of polymeric complex-shape parts. Because of economic and technological reasons plasma-assisted thin film deposition (plasma-chemical vapour phase deposition) is also conducted *in vacuo* or at low pressure. Items to be processed are placed in a vacuum chamber, the pressure is reduced as prescribed and then the chamber is filled with constant gas flow under continuous pumping. Plasma is formed upon electromagnetic excitation. The necessary treatment regimes are chosen by varying reaction conditions (medium, process duration, pressure in the reactor, power, and frequency).

Methods of vapour-phase syntheses include pyrolysis, electric explosion, laser ablation, high-temperature evaporation and plasma synthesis. Plasma-assisted pyrolysis has been utilized for long to produce simple materials, such as soot and colloidal silica. At present, the method is used to prepare many compound materials. Laser ablation enables fabrication of almost all imaginable nanomaterials since the technology combines physical erosion and evaporation. However, the process takes a very long time, so this technology seems to be more appropriate for research usage. High-frequency discharge plasma and d.c. plasma are successfully used in materials design. These thermal sources are environmentally safe and controllable; the plasma temperature can exceed 9000 °C, which allows one to process and sputter even refractory materials. On the

other hand, this plasma is inapplicable for treatment of the surface of organic materials.

All kinds of plasma seem to be promising for utilization in additive manufacturing technologies, although each of them has certain advantages and drawbacks. It is impossible to draw general conclusions about future use of certain fields and methods, in, *e.g.*, additive manufacturing technologies since this depends on the demand for production of structures made of particular materials.

Plasma-assisted treatment is a promising and environmentally safe method of modification of synthetic fibres [121, 125, 126] and textiles in order to improve their hydrophilic properties. Treatment with nonequilibrium low-temperature plasma causes efficient and stable changes in the surface properties of fibres with retention of their bulk (including physicomechanical) properties; no degradation of the material occurs in this case. By varying the discharge parameters and the nature of the plasma-forming gas one can control the composition of the reactive species and, therefore, the character of the action of high-frequency discharge on fibres and materials.[121]

8. Radiation-induced polymerization

Radiation-induced processes occur in systems exposed to α-, β-,or γ-radiation. The first (physical) stage of radiation-induced polymerization [127] takes 10^{-15} to 10^{-16} s and involves absorption of energy and rapid formation of different-type active sites. The overall radiation output of primary charged and excited particles is 7–10 particles per 100 eV. In the next (physicochemical) stage the system under study goes to thermal equilibrium within 10^{-13}–10^{-10} s. Then, in the chemical stage, ions, electrons and free radicals interact with one another and with molecules of the medium. Although research in this field has been carried out for nearly five decades, the results obtained are inconsistent in respect to primary radiation-induced and secondary post-radiation effects.[128]

Radiolysis is a common name for various kinds of transformation of matter [127] including radiation-induced polymerization and modification of polymers through grafting of monomers to obtain high-purity polymeric materials from, *e.g.*, ethylene, trioxane, acrylamide and their copolymers with vinyl chloride, tetrafluoroethylene, 1,3-dioxolane, *etc*. Radiation-induced vulcanization of rubbers and manufacturing of wood–polymer composite materials, as well as production of oleophobic, noncombustible and light-resistant materials are of great importance.

In the last decade, there has been considerable progress in understanding the dynamics of the processes under study and radiation technologies (including nanotechnologies).[129–131] It is safe to assume that radiation-induced polymerization will become an integral part of additive manufacturing technologies in line with photopolymerization. However, this method is still of limited use due to the need for protection against ionizing radiation. At present, products obtained using radiation-chemical technologies occupy a modest place in the total production of polymers. However, the production growth rates for radiation methods are rather high, which gives grounds to hope for successful competition between radiation-chemical and conventional technologies.[127]

9. Photopolymerization, photoconductivity and certain accompanying effects in polymers

9.1. Photopolymerization and its role in additive manufacturing and other technologies

Photoinduced (mainly UV-irradiated) reactions occur in the gas, liquid and solid phases. The term 'photopolymerization' refers to all photochemical processes used to prepare polymers that proceed by the chain (polymerization) or stepwise (polycondensation) mechanisms. In the case of chain photopolymerization radiation can be absorbed immediately by monomer or initiator molecules as well as by sensitizer molecules used to transfer the radiant energy to the monomer or initiator molecules. In the former case, a photon only initiates a reaction that subsequently proceeds according to the conditions in the reaction volume. In the latter case, chain propagation event requires absorption of a new photon.

Gas-phase photopolymerization is most often sensitized with mercury vapours and ketones. Typical sensitizers of liquid-phase photopolymerization processes include dyes, polynuclear aromatic compounds, carbonyls, as well as transition metal salts and acetylacetonates. Large-scale production mainly utilizes chain photopolymerization to prepare, *e.g.*, optically homogeneous products like plexiglas and certain coatings. At present, photopolymerization can be treated as individual line of research in physical chemistry of polymers.[132, 133]

Photopolymerization processes are often studied by the same methods as those used to investigate the kinetics of fast reactions in solutions. They are thoroughly considered in a book by Caldin.[133] A number of methods based on relaxation and pulsed techniques using electromagnetic fields are combined with EPR and other physical methods. Research into the field effects on the polymerization kinetics requires the development of high-precision methods for kinetic measurements.

A schematic of a dilatometer used to study thin-film photopolymerization kinetics is shown in Fig. 5. The instrument is designed to visually monitor the dynamics of photopolymerization (incident light is shown by vertical

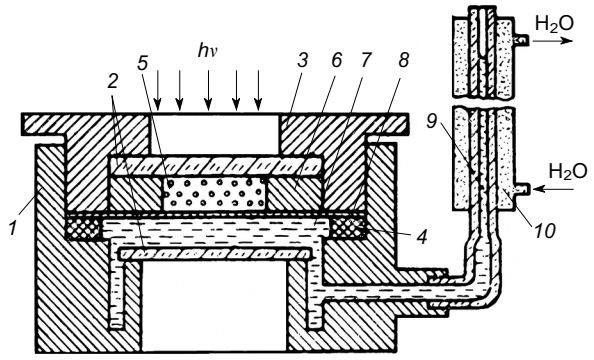


Figure 5. Dilatometer for photopolymerization studies: a schematic.[132]
Metal case (*1*), optical glasses for irradiation of reaction mixture (*2*), nut (*3*), gasket (*4*), reaction volume (*5*), different-thickness gasket to change the reaction volume (*6*), dilatometric liquid (*7*), elastic separating film (*8*) and a capillary with thermostatted jacket (*9*).

arrows). As the monomer is consumed and a polymer formed, the volume of the reaction mixture decreases, the elastic separating film bows and so does the dilatometric liquid, and the liquid column in the capillary moves downward. The capillary is thermostatted to exclude motions of the liquid due to the temperature fluctuations in the environment.

Photopolymerization in thick films in the self-sustained travelling wave mode was studied.[134] This kind of polymerization is used to manufacture polymeric optical products. The technique involves monitoring the temperature difference in the films under study using a number of thermocouples arranged at a distance of 10 to 15 mm from one another along the length of the sample. On an industrial scale, chain photopolymerization is most often used to, *e.g.*, produce optically homogeneous products like plexiglas and certain stereoregular polymers. Thin-film photopolymerization is used for curing of coatings, manufacturing of printing plates, microchips, *etc*. In laboratory practice the method is often utilized to determine the rate constants for radical reactions that typically proceed by the radical and cationic (ionic) mechanisms.[135, 136]

Photoinitiation of radical polymerization involves (i) absorption of light by a certain component of the reaction mixture, *e.g.*, a photoinitiator molecule; (ii) transition of this molecule to an excited state and (iii) dissociation of a chemical bond (typically, one of the weakest bonds in the molecule is cleaved). Compounds used as photoinitiators (Ini) dissociate into two radicals

$$\mathrm{Ini}^{*} \longrightarrow (\mathrm{R}^{1})^{\bullet} + (\mathrm{R}^{2})^{\bullet} \qquad (2)$$

or intramolecular rearrangement results in the formation of a biradical

$$\mathrm{Ini}^{*} \longrightarrow (\mathrm{R}^{1})^{\bullet}(\mathrm{R}^{2})^{\bullet} \qquad (3)$$

that is, the molecule bearing two free valences in different structural fragments. If a sensitizer (Sens) is used, photoexcitation can be followed by transfer of the absorbed energy from Sens to the initiator

$$\mathrm{Sens}^{*} + \mathrm{Ini} \longrightarrow \mathrm{Sens} + \mathrm{Ini}^{*} \qquad (4)$$

or Sens interacts with Ini to give a pair of free radicals

$$\mathrm{Sens}^{*} + \mathrm{Ini} \longrightarrow (\mathrm{R}^{1})^{\bullet} + (\mathrm{R}^{2})^{\bullet} \qquad (5)$$

The excited photoinitiator molecule can also dissociate into more than two species. In this case, only two of them become free radicals, whereas other fragments that typically have low molecular masses retain electrical neutrality

$$\mathrm{Ini}^{*} \longrightarrow (\mathrm{R}^{1})^{\bullet} + (\mathrm{R}^{2})^{\bullet} + \ldots + \mathrm{R}^{m-1} + \mathrm{R}^{m} \qquad (6)$$

The radical produced upon the decomposition of photoinitiator can add to a monomer (M) containing a C=C double bond (*e.g.*, to vinyl or acryl monomer); as a result, this bond is cleaved and a new radical with higher molecular mass is formed

$$\mathrm{R}^{\bullet} + \mathrm{H_2C{=}CH{-}M} \longrightarrow (\mathrm{R{-}HC{-}CH{-}M})^{\bullet} \qquad (7)$$

In turn, this radical interacts with the next monomer molecule, thus forming a polymer molecule with a free valence. If the molecule of monomer M contains more than one unsaturated bond, polymerization results in the formation of a 3D cross-linked polymer molecule with a large number of free valences

$$\mathrm{R}^{\bullet} + n\,\mathrm{M} \longrightarrow \mathrm{RM}_{n}^{\bullet} \qquad (8)$$

The interaction of the free radical $\mathrm{R}^{\bullet}$ with the monomer molecule can be accompanied by hydrogen abstraction without cleavage of the double bond. This is the case for chain transfer to monomer

$$\mathrm{R}^{\bullet} + \mathrm{M} \longrightarrow \mathrm{RM}^{\bullet} \qquad (9)$$

The chain reaction terminates as a result of interaction between the radical and either a radical (recombination) or inhibitor of radical polymerization. In the latter case, a radical with a very low reactivity is formed. A classical inhibitor is oxygen. The interaction of oxygen molecule with a reactive radical results in peroxy radical, a stable compound of low reactivity. Chain radical polymerization also terminates if the radical becomes isolated in an inert polymer matrix. Nevertheless, the free valence still can migrate along the polymer chain through intramolecular rearrangements.

In ionic photopolymerization a photoinitiator absorbs a photon and forms a $\mathrm{Cat^{+}An^{-}}$ ion pair, which can either exist as a compound with ionic bond or dissociate into cation (Cat) and anion (An). Usually, the ions differ in reactivity, so only one ion of the pair initiates a chain process even if there is a potentiality of both anionic and cationic polymerization of the monomer (oligomer). Since dissociation of known ionic photoinitiators produces a reactive cation and a low-reactive anion, 'ionic photopolymerization' typically implies cationic photopolymerization. This is the case for polymerization of vinyl and diene monomers and oligomers, acrylates and their derivatives and heterocyclic compounds. Like the polymerization of 1,3-dioxolane and trioxane (see above), that of heterocyclic systems involves ring opening. Polymerization of compounds containing, *e.g.*, a vinyl group is described by the equation

$$\mathrm{R{-}CH{=}CH_2} + \mathrm{Cat^{+}} \longrightarrow \mathrm{R{-}CHCat{-}CH_2^{+}} \qquad (10)$$

The cation interacts with the next monomer (oligomer) molecule, *etc*. If the ion pair does not dissociate into anion and cation, the chain initiation reaction is as follows:

$$\mathrm{R{-}CH{=}CH_2} + \mathrm{Cat^{+}An^{-}} \longrightarrow \mathrm{R{-}CHCatAn^{-}{-}CH_2^{+}} \qquad (11)$$

As to heterocyclic compounds, the equation of the chain initiation and ring opening reaction has the form

$$\mathrm{R{-}\underset{\diagdown\,\mathrm{O}\,\diagup}{CH}{-}CH_2} + \mathrm{Cat^{+}} \longrightarrow \mathrm{R{-}CHCat{-}CH_2{-}O^{+}} \qquad (12)$$

The cation thus produced interacts with another monomer molecule, which also causes ring opening.

The application of photopolymerization in additive manufacturing technologies is promising and justified. As

to new spots of R&D activity, mention may be made of the design of polymers whose damaged structure (cracks) is repaired under the action of UV radiation.[137, 138] In recent decades, intensive research efforts have been made to design self-healing materials. These systems can be conditionally divided into two large groups. One of them includes materials made of covalently bound extended organic macromolecules. They exhibit rather high mechanical rigidity, thus being promising for construction engineering (repair of water pipes) and other industries. These polymeric materials contain microvessels filled with monomeric compounds necessary for self-healing. At occurrence of damages, microvessels break up and release monomers that react with the damaged fragments of macromolecules. This approach has a clearly seen drawback, *viz*., the loss of the self-healing ability as the monomers are consumed. The second group includes polymeric materials with weaker chemical bonds that form supramolecular complexes. Inter-chain bonds in such systems are formed through weak (metallic or hydrogen) bonds or π-bonds rather than strong covalent interactions. As temperature increases, these bonds readily dissociate but form again with ease on cooling. Self-healing polymers are thought to be promising for long-term use of products made of them.

Currently, the key problem is to find a method to make these polymers more rigid. An example is provided by the studies carried out by the research group headed by Professor C.Weder,[139] who work with block copolymers comprised of a mixture of different (two and more) monomers that form an ordered structure of alternating blocks or layers connected through weak interactions. Monomers represent conventional carbon chain compounds with negatively charged terminal groups and metal (zinc and lanthanum) compounds. Positively charged metal particles attract negatively charged termini, thus creating an extended polymer chain. The polymeric material has a layered structure, namely, charged layers of terminal groups linked to metal atoms alternate with nonpolar carbon chain layers. Although macromolecules are linked through noncovalent bonds, it is believed [139] that the structure is comparable in mechanical strength with covalently bound polymers. The use of zinc or lanthanum compounds is due to the fact that these metals absorb UV radiation; the absorbed energy is converted to heat and the material is softened at cracks. Metal ions interact with the negatively charged groups and again form chemical bonds with them.

Photopolymerization allows one to extend methods of formation of polymeric systems. It was shown [140] that photopolymerization of mixed monolayers of diacetylene derivatives on the surface of gold nanoparticle hydrosol affords nanostructured polymer films containing gold nanoparticles. Moreover, the bilayer structure formed upon coating the film with conductive polyaniline layer demonstrates a strong synergistic effect that manifests itself in increased photoconductivity at the plasmon frequency of gold nanoparticles. Polymeric systems thus obtained and the method for their preparation are promising for the development of ultrathin optoelectronic devices on flexible substrates.

9.2. Photoconductivity

Photoconductivity involves three key processes, *viz*., photogeneration, transport and recombination of charge carriers. Weak intermolecular interactions in polymers predetermine

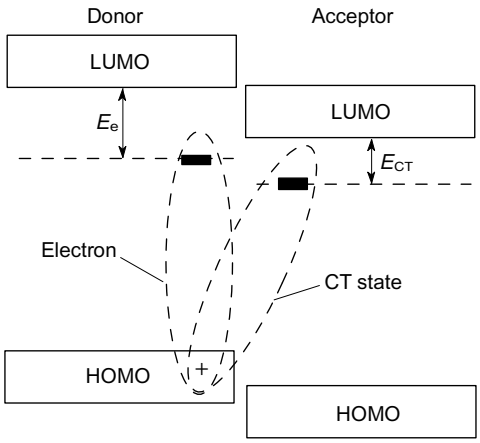


Figure 6. The formation of a charge-transfer (CT) state: a schematic.
The binding energies of exciton (E_e) and CT state (E_{CT}) are shown relative to the LUMO energy levels.

(i) absorption of light by certain fragments and photogeneration of charge carriers with quantum yields less than unity and (ii) localization and relatively low mobility of charge carriers. There are a variety of original publications, reviews and monographs (see, *e.g*., Refs 141 and 142) devoted to photogeneration of charge carriers. An absorbed photon causes excitation of the photoactive fragment of the polymer. In terms of molecular orbitals, an electron goes from the HOMO to the LUMO of this fragment (Fig. 6). The HOMO–LUMO energy difference (E_g) is treated as an analogue to the band gap (in terms of the energy band model).

In the photoactive fragment of the polymer, an electron and an ion represent a bound electron–hole pair, or exciton. Owing to Coulomb attraction between particles in the pair the exciton has a rather high binding energy (E_e) which is typically 0.2–0.5 eV in polymers. Decay of an exciton is accompanied by electron transfer from the initial electron-donor (D) fragment of the polymer to electron acceptor (A), for instance, the electronegative moiety of the polymer or some other species. The process is facilitated by the LUMO energy difference between D and A (see Fig. 6). After electron transfer, the electron and hole remain Coulombically bound in a state that is called charge-transfer (CT) state. Although the binding energy of the CT state (E_{CT}) is lower than E_e, thermal energy (kT) at room temperature (0.025 eV) is too low to split the CT state into free electron and hole. Opinions are different as to the mechanisms of formation of free charge carriers;[142] however, an important role of the degree of delocalization of electron and hole on the acceptor and donor fragments of polymers (molecules, clusters) was pointed out.

Application of an external electric field to a polymer film considerably increases the probability of splitting of the CT state into free charge carriers, which facilitates their intermolecular transport. Electrons and holes moving in opposite directions can collide. This will be followed by bimolecular recombination[143] and, therefore, by a decrease in the concentration of charge carriers and, consequently, in the photoconductivity of the polymer, thus deteriorating the properties of the photodiode and photovoltaic device.

9.3. Photovoltaic effect

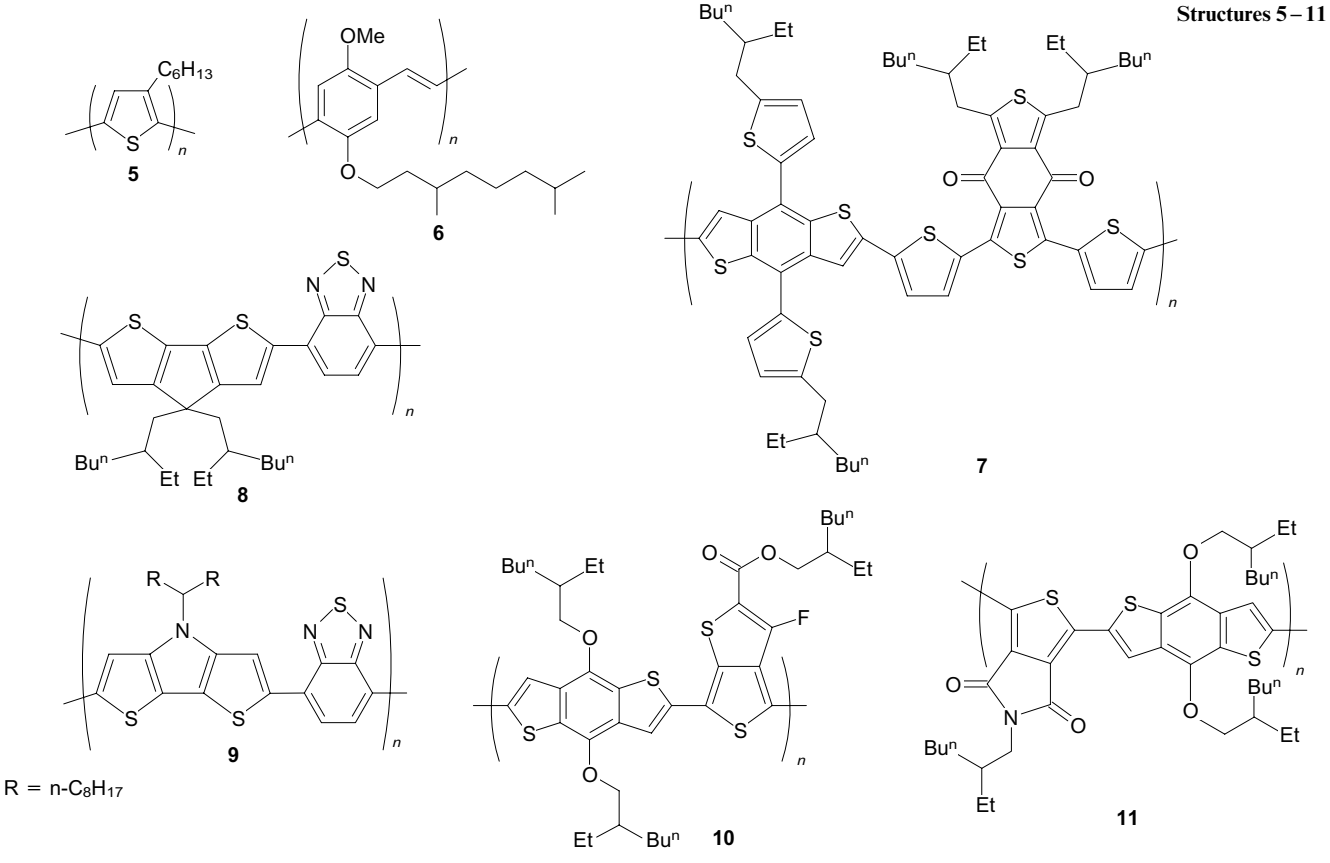
Recently, there has been considerable interest in photoconverters of solar energy to electricity based on the photovoltaic effect in thin polymer films. The most pronounced photovoltaic effect is observed in films of donor – acceptor (D – A) composites with polymers most often acting as donors (Table 3) and [6,6]-phenyl-C_{61} butyric acid methyl ester (PCBM) acting as acceptor. The HOMO and LUMO energies of PCBM are −6.0 and −4.3 eV, respectively. The polymer also serves as the film-forming material. Free charge carriers are generated at the D/A interface; therefore, it is necessary that a continuous network of interpenetrating phases of the D and A components be formed in D – A mixtures (see, *e.g.*, a review [144]). Such a structure of the photoactive layer is called the bulk heterojunction, can be practically implemented with ease in polymeric composites and represents an advantage of the systems in question over inorganic semiconductors. To date, the maximum efficiency of 12.2% (see Ref. 145) was attained using a ptotoconverter with a bulk heterojunction based on narrow-gap (E_g = 1.8 eV) copolymers 2,6-{4,8-bis[5-(2-ethylhexyl)thiophen-2-yl]benzo[1,2-*b*:4,5-*b*′]dithiophene} and 1,3-di(5-thiophen-2-yl)-5,7-bis(2-ethylhexyl)benzo[1,2-*c*:4,5-*c*′]-dithiophene-4,8-dione.[146] A mechanism was proposed of photogeneration of charge carriers in the photovoltaic photocurrent mode in the bulk heterojunction of D – A systems.[147, 148]

Table 3. Characteristics of typical electron-donor polymers.

Compound	$-E_D$(LUMO) /eV	$-E_D$(HOMO) /eV	Ref.
5	3.00	5.10	153, 154
2	2.70	5.10	155 – 160
6	3.00	5.30	155 – 160
7	3.53	5.33	146
8	3.60	5.30	155 – 160
9	3.10	4.90	155 – 160
10	3.30	5.15	155 – 160
11	3.75	5.55	155 – 160

The development of photoactive polymers for solar cell components follows two research avenues:[149 – 151] the synthesis of polymers with π-conjugated system [152] and the formation of D – A charge-transfer complexes in polymers. The charge-transfer complexes can represent either monomer units of corresponding polymers or composites of a polymer and a low-molecular-mass compound, in particular, PCBM. Donor-acceptor interaction between components of the composite leads to an increase in photoconductivity and to extension of the spectral range of absorption, *i.e.*, to sensitization of the photoeffect. Possible sensitizers include dye molecules that create photoactive sites in the polymer for absorption in the visible or IR range (spectral sensitization) as well as molecules involved in D – A-interaction with aromatic fragments of the polymer (structural chemical sensitization). The HOMO and LUMO energies play a significant role when choosing the D and A components of the polymeric system. The structural formulas and the energies E_D(HOMO) and E_D(LUMO) of the polymers that are most widely used in the design of bulk heterojunctions in polymer – fullerene composites are presented in Table 3. These polymers can be classified as homopolymers (**2**, **5**, **6**), donor – acceptor polymers (**8**, **9**) [161] and quinoid type polymers (**7**, **10**, **11**).[146, 162]

Structures 5 – 11



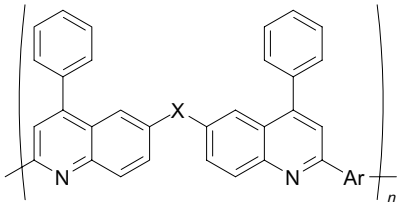
Donor–acceptor polymers contain alternating donor and acceptor fragments. Intramolecular charge transfer from D to A favours polarization of the main chain and causes E_g to decrease. An advantage of D–A-polymers consists in the possibility to vary E_D(HOMO) and E_D(LUMO)[163] by varying the electron-donating ability and electron affinity of the corresponding moieties.[162] The weaker the electron-donating ability the lower the energy E_D(HOMO), while the stronger the electron-withdrawing ability the lower the energy E_g. The HOMO and LUMO positions can also be varied by introducing a third monomer (D or A) into the monomer unit of the polymer, that is, by creating copolymers of the types A1–D–A2–D or D1–A–D2–A.[164]

A fruitful strategy to decrease E_g is to synthesize polymers prone to form a quinoid structure in the main chain.[165] Within the framework of the resonance theory the quinoid form has a lower resonance energy than aromatic moieties. For instance, the resonance energy of benzene ring in polybenzo[*c*]thiophene (1.56 eV) is somewhat higher than that of thiophene (1.26 eV); therefore, thiophene tends to adopt a quinoid structure to retain the aromaticity of the benzene ring.[162]

The energy E_D(HOMO) in semiconductor polymers can be reduced using various substituents.[166] For instance, the fluorine-containing moiety has high electronegativity and therefore E_D(HOMO) decreases.[159, 164] At the same time, E_D(HOMO) increases upon introducing electron-donating groups into the polymer.[167] Substituents can influence the electronic properties and the overall degree of crystallinity of photoactive layers. For instance, a study[168] of diketopyrrolopyrrole polymers where the branching points in the alkyl chain were moved away from the main chain revealed improved crystallinity and, as a consequence, higher efficiency of photovoltaic process.

An example of polymers with intramolecular charge transfer is provided by a polyphenylquinoline (PPQ) (structure **12**) representing a D–A complex formed by the donor arylene (Ar) fragment and phenylquinoline acceptor rings.[169–171] This complex, especially if the arylene moiety is a strong donor (*e.g.*, of carbazole or indolocarbazole type), can[141] interact with structurally similar acceptor molecules. Such a sensitization of the photoeffect improves the photophysical properties (photosensitivity or photoconductivity) of polyvinylquinolines and extends the spectral sensitivity range.

Structure 12



12

An acceptor molecule of 2,1,3-benzothiadiazole (BTDA) is structurally similar to carbazole or indolocarbazole molecules. Indeed, sensitization of photoeffect in the PPQ = BTDA composites manifests itself efficiently. Namely, the introduction of BTDA (10 mass %) causes extension of the spectral sensitivity range and an increase in the integral photosensitivity and photocurrent by a factor of 4.5 and more than 6, respectively. The photoeffect is due to complexation between donor arylene moieties and acceptor (BTDA), whereas the larger increase in the photocurrent compared to the change in the photosensitivity is probably caused by the transport of free electrons to molecules.[172]

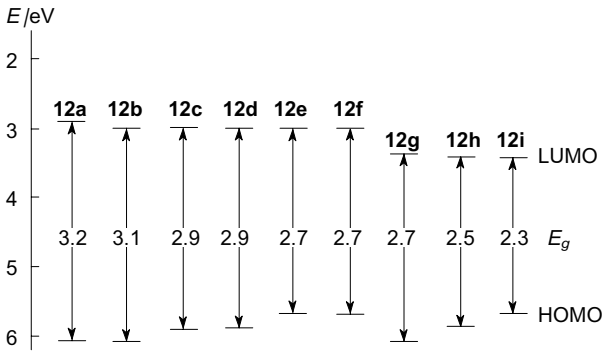


Figure 7. HOMO–LUMO energy diagram characterizing the band gap of polyphenylquinolines (PPQ).[173]
For **12a**–**12i**, see Table 4.

Figure 7 presents the HOMO and LUMO energy diagram and the E_g values determined using the results of studies on absorption spectra, photosensitivity, quantum yield of photogeneration of charge carriers and luminescence of polyvinylquinoline solutions and films of different structure and composition (Table 4). The narrowest band gap (E_g = 2.3 eV) corresponds to the indolocarbazole-containing complex. These studies demonstrated the efficiency of targeted synthesis of photosensitive polymers with D- and A-moieties in the main chain.[173]

9.4. Electroluminescence

Polymers with D- and A-fragments can exhibit electroluminescence that emerges upon radiative recombination

Table 4. Bridging groups (X) between electron-withdrawing phenylquinoline rings and aromatic arylene moieties (Ar) in the structure of polyphenylquinolines **12**.[170, 173]

Compound in Fig. 7	X	Arylene moiety
12a	–O–Ph–O–	Diphenyl oxide
12b	–O–	The same
12c	–O–	Dodecylcarbazole
12d	–O–	Cbz(C_6F_4)(C_6F_5) (see [a])
12e	–O–	Cbz($C_6H_4NO_2$) (see [a])
12f	–O–	Dioctylindolo[3,2-*b*]-carbazole
12g	>N—Ph	Diphenyl oxide
12h	>N—Ph	Octylcarbazole
12i	>N—Ph	Dioctylindolo[3,2-*b*]-carbazole

[a] Cbz is carbazole.

of electrons and holes injected into the polymer film from the cathode and anode, respectively. Since efficient bimolecular recombination is achieved when electrons and holes arrive at the recombination region with equal velocities, in the case of single-layer light-emitting diode it is desired that the polymer have ambipolar conductivity.[174] Key principles of the design of light-emitting organic materials and corresponding devices were reviewed.[175]

Industrial production of displays utilizes organic light-emitting diodes based on low-molecular-mass compounds. Thin (up to a few nanometres) and homogeneous layers of appropriately chosen compounds are prepared by vacuum thermal deposition on substrates. Research and development in the field of white light sources are carried out using polymeric materials[176] since liquid polymer solutions allow one to form thin-layer coating by simply casting relatively large areas. The key problem in manufacturing of light-emitting diodes with white emission is to attain an intensity balance in the blue, green and red ranges of the visible spectrum. To solve the problem, it was proposed to augment the colour of the polymer electroluminescence with the emission of semiconductor quantum dots.[177,178] A successful strategy is to design a bicomponent light-emitting diode[179] based on modified polyfluorene with bright blue-green emission and semiconductor quantum dots CdSe/ZnS/CdS/ZnS with orange-red emission with a quantum yield fluorescence of more than 90%. By varying the component ratio (by mass) in the light-emitting composite one can vary the white tone without loss of emission efficiency.

10. Polymeric materials under the action of electromagnetic fields in additive manufacturing technologies

At present, additive manufacturing technologies widely use photochemical methods of synthesis for layer-by-layer buildup of physical parts to attain a necessary size.[180] At the same time, there have been increasingly frequent attempts to utilize methods for the design of new forms of polymers and composite materials.

Electrospinning is a method of fabrication of nano- and microfibres. Renewed interest in the technique is due to a new stage in the development of modern materials science. In the 1930s, I.V.Petryanov-Sokolov, N.D.Rosenblyum and N.A.Fuks, who worked at the Laboratory of Aerosols, Karpov Scientific Research Institute of Physics and Chemistry (Moscow, Russia), studied the generation of monodisperse aerosol droplets from nitrocellulose solution by electrostatic spraying and revealed the formation of very thin long filaments that form uniform layers instead of droplets. These layered materials were named 'Petryanov's filters' (PFs). In the USSR, for more than 50 years they were the one and only system for fine purification of air from

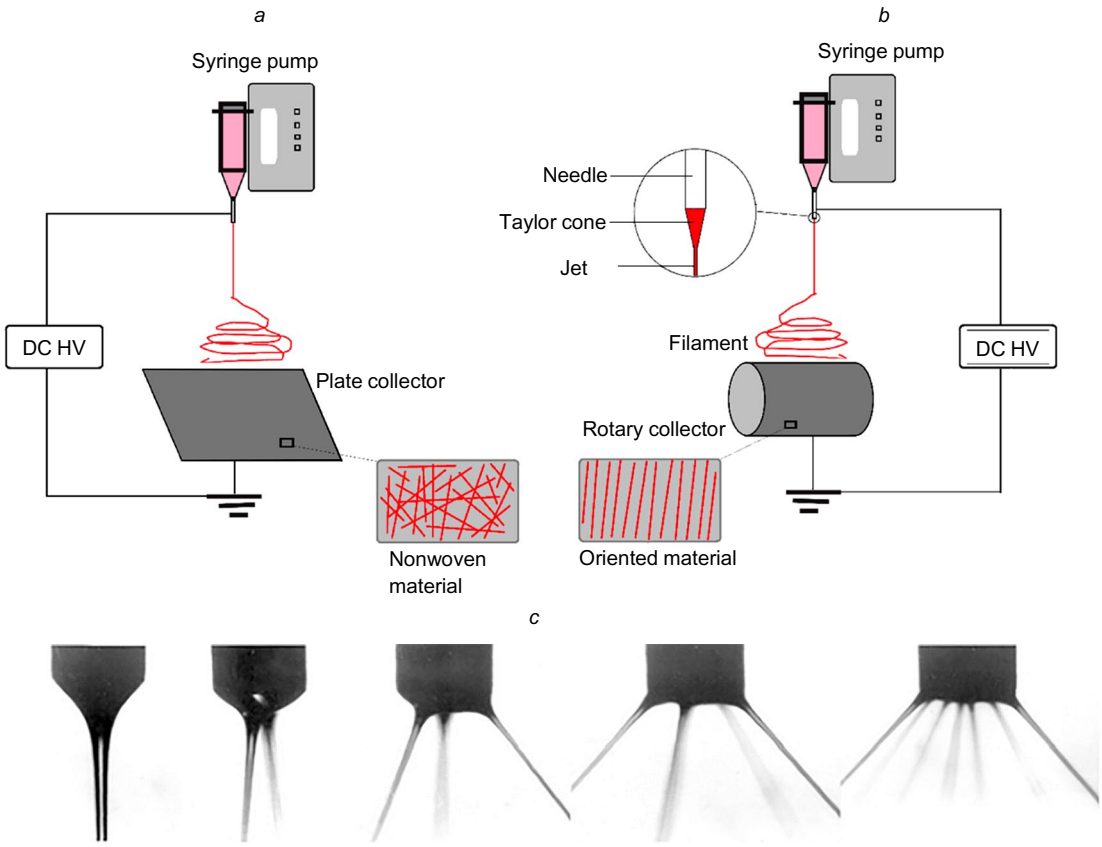


Figure 8. Two types of electrospinning setup (*a*, *b*)[185] and initial steps of electrospinning process (*c*).[183]
Shown are two versions of electrospinning that require polarization of a polymer solution or melt droplet in electric field created between the syringe pump needle tip and grounded plate collector (*a*) or rotary collector (*b*). Shown in Fig. *c* are jets stretched into filaments; the rate of formation and diameter of filaments can be assessed from the appearance of jets. 'DC HV' stands for a d.c. high-voltage source.

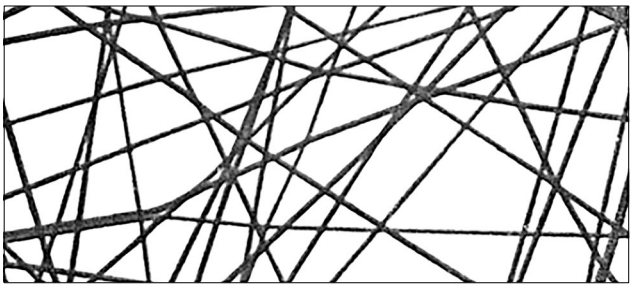


Figure 9. A photomicrograph of electrospun filaments.[183] Average filament diameter is about 1 μm.

submicrometre particles. Detailed information on the filtering properties and application of PFs was for the first time published only in 1968 (see Ref. 181). More recently, Academician I.V.Petryanov's entourage have published a series of studies on industrial applications of PFs (see, *e.g.*, Refs 182–184). A schematic of a typical electrospinning setup[185] and the steps of splitting the polymer solution or melt jet into nanofibres[158] and a photomicrograph of electrospun filaments are shown in Figs 8 and 9.

In this technology a thin jet of polymer melt (solution) or polymer with filler, having a dog bone cross-section and high density of surface charge, is split into two or three nearly identical jets that are subsequently deposited on a surface and form micro- or nanofibres. A study[186] on jet formation process deserves attention. The author[186] analyzed the mechanism and dynamics of formation of polymer fibres and relevant methods of control. Fibres thus fabricated can be used to obtain composites using additive manufacturing technologies. It should be noted that the fibre thickness can be controlled by, *e.g.*, varying the component concentrations in solution or the concentration of the polymer with finely disperse fillers (see Refs 181–184 and 186).

It seems likely[186] that charged fibres in PFs are similar in nature to electret fibres. Note that electric charges on PF fibres mainly influence the deposition of charged particles and are therefore used in filters for air purification. Studies on electrospinning of polymer fibres carried out at the Karpov Scientific Research Institute of Physics and Chemistry led to the development of a technology for fabrication of PFs from nanofibres. At present, compact laboratory-scale electrospinning setups using concentrated polymer solutions or melts are available.

Magnetospinning[187] is a new magnetic-field-driven method of fabrication of fibres. The technique resembles electrospinning. A schematic of a magnetospinning setup is presented in Fig. 10. Shown are the initial stages of the process using a polymer solution or melt containing ferromagnetic particles. To initiate the stretching of fibres, it is required that a liquid droplet (*a*) be pushed through the needle of a syringe pump to meet a permanent magnet (red-and-blue ball), drawn by the magnet (*b*, *c*) and then the fibre spooled on a reel (*d*). Apparent simplicity of magnetospinning should not mislead since the development of the technique required considerable efforts.

There is a variety of methods of research into physical chemistry of polymerization processes and modification of polymeric materials. This allows one to study and design polymeric materials with specified properties and to solve new scientific and technological problems on a new stage of development of natural science. From the aforesaid it follows that the structure of the polymer chain can be altered either upon branching in the course of polymerization or in later stages of the process under the action of various factors including electromagnetic fields. Considering polycondensation of monomers bearing three functional groups, cross-linking unavoidably becomes a key factor in polymerization. Moreover, in such systems the polymer undergoes rapid transformation into a giant cross-linked molecule or gel as two thirds of the total amount of reactive groups are consumed. The formation of the 3D network begins with abrupt increase in the molecular mass in a narrow interval of conversions. High-cross-linked polymers, such as thermosetting resins, represent solid materials that show no flow at high temperatures. To attain specific goals, linear polymers are cross-linked by, *e.g.*, heating (including microwave heating) in the presence of peroxides.

In rubber industry, weak cross-linking using sulfur (vulcanization) is used for conversion of the starting poly-

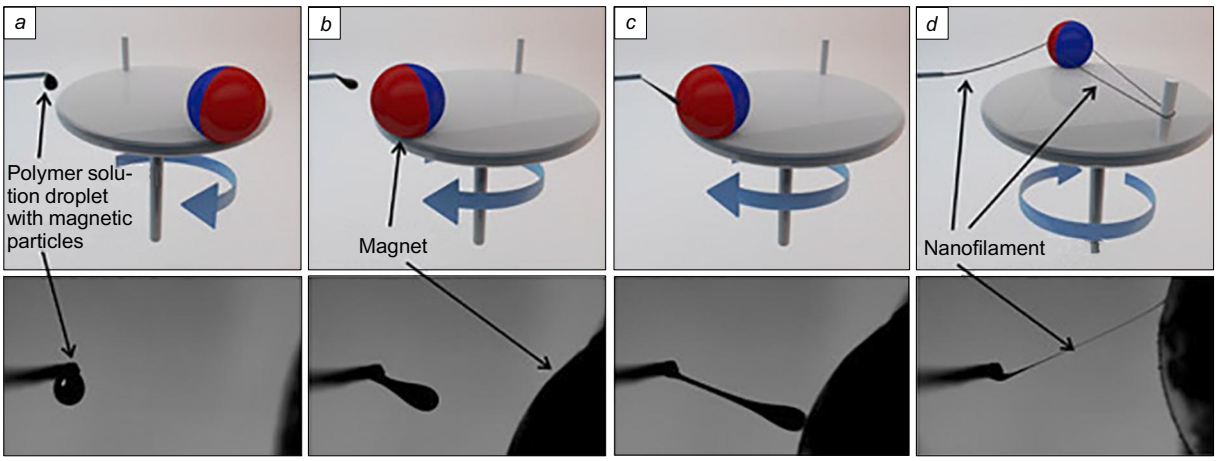


Figure 10. A schematic of the magnetospinning setup: a magnet fixed on a rotating stage approaches a droplet of the ferromagnetic liquid and attracts the droplet, and a liquid bridge between the magnet and the needle is formed; as the solvent evaporates, the liquid bridge is transformed into the nanofibre.[187] For *a*–*d*, see text.

mer (natural or synthetic latex) to a solid elastic product. Electrochemical polymerization of conjugated polymers from multifunctional monomers also results in cross-linked polymers. Contrary to this, uncross-linked saturated thermoplastic polymers soften and flow at high temperatures. This behaviour is also typical of conjugated polymers with bulky side fragments since the disordering action dominates the main-chain rigidity. In the absence of bulky side groups, conjugated polymers often degrade on heating without transition to the flow state.

In the text above we considered bulk effects; however, local treatment of the surface in, *e.g.*, the design of electronic devices becomes important.

An analysis of published data on the state of the art in modern materials science revealed two avenues of research:[16]

— search for new effects that arise in response to the action of electromagnetic fields on processes and materials; and

— search for methods and ways of realization of additive manufacturing technologies.

In the near future, where the micrometre size will be reduced by three orders of magnitude, the era of quantum technologies will begin and it will become possible to go to atom-structured matter.[137] Clearly, the first example of application of quantum chemistry to solution of practical tasks in nanotechnologies is provided by the so-called atomic writing on the film surface[137] using, *e.g.*, grafting of trichloroethylene molecules to the film surface in electric field (Fig. 11).

According to M.Aono,[138] local treatment of a polymer or polymeric composite requires the following:

— to select a spot on the surface with atoms,

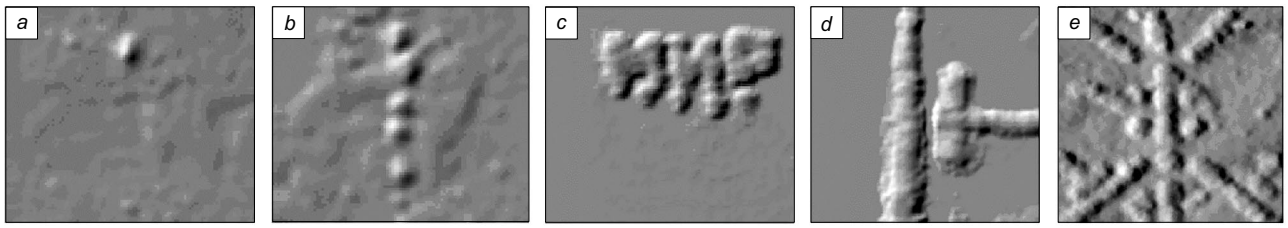


Figure 11. Atomic writing.[137]
Dots that make up symbols represent fragments of trichloroethylene molecules prepared by grafted oligomerization induced by electric field of the cantilever of a scanning tunnelling microscope. Frame size: 0.4×0.4 μm and dot cross-section size is 40 nm (*a*–*c*); image of field-emitting transistor (*d*); and a neuron quantum integrated circuit (frame size 0.4–0.4 μm).

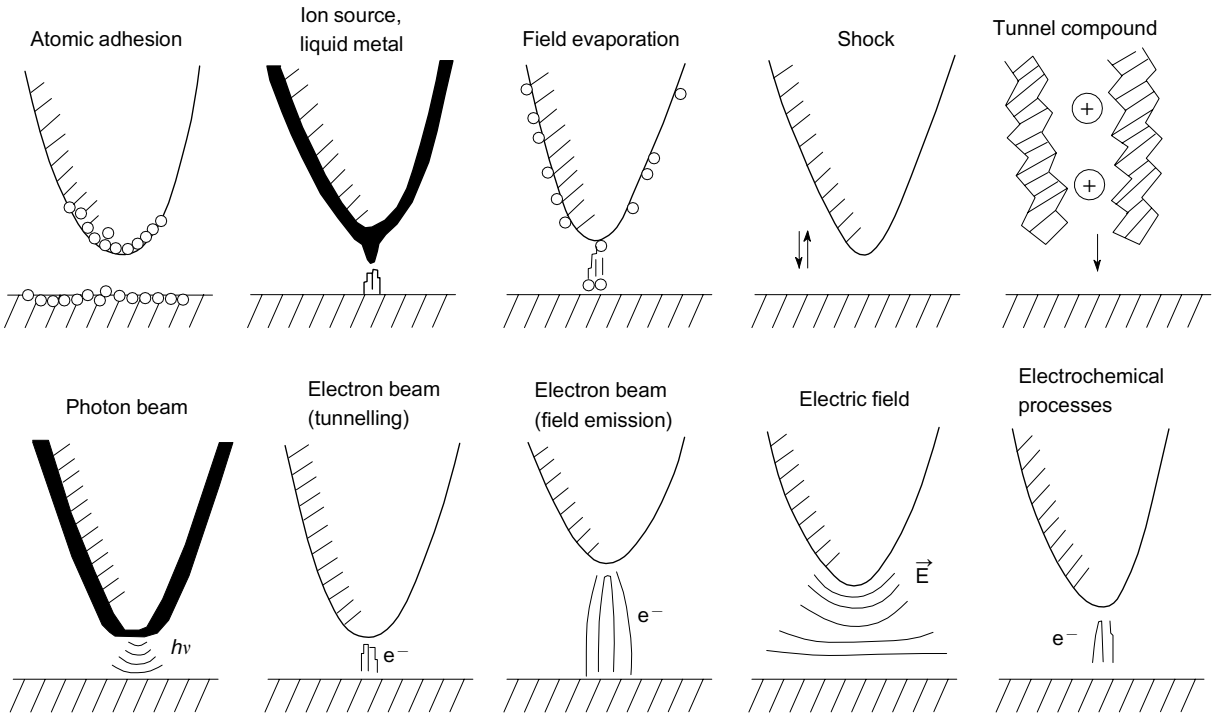


Figure 12. Physical processes and methods used for treatment of polymeric systems on atomic level.[138]
Shown are schemes of manipulation of particular atoms on silicon surface to assembly nanostructures. The physical effects indicated were used to extract, move and exactly locate atoms. All manipulations were carried out using a scanning tunnelling microscope.

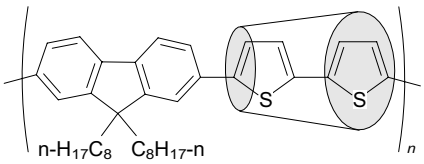
— to move atoms, and

— to pick atoms on the tip apex and supply them to the spot of interest on the substrate surface.

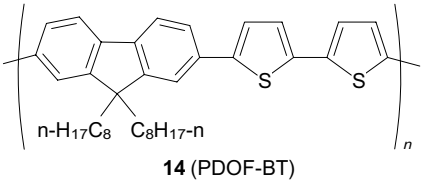
Appropriate physical processes and methods are shown in Fig. 12.

Among promising present-day chemical apparoaches to modification of polymers, there are supramolecular chemistry methods. In 1987, J.-M.Lehn, Ch.J.Pedersen and D.J.Cram were awarded the Nobel Prize in chemistry 'for their development and use of molecules with structure-specific interactions of high selectivity'. To date, the list of known supramolecular systems includes, *e.g.*, catenanes, rotaxanes, molecular knots[188] and molecular Borromean rings whose components are linked by noncovalent (first of all, hydrogen) bonds. For instance, rotaxanes consist of one or more macrocycles encircling a linear macromolecule and holding on it through noncovalent interactions.[189–191] Threading of the macrocycle onto conjugated macromolecular chains does not violate π-conjugation along the chain and favours improvement of the solubility, morphology, thermal stability and film-forming ability of the complex thus obtained.[192, 193] The mobility of charge carriers in thin films of polyrotaxane, that is, a supramolecular complex of a fluorene/bithiophene copolymer (PDOF-BT) with macrocyclic methylated β-cyclodextrin (PDOF-BT·RM-βCD) (structures **13**–**15**)[194] in external electric field is nearly halved compared to that in the PDOF-BT film.[195] In this case, the macrocycle (β-cyclodextrin) insulates a proportion of thiophene moieties of the macromolecule, thus reducing the concentration of transport centres involved in the intermolecular transfer of charge carriers. The use of macrocycles bearing fragments containing charge-transport or photoactive centres may appear to be a fine tool for controlling the conductivity and photoconductivity of polyrotaxanes. Successful attempt of synthetic chemists to thread macrocycles onto two adjacent macromolecular chains will be a landmark event on the way towards molecular gates, diodes and other elements of molecular electrical chains.

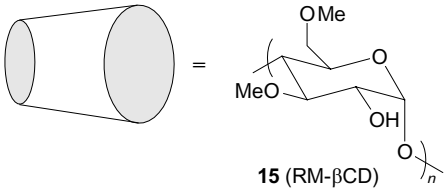
Structures 13–15



13 (PDOF-BT·RM-βCD)



14 (PDOF-BT)



15 (RM-βCD)

Most recently designed types of composites that proved themselves materially can be considered promising for fabrication of corresponding prototypes using additive manufacturing technologies. It is of great importance to take into account the character of connectivity of structural fragments in these materials, the change in their size compared to the size of the functional structure, the function of these fragments and the intensity of their response to the action of external factors. A classification of composites initially proposed by Newnham *et al.*[196] for materials with ferroelectric fillers appears to be suitable for composites with other functional fillers.

11. Conclusion

Our analysis of published data showed that studies on the field effects and relaxation processes induced by them in physical chemistry of polymers began in the early stage of development of synthetic polymer chemistry and polymer materials science. Initially, they were mainly aimed at establishing consequences of the action of physicomechanical factors, although important results concerning degradation of polymeric materials under the action of thermal loads, light, electric breakdown and ionizing radiation were obtained. These investigation lines and the discovery of new effects associated with the dynamics of chemical reactions formed the basis of a new branch of chemical science, *viz.*, polymerization under nonclassical conditions, in particular, in electromagnetic and other physical fields. Successful development of this avenue of research is, in particular, due to intensification of activity in the field of additive manufacturing technologies. We believe that symbiosis of these two important branches of modern materials science has great potential for practical application.

As applied to physical chemistry of polymers, the state-of-the-art in the studies of electromagnetic field effects has much in common with the situation in molecular biology described by Academician A.L.Buchachenko. The results obtained are ambiguous, irreproducible and contradictory. This is particularly clearly seen when analyzing data of studies on microwave heating of reaction mixtures containing polar components (ambiguity is mainly due to the problems with high-precision measurements of the synthesis temperatures) reported by different authors. Besides, with few exceptions, there are no methods for predicting how electromagnetic fields will act on new reaction mixtures and materials.

In connection with the aforesaid emphasize that not so important are the random positive effects as the regularities established in properly designed experiments (*i.e.*, undistorted, reliable and reproducible results of the action of each kind of electromagnetic field on particular reaction mixtures or other polymeric systems).

As mentioned above, retardation of cationic polymerization of 1,3-dioxolane in the presence of carbonyl salt Ph_3CSbF_6 is an important result[49] which, in particular, suggested that polymerization in this reaction mixture proceeds on active sites representing free ions. It remains unclear why the yield of polymer in radical polymerization of acrylamide in a water–methanol mixture (1 : 1) decreased from 52.80% under ambient conditions to 38.56% and 35.01%, upon switching on a magnetic field of 1.72% and 7.24 kGs, respectively, although the molecular mass of the polymer increased in both cases under magnetic field.[197]

However, these changes were not observed in the polymerization in water. The yield of polymer was 72.83% in the absence of magnetic field and 71.34%, 70.77% and 73.08% in a magnetic field of 3.50, 5.50 and 7.30 kGs, respectively, being dependent on the monomer concentration in the starting mixture (the lower the monomer concentration in the starting mixture the larger the decrease in the polymer yield in the magnetic field). These unusual regularities of radical polymerization in magnetic field were previously unknown. In this connection further experiments are required to gain a better insight into these effects and to study the effect of solvents on the magnitude and character of the response to the action of magnetic field.

Also, a large array of reliable results confirmed by many researchers includes those which point to the lack of conscientiousness, incompetency or misbelief of the authors presenting their results that can be treated as science fiction. The breeding grounds for this consist in the fact that the experimental conditions and exact composition of systems under study are not always specified in detail, so certain results cannot be verified at all. Examples are provided by the statements that (i) rubber polymer is transformed into superconductor under UV irradiation, (ii) there always exists a nonthermal contribution of the effect of microwave radiation on the syntheses and synthetic polymers,[198] and (iii) pulsed magnetic field makes it possible to improve the physicomechanical properties of natural and artificial polymer fibres.[199] There is good reason to agree with the author of a review [200] on the magnetooptical effects in diamagnetics (including polymers) in that elucidation of magnetic field effects on diamagnetic materials requires the use of high-resolution methods.

Additionally, quasi-sensational results (luckily, isolated cases) reduce confidence in this promising avenue of research and deserve criticism in the scientific community. This type of reasoning is called sophism according to Aristotle, or *renyxa* according to Professor A.I.Kitaigorodskii.[201] Meanwhile this should be treated with care since spin chemistry was also once erroneously called *renyxa*; this could influence the progress in this field of knowledge.

Summing up, emphasize the following: if the mid-20th century and late-20th century can be called the kinetic period in relation to physical chemistry of polymers, the early 21th century is the era of polymer materials science, associated with expectations of solving various scientific and technological problems including those based on the effects considered in this review.

We believe that our review on the effects of electromagnetic fields on polymer syntheses and polymeric materials would be incomplete without information on feasible and prospective studies aimed to solve new scientific and social problems. Their efficiency can, in particular, be illustrated considering widely used electroflocculation technique for manufacturing of carpet products for household use.[202] Considerable advances have been made in photopolymerization; the method has great potential for practical application in advanced nano- and microadditive manufacturing technologies.[203 – 206] It is highly plausible that fabrication of highly porous fibres by electrospinning will be widely used in the design of more efficient media for chemical power sources.[207, 208] Magnetospinning [187] allows one to obtain highly porous magnetic fibres for nanorobotics, smart structures [209] and other nanoscale devices.[210] This offers prospects for solving immediate tasks in microelectronics. Solution of problems typical of polymer chemistry requires answers to the following questions:[210 – 212]

— do electromagnetic fields influence the molecular mass distribution of polymers being syntheszied?

— how can the molecular mass distribution be controlled?

— what are minimum electric field strengths for controlling the polymer microstructure in various polymerization systems since the microstructure of polymers is invaluable source of information?

All research avenues considered in the review have passed the initial stage of development. They have great potential for future progress (see above), as indicated by recent advances in studies of dendrimers [213] and organic electronics.[214]

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Figure 4 is a courtesy of Springer Nature.

Figure 10 is a courtesy of Wiley.

Figure 12 is a courtesy of the American Chemical Society.

References

1. A.L.Buchachenko. *Russ. Chem. Rev.*, **68**, 85 (1999)
2. A.L.Buchachenko. *Novaya Izotopiya v Khimii i Biologii*. (New Isotopy in Chemistry and Biology). (Moscow: Nauka, 2007)
3. V.V.Logvinov. *Vse Otkrytiya i Dostizheniya Nauki i Tekhniki za Poslednie 200 Let*. (All Discoveries and Achievements of Science and Engineering in the last 200 years). (Moscow: Knizhnyi Dom Librokom, 2014)
4. A.A.Berlin, E.V.Prut. *Soros Educ. J.,* **6** (4), 30 (2000)
5. V.I.Irzhak. *Arkhitektura Polimerov*. (Polymer Architecture). (Moscou: Nauka, 2012)
6. K.K.Kalnin'sh, E.F.Panarin. *Vozbuzhdennye Sostoyaniya v Khimii Polymerov)*. (Excited States in the Chemistry of Polymers). (St. Petersburg: SPGUTD Polygraphic Center, 2007)
7. A.D.Stadnik, G.V.Kirik. *Polimernye Kompozity i Nanokompozity v Magnitnykh Polyakh)*. (Polymer Composites and Nanocomposites in Magnetic Fields). (Sumy: Universitetskaya Kniga, 2005)
8. W.Schnabel. *Polymers and Electromagnetic Radiation: Fundamentals and Practical Application*. (Weinheim: Wiley, 2014)
9. A.R.Blythe, D.Bloor. *Electrical Properties of Polymers*. (Cambridge: Cambridge University Press, 2005)
10. G.A.Lushcheikin. *Polimernye Elektrolity*. (Polymeric Electrolytes). (Moscow: Khimiya, 1976)
11. J.A.Gorokhovatskij. *Osnovy Termodepolyarizatsionnogo Analiza*. (The Fundamentals of Thermodepolarization Analysis). (Moscow: Nauka, 1981)
12. A.N.Lachinov, N.V.Vorob'eva. *Phys.-Uspekhi*, **49**, 1223 (2006)
13. H.Hayden, S.Park, V.Zhirnov, R.Cavin, P.A.Kohl. *J. Nanopart. Res.*, **12**, 2335 (2010)
14. N.S.Enikolopyan, Yu.A.Berlin, S.I.Beshenko, V.A.Zhorin. *JETP Lett.*, **33**, 492 (1981)
15. M.Lauters, B.McCarthy, D.Sarid, G.E.Jabbour. *Appl. Phys. Lett.*, **89**, 013507 (2006)

16. V.A.Kolesnikov, M.G.Tedoradze, A.R.Tameev, A.V.Vannikov. *Polym. Sci., Ser. B*, **50**, 305 (2008)
17. X.Liu, Z.Ji, D.Tu, L.Shang, J.Liu, M.Liu, C.Xie. *Org. Electron.*, **10**, 1191 (2009)
18. A.R.Tameev, A.N.Lachinov, R.B.Salikhov, A.A.Bunakov, A.V.Vannikov. *Russ. J. Phys. Chem., A*, **79**, 2025 (2005)
19. S.-H.Hong, O.Kim, S.Choi, M.Reea. *Appl. Phys. Lett.*, **91**, 093517 (2007)
20. A.R.Tameev, R.G.Rakhmeev, V.R.Nikitenko, R.B.Salikhov, A.A.Bunakov, A.N.Lachinov, A.V.Vannikov. *Phys. Solid State*, **53**, 195 (2011)
21. A.Zherebov, A.Lachinov, J.Genoe, A.Tameev. *Appl. Phys. Lett.*, **92**, 193302 (2008)
22. J.C.C.Fan, J.B.Goodenough. *J. Appl. Phys.*, **48**, 3524 (1977)
23. V.R.Nikitenko, A.R.Tameev, A.V.Vannikov, A.N.Lachinov, H.Bässler. *Appl. Phys. Lett.*, **92**, 153307 (2008)
24. E.A.Lebedev, E.L.Alexandrova, A.N.Aleshin. *Phys. Solid State*, **51**, 208 (2009)
25. O.A.Ponomarev, E.S.Shikhovtseva. *J. Exp. Theor. Phys.*, **80**, 346 (1995)
26. S.N.Salazkin, V.V.Shaposhnikova, L.N.Machulenko, N.G.Gileva, V.A.Kraikin, A.N.Lachinov. *Polym. Sci., Ser. A*, **50**, 243 (2008)
27. B.G.Zykov, Yu.V.Vasil'ev, V.S.Fal'ko, A.N.Lachinov. V.I.Khvostenko, N.G.Gileva. *JETP Lett.*, **64**, 439 (1996)
28. L.N.Grigorov. *Pis'ma Zh. Tekh. Fis.*, **17** (10), 45 (1991)
29. M.N.Nikolaeva. Candidate Thesis in Physical and Mathematical Sciences. PTI RAS, 2007
30. A.N.Ionov. *J. Exp. Theor. Phys.*, **116**, 834 (2013)
31. A.T.Ponomarenko, A.R.Tameev, V.G.Shevchenko. *Intern. Sci. J. Alternat. Energy Ecol.*, (1–2), 88 (2016)
32. A.T.Ponomarenko, A.R.Tameev, V.G.Shevchenko. *Intern. Sci. J. Alternat. Energy Ecol.*, (3–4), 93 (2016)
33. *Electrochemistry of Polymers*. (Eds M.P.Tarasevich, E.I.Khrushcheva). (Moscow: Nauka, 1990)
34. V.F.Ivanov. Doctoral Thesis in Chemical Sciences. IPCE RAS, 2007
35. O.D.Omel'chenko, O.L.Gribkova, A.A.Nekrasov, V.A.Tverskoi, V.F. Ivanov, A.V.Vannikov. *Prot. Met. Phys. Chem. Surf.*, **47**, 503 (2011)
36. J.W.Breitenbach, O.F.Olaj, F.Sommer. *Adv. Polym. Sci.*, **9**, 48 (1972)
37. G.S.Shapoval, A.V.Gorodyskii. *Russ. Chem. Rev.*, **42**, 370 (1973)
38. G.S.Shapoval, T.E.Lipatova. *Elektrokhimicheckoe Initsiirovaniye Polymerisatsii*. (Electrochemical Initiation of Polymerization) (Kiev: Naukova Dumka, 1977)
39. *The New Frontiers of Organic and Composite Nanotechnology*. (Eds V.Erokhin, M.Kumar Ram, O.Yavuz). (Oxford, Amsterdam: Elsevier, 2008)
40. *Handbook of Organic Conductive Molecules and Polymers*: *Conductive Polymers: Synthesis and Electrical Properties*. Vol. 2. (Ed. H.S.Navla). (Chichester: Wiley, 1997)
41. *Elektroanaliticheskiye Metody (Teoriya i Praktika)*. [Electroanalytical Methods (Theory and Practice)] Moscow: Binom. Laboratoriya Znanii, 2009)
42. T.V.Vernitskaya, O.N.Efimov. *Russ. Chem. Rev.*, **66**, 443 (1997)
43. *Electropolymerization. Concepts, Materials and Application*. (Eds S.Cosnier, A.Karyakin). (Weinheim: Wiley-VCH, 2010)
44. P.Chmielarz, M.Fantin, S.Park, A.A.Isse, A.Gennaro, A.J.D.Magenau, A.Sobkowiak, K.Matyjaszewski. *Prog. Polym. Sci.*, **69**, 47 (2017)
45. E.H.Discekici, A.Anastasaki, R.Kaminker, J.Willenbacher, N.P.Truong, C.Fleishman, B.Oschman, D.J.Lunn, J.R.de Alaniz, T.P.Davis, C.M.Bates. *J. Am. Chem. Soc.*, **39**, 5939 (2017)
46. M.Szwarc. *Carbanions, Living Polymers and Electron Transfer Processes*. (New York: Wiley, 1968)
47. Yu.D.Semchikov, in *Vysokomolekulyarnye Soedineniya* (High-Molecular Compounds). (Moscow Akademiya, 2005). P. 25
48. N.Ise. *Adv. Polym. Sci.*, **6**, 347 (1969)
49. A.T.Ponomarenko, A.R.Tameev, V.G.Shevchenko. *Bull. Russ. Acad. Sci. Phys.*, **80**, 1131 (2016)]
50. A.P.Persoons. *J. Phys. Chem.*, **78**, 1210 (1974)
51. S.S.Dukhin, B.V.Derjaguin.*Elektroforez*. (Electrophoresis). (Moscow: Nauka, 1976)
52. M.M.Khaletskii, B.I.Sukhorukova. *Vysokomol. Soedin.*, **3**, 1347 (1961)
53. *Electromigration Techniques. (Springer Ser. in Chemical Physics)*. Vol. 105. (Eds B.Buszewski, E.Dziubakievicz, M.Szumski). (Berlin, Heidelberg: Springer-Verlag, 2013)
54. E.Du, S.Manoochehri. *Electrophoresis*, **29**, 5017 (2008)
55. H.A.Pohl. *J. Appl. Phys.*, **29**, 1182 (1958)
56. H.A.Pohl. *Dielectrophoresis: the Behavior of Neutral Matter in Nonuniform Electric Fields*. Vol. 80. (Cambridge: Cambridge University Press, 1978)
57. X.D.Wang, J.Vykoukal, F.F.Becker, P.R.C.Gascoyne. *Biophys. J.*, **74**, 2689 (1998)
58. K.M.Gorbunova, P.D.Dankov. *Uspekhi Khimii*, **17**, 710 (1948)
59. K.J.Vetter. *Electrochemical Kinetics*. (Academic Press, 1967)
60. R.Kaishev. *Izbrannye Trudy*. (Selected Works). (Sofia: Bulgarian Academy of Sciences, 1980)
61. A.I.Danilov, Yu.M.Polukarov. *Russ. Chem. Rev.*, **56**, 619 (1987)
62. S.A.Vshivkov. *Fazovye Perekhody Polimernykh Sistem vo Vneshnikh Polyakh*. (Phase Transitions of Polymer Systems in External Fields). (Ekaterinburg: AMB, 2011)
63. Al.Al.Berlin, R.Ya.Deberdeev, Yu.V.Petrukhin, R.M.Garipov. *Polioksimetileny*. (Polyoxymethylenes). (Moscow: Nauka, 2008)
64. H.Roth, F.Keller, G.Fleisher. *Fazerforsch. Textiltechn.*, **25**, 539 (1974)
65. Yu.B.Amerik, B.A.Krentsel, M.V.Shishkina. *Dokl. Akad. SSSR*, **163**, 364 (1965)
66. H.J.Kreuzer. *Surf. Interface Anal.*, **36**, 372 (2004)
67. Y.W.Li, J.H.Zhu, C.J.Liu, J.Q.Jiang. *Polym. Lett.*, **3**, 684 (2009)
68. *Strong and Ultrastrong Magnetic Fields and their Applications. Topics in Applied Physics*. Vol. 67. (Ed. F.Herlach). (Berlin, Heidelberg, New York, Tokyo: Springer Verlag, 1985)
69. A.P.Chiriac. *J. Appl. Polym. Sci.*, **98**, 1025 (2005)
70. A.P.Chiriac. *J. Polym. Sci., Part A: Polym. Chem.*, **42**, 5678 (2004)
71. A.P.Chiriac, I.Neamtu, C.I.Simionescu. *Angew. Makromol. Chem.*, **273**, 75 (1999)
72. D.S.Bag, S.Maiti. *Polymer*, **39**, 525 (1998)
73. I.Rintoul, C.Wandrey. *Macromol. Symp.*, **261**, 121 (2008)
74. D.S.Bag, S.Maiti. *J. Polym. Sci., Part A: Polym. Chem.*, **36**, 1509 (1998)
75. A.A.Kipriyanov Jr., P.A.Purtov. *Vestn. NGU. Ser. Fiz.*, **2** (4), 88 (2007)
76. G.Filipcsei, I.Csetneki, A.Szilagyi, M.Zriny. *Adv. Polym. Sci.*, **206**, 137 (2007)
77. I.V.Kubrakova. *Russ. Chem. Rev.*, **71**, 283 (2002)
78. A.T.Ponomarenko, V.G.Shevchenko. *Nanosist., Nanomater., Nanotekhnol.*, **13**, 117 (2015)
79. R.A.Kuznetsov, A.N.Mudrov, T.A.Ageeva, O.A.Koifman. *Izv. Vyssh. Uchebn. Zaved., Khim., Khim. tekhnol*, **51** (12), 58 (2008)
80. Yu.V. Rumyantseva, R.A.Kuznetsov, A.N.Mudrov, T.A.Ageeva O.A.Koifman. *Izv. Vyssh. Uchebn. Zaved., Khim., Khim. tekhnol*, **55** (12), 114 (2012)
81. D.Bogdal, P.Penczec, J.Pielichovsky, A.Prociak. *Adv. Polym. Sci.*, **163**, 194 (2003)

82. D.Bogdal, A.Prociak. *Microwave-Enhanced Polymer Chemistry and Technology*. (Austin: Blackwell Publishing Professional, 2007)
83. V.Ch.Bokun, V.A.Tarasenko, Yu. P.Bass, A.N.Ponomarev. *Khim. Fiz.*, **21**, 83 (2002)
84. A.P.Magunov. *Lazernaya Termometriya Tverdykh Tel*. (Laser Thermometry of Solids) (Moscow: Fizmatlit, 2001)
85. M.I.Bil'ko, A.K.Tomashevskii. *Izmerenie Moshchnosti na SVCh*. (Measurement of Power on a Microwave). (Moscow: Radio i Svyas', 1986)
86. R.Correa, G.Gonzalez, V.Dougar. *Polymer*, **39**, 1471 (1998)
87. A.F.Porto, L.B.Sadicoff, C.V.M.Amorim, M.C.S.Mattos. *Polym. Test.*, **21**, 145 (2002)
88. Z.Cheng, X.Zhu, N.Zhou, J.Zhu, Z.Zhang. *Radiat. Phys. Chem.*, **72**, 695 (2005)
89. C.Koopmans, M.Iannelli, P.Kerep, M.Klink, S.Schmitz, S.Sinnwell, H.Ritter. *Tetrahedron*, **62**, 4709 (2006)
90. M.S.Cortizo, S.Laurella, J.L.Alessandrini. *Radiat. Phys. Chem.*, **76**, 1140 (2007)
91. A.G.Alekseev, E.V.Shtager, S.V.Kozyrev. *Fizicheskie Osnovy Tekhnologii Stealth*. (Physical Bases of Stealth Technology). (Saint Petersburg: Izd. VVM, 2007)
92. A.N.Lagar'kov, M.A.pogosyan. *Vestn. RAS* , **73**, 779 (2003)
93. A.N.Didenko, B.V.Zverev. *SVCh-Energetika*. (Microwave Energy). (Moscow: Nauka, 2000)
94. T.Ershova. *Electronica*, (3), 64 (2013)
95. V.G.Shevchenko, V.N.Apletalin, A.T.Ponomarenko, Yu.N.Kazantsev. *Proc. SPIE*, **2722**, 216 (1996)
96. N.N.Trofimov, M.Z.Kanovich, E.M.Kartashov, V.I.Natrusov, A.T.Ponomarenko, V.G.Shevchenko, V.I.Sokolov, I.D.Simonov-Emel'yanov, in *Fizika Kompozitnykh Materialov*. (Physics of Composite Materials). (Moscow: Mir, 2005). Vol. 2, P. 246
97. *Microwaves in Organic Synthesis*. (Ed. A.Loupy). Wiley-VCH, Weinheim, 2002
98. R.Haberkorn, M.E.Mechel-Beyerle. *Biophys. J.*, **26**, 489 (1979)
99. N.J.Turro, G.C.Weed. *J. Am. Chem. Soc.*, **105**, 1861 (1983)
100. A.L.Buchachenko, E.L.Frankevich. *Chemical Generation and Reception of Radio and Microwaves*. (Weinheim, New York, Basel, Cambridge, Tokyo: VCH, 1994)
101. U.E.Steiner, T.Ulrich. *Chem. Rev.*, **89**, 51 (1989)
102. M.R.Wasielewski, C.H.Bock, M.K.Bowman, J.R.Norris. *Nature (London)*, **303**, 520 (1983)
103. M.Okazaki, Y.Konishi, K.Toriyama. *Chem. Lett.*, **23**, 737 (1994)
104. M.Mukai, Y.Fujiwara, Y.Tanimoto, Y.Konishi, M.Okazaki. *Z. Phys. Chem.*, **180**, 223 (1993)
105. K.M.Salichov, Y.N.Molin, R.Z.Sagdeev, A.L.Buchachenko. *Spin Polarization and Magnetic Field Effect in Radical Reactions*. (Amsterdam: Elsevier, 1984)
106. *Biophysical Effects of Steady Magnetic Fields*. (Eds G.Maret, J.Kiepenheuer, N.Boccara). (Berlin, Heidelberg: Springer-Verlag, 1986)
107. C.R.Timmel, U.Till, B.Brocklehurst, K.A.McLauchlan, P.J.Hore. *Mol. Phys.*, **95**, 71 (1998)
108. U.Till, C.R.Timmel, B.Brocklehurst, P.J.Hore. *Chem. Phys. Lett.*, **298**, 7 (1998)
109. B.Brocklehurst. *J. Chem. Soc., Faraday Trans*, **72**, 1869 (1976)
110. B.Brocklehurst, K.A.McLauchlan. *Int. J. Radiat. Biol.*, **69**, 3 (1996)
111. J.R.Woodward, R.J.Jackson, C.R.Timmel, K.A.McLauchlan, P.J.Hore. *Chem. Phys. Lett.*, **272**, 376 (1997)
112. D.V.Stass, J.R.Woodward, C.R.Timmel, P.J.Hore, K.A.McLauchlan. *Chem. Phys. Lett.*, **329**, 15 (2000)
113. C.R.Timmel, J.R.Woodward, P.J.Hore, K.A.McLauchlan, D.V.Stass. *Meas. Sci. Technol.*, **12**, 635 (2001)
114. A.J.Hoff, B.Cornelissen. *Mol. Phys.*, **45**, 413 (1982)
115. C.T.Rodgers. *Pure Appl. Chem.*, **81**, 19 (2009)
116. K.Miyamoto. *Fundamentals of Plasma Physics and Controlled Fusion*. (Tokyo: Tokyo University, 2005)
117. *Entsiklopediya Nizkotemperaturnoi Plazmy*. (Encyclopedia of Low-Temperature Plasma) Vol 3. (Ed. V.E.Fortov). (Moscow: Nauka, 2000)
118. P.Tipler, G.Mosca. *Physics for Scientists and Engineers: Electricity, Magnetism, Light, and Elementary Modern Physics*. (New York: Freeman, 2004)
119. N.D.Andreev. *Organicheskii Sintez v Electricheskikh Razryadakh*. (Organic Synthesis in Electric Discharge) (Leningrad, Moscow: RISO AN SSSR, 1953)
120. V.I.Zyn'. *Predpolimerizatsiya v Plazme*. (Pre-polymerization in Plasma). (Samara: NTs RAN, 2016)
121. M.V.Akulova, B.N.Mel'nikov, S.V.Fedosov, L.V.Sharnina. *Primenenie Tleyushchego Razryada v Tekstil'noi i Stroitel'noi Promyshlennosti*. (The Use of Glow Discharge in the Textile and Construction Industry) (Ivanovo: IGKhTU, 2008)
122. A.I.Drachev, A.B.Gil'man. *Russ. J. Phys. Chem.*, **82**, 1733 (2008)
123. A.N.Ponomarev, V.N.Vasilets, R.V.Tal'roze. *Khim. Fiz.*, **21**, 96 (2002)
124. X.Yasuda *Plasma Polymerization*. (London: Academic Press, 1985)
125. E.A.Sergeeva, V.S.Zheltukhin, I.Sh.Abdulin. *Modifikatsiya Sinteticheskikh Voloknistykh Materialov i Izdeliy Neravnovesnoy Nizkotemperaturnoy Plazmoy. Teoriya, Modeli, Metody*. (Modification of Synthetic Fibrous Materials and Products by Nonequilibrium Low-temperature Plasma. Theory, Models, Methods). (Kazan': GKTU, 2011). Pt. 1
126. E.A.Sergeeva, N.V.Korneva, L.A.Zenitova, I.Sh.Abdulin. *Modifikatsiya Sinteticheskikh Voloknistykh Materialov i Izdeliy Neravnovesnoy Nizkotemperaturnoy Plazmoy. Svoistva, Struktura, Tekhnologii*. (Modification of Synthetic Fibrous Materials and Products by Nonequilibrium Low-temperature Plasma. Properties, Structure, Technologies). (Kazan': GKTU, 2011). Pt. 2
127. V.K.Milinchuk. *Soros Educ. J. Chem.,* **6** (4), 24 (2000)
128. V.Ya.Kabanov, V.I.Feldman, B.G.Ershov, A.I.Polikarpov, D.P.Kiryukhin, P.Yu.Apel'. *High Energy Chem.*, **43**, 1 (2009)
129. S.Ya. Pshezhetskyi. *Mekhanizm Radiatsionno-Khimicheskikh Reaktsiy*. (Mechanism of Radiation-Chemical Reactions). (Moscow: Gos. Nauch.-Teh. Izd. Khim. Lit., 1962)
130. A.P.Tyutnev, V.P.Saenko, E.D.Pozhidaev, N.S.Kostyukov. *Dielektricheskiye Svoystva Polimerov v Polyakh Ioniziruyushchikh Izlucheniy*. (Dielectric Properties of Polymers in Ionizing Radiation Fields). (Moscow: Nauka, 2005)
131. *Radioliz Uglevodorodov*. (Radiolysis of Hydrocarbons). (Eds A.V.Topchiev, L.S.Polak). (Moscow: Izd. Akad. Nauk SSSR, 1962)
132. V.K.Grishchenko, A.F.Maslyuk, S.S.Gudzera. *Zhidkiye Fotopolimerizuyushchiyesya Kompozitsii*. (Liquid Photopolymerizable Compositions). (Kiev: Naukova Dumka, 1985)
133. E.Caldin. *Fast Reactions in Solutions*. (New York: Willey, 1964)
134. S.A.Chesnokov, V.M.Treushnikov, Yu.V.Chechet, V.K.Cherkasov, O.N.Mamusheva. *Polym. Sci., Ser. A*, **50**, 291 (2008)
135. W.Schnabel. *Polymers and Light (Fundamental and Technical Application)*. (Weinheim: Wiley-VCH, 2007)
136. A.Ravve. *Light Associated Reaction of Synthetic Polymers*. (Berlin, Heidelberg: Springer-Verlag, 2006)
137. E.F.Sheka *Ros. Khim. Zh.*, **46** (5), 15 (2002)
138. P.S.Weiss. *ACS Nano*, **1**, 379 (2007)
139. M.Burnworth, L.Tang, J.R.Kumpfer, A.J.Duncan, F.L.Beyer, G.L.Fiore, S.J.Rowan, C.Weder. *Nature (London)*, **472**, 334 (2011)
140. E.F.Abdrashitov, D.A.Kritskaya, V.Ch.Bokun, A.N.Ponomarev. *High Energy Chemistry*, **46**, 24 (2012)

141. C.Deibel, T.Strobel, V.Dyakonov. *Adv. Mater.*, **22**, 4097 (2010)
142. F.Gao, O.Inganäs. *Phys. Chem. Chem. Phys.*, **16**, 20291 (2014)
143. A.P.Tyutnev, R.Sh.Ikhsanov, A.R.Tameev, V.S.Saenko. *Polym. Sci., Ser. A*, **55**, 778 (2013)
144. L.Lu, T. Zheng, Q. Wu, A.M.Schneider, D.Zhao, L.Yu. *Chem. Rev.*, **115**, 12666 (2015)
145. W.Zhao, S.Li, S.Zhang, X.Liu, J.Hou. *Adv. Mater.*, **29**, 1604059 (2017)
146. S.Li, L.Ye, W.Zhao, S.Zhang, S.Mukherjee, H.Ade, J.Hou. *Adv. Mater.*, **28**, 9423 (2016)
147. S.D.Dimitrov, J.R.Durrant. *Chem. Mater.*, **26**, 616 (2014)
148. H.van Eersel, R.A.J.Janssen, M.Kemerink. *Adv. Funct. Mater.*, **22**, 2700 (2012)
149. D.Gendron, M.Leclerc. *Energy Environ. Sci.*, **4**, 1225 (2011)
150. Z.Zuo, Y.Li. *Polym. Bull.*, **68**, 1425 (2012)
151. G.V.Bulavko, A.A.Ishchenko. *Russ. Chem. Rev.*, **83**, 575 (2014)
152. S.Beaupré, M.Leclerc. *J. Mater. Chem. A*, **1**, 11097 (2013)
153. M.C.Scharber, D.Mühlbacher, M.Koppe, P.Denk, C.Waldauf, A.J.Heeger, C.J.Brabec. *Adv. Mater.*, **18**, 789 (2006)
154. Y.Kim, S.A.Choulis, J.Nelson, D.D.C.Bradley, S.Cook, J.R.Durrant. *Appl. Phys. Lett.*, **86**, 063502 (2005)
155. Y.Zhou, Y.Li, H.Zhong, J.Hou, Y. Ding, C.Yang, Y.Li. *Nanotechnology*, **17**, 4041 (2006)
156. D.Mühlbacher, M.Scharber, M.Morana, Z.Zhu, D.Waller, R.Gaudiana, C.Brabec. *Adv. Mater.*, **18**, 2884 (2006)
157. I.H.Campbell, T. W.Hagler, D.L.Smith, J.P.Ferrais. *Phys. Rev. Lett.*, **76**, 1900 (1996)
158. W.Yue, Y.Zhao, S.Shao, H.Tian, Z.Xie, Y. Geng, F.Wang. *J. Mater. Chem.*, **19**, 2199 (2009)
159. Y.Liang, Z.Xu, J.Xia, S.T.Tsai, Y.Wu, G.Li, C.Ray, L.Yu. *Adv. Mater.*, **22**, E135 (2010)
160. Y. Zou, A.Najan, P.Berrouard, S.Beaupré, B.R.Aich. *J. Am. Chem. Soc.*, **132**, 5330 (2010)
161. L.Pandey, C.Risko, J.E.Norton, J.-L.Brédas. *Macromolecules*, **45**, 6405 (2012)
162. H.Zhou, L.Yang, W.You. *Macromolecules*, **45**, 607 (2012)
163. L.Bian, E.Zhu, J.Tang, W.Tang, F.Zhang. *Prog. Polym. Sci.*, **37**, 1292 (2012)
164. M.L.Keshtov, S.A.Kuklin, A.R.Khokhlov, I.O.Konstantinov, N.V.Nekrasova, Z.Xie, G.D.Sharma. *Polymer*, **133**, 195 (2017)
165. H.-Y. Chen, J.Hou, S.Zhang, Y. Liang, G.Yang, Y.Yang, L.Yu, Y.Wu, G.Li. *Nat. Photon.*, **3**, 649 (2009)
166. C.Piliego, T.W.Holcombe, J.D.Douglas, C.H.Woo, P.M.Beaujuge, J.M.J.Fréchet. *J. Am. Chem. Soc.*, **132**, 7595 (2010)
167. J.L.Brédas, A.J.Heeger. *Chem. Phys. Lett.*, **217**, 507 (1994)
168. I.Meager, R.S.Ashraf, S.Mollinger, B.C.Schroeder, H.Bronstein, D.Beatrup, M.S.Vezie, T. Kirchartz, A.Salleo, J.Nelson, I.McCulloch. *J. Am. Chem. Soc.*, **135**, 11537 (2013)
169. V.M.Svetlichnyi, E.L.Aleksandrova, L.A.Myagkova, N.V.Matyushina, T.N.Nekrasova, R.Yu.Smyslov, A.R.Tameev, S.N.Stepanenko, A.V.Vannikov, V.V.Kudryavtsev. *Semiconductors*, **45**, 1339 (2011)
170. V.M.Svetlichnyi, E.L.Aleksandrova, T.N.Nekrasova, R.Yu.Smyslov, L.A.Miagkova, N.V.Matyushina. *Semiconductors*, **46**, 496 (2012)
171. V.M.Svetlichnyi, E.L.Aleksandrova, A.R.Tameev, L.A.Miagkova, N.V.Matyushina. *Semiconductors*, **46**, 491 (2012)
172. E.L.Aleksandrova, V.M.Svetlichnyi, N.V.Matyushina, L.A.Myagkova, V.V.Kudryavtsev, A.R.Tameev. *Semiconductors*, **48**, 1481 (2014)
173. E.L.Aleksandrova, V.M.Svetlichnyi, L.A.Myagkova, N.V.Matyushina, T.N.Nekrasova, R.Yu.Smyslov, V.D.Pautov, A.R.Tameev, A.V.Vannikov, V.V.Kudryavtsev. *Opt. Spectrosc.*, **114**, 737 (2013)
174. G.I.Nosova, A.V.Yakimanskii, N.A.Solovskaya, E.V.Zhukova, R.Yu.Smyslov, A.R.Tameev, E.L.Aleksandrova, T.V.Magdesieva. *Polym. Sci., Ser. B*, **53**, 16 (2011)
175. M.Kuik, G.-J.A.H.Wetzelaer, H.T.Nicolai, N.I.Craciun, D.M.De Leeuw, P.W.M.Blom. *Adv. Mater.*, **26**, 512 (2014)
176. H.Wu, L.Ying, W.Yang, Y.Cao. *Chem. Soc. Rev.*, **38**, 3391 (2009)
177. J.H.Park, J.Y.Kim, B.D.Chin, Y.C.Kim, J.K.Kim, O.O.Park. *Nanotechnology*, **15**, 1217 (2004)
178. C.-H.Chou, C.-H.Yang, C.-S.Hsu, T.-M.Chen. *J. Nanosci. Nanotechnol.*, **7**, 2785 (2007)
179. S.V.Dayneko, D.A.Lypenko, P.S.Samokhvalov, A.A.Chistyakov, I.Nabiev, G.I.Nosova, I.A.Berezin, A.V.Yakimanskii. *Opt. Spectrosc.*, **122**, 12 (2017)
180. I.Gibson, D.V.Rosen, D.Stuker. *Additive Manufacturing Technologies*. (Berlin, Heidelberg, New York, London: Springer-Verlag, 2010)
181. I.V.Petryanov-Sokolov, V.I.Kozlov, P.I.Basmanov, B.I.Ogorodnikov. *Voloknistye Filtruyushchie Materialy*. (Fibrous Filter Materials). (Moscow: Khimiya, 1968)
182. P.I.Basmanov, V.N.Kirichenko, Yu.N.Filatov, Yu.L.Yurov. *Vysokoeffektivnaya Ochistka Gazov ot Aerozoley Filtrami Petryanova*. (Highly Effective Gas Cleaning From Aerosols with Petryanov Filtres) (Moscow: Nauka, 2003)
183. A.A.Shutov. Doctoral Thesis in Physical and Mathematical Sciences. Karpov Institute of Physical Chemistry, Moscow, 2008
184. A.K.Budyka, B.I.Ogorodnikov, V.I.Skitovich. *J. Aerosol Sci.*, **24** (Suppl. 1), S205 (1993)
185. H.Esfahani, R.Jose, S.Ramakrishna. *Materials*, **10**, 1238 (2017)
186. S.L.Bazhenov. *Dokl. Phys. Chem.*, **441**, 227 (2011)
187. O.Tokarev, O.Trotsenko, I.M.Griffits, H.A.Stone, S.Minko. *Adv. Mater.*, **27**, 3560 (2015)
188. G.Schill. *Catenanes, Rotaxane, and Knots*. (New York: Academic Press, 1971)
189. J.A.Bravo, F.M.Raymo, J.F.Stoddart, A.J.P.White, D.J.Williams. *Eur. J. Org. Chem.*, 2565 (1998)
190. F.Huang, H.W.Gibson. *Prog. Polym. Sci.*, **30**, 982 (2005)
191. A.Harada, A.Hashidzume, H.Yamaguchi, Y.Takashima. *Chem. Rev.*, **109**, 5974 (2009)
192. S.Brovelli, G.Sforazzini, M.Serri, G.Winroth, K.Suzuki, F.Meinardi, H.L.Anderson, F.Cacialli. *Adv. Funct. Mater.*, **22**, 4284 (2012)
193. A.Farcas, G.Tregnago, A.-M.Resmerita, S.T.Dehkordi, S.Cantin, F.Goubard, P.-H.Aubert, F.Cacialli. *J. Polym. Sci., Part A: Polym. Chem.*, **52**, 460 (2014)
194. A.Farcas, I.Ghosh, V.C.Grigoras, I.Stoica, C.Peptu, W.M.Nau. *Macromol. Chem. Phys.*, **212**, 1022 (2011)
195. S.V.Kostromin, V.V.Malov, A.R.Tameev, S.V.Bronnikov, A.Farcas. *Techn. Phys. Lett.*, **43** (2), 173 (2017)
196. R.Newnham, D.P.Skinner, L.F.Gross. *Mater. Res. Bull.*, **13**, 525 (1978)
197. D.S.Bag, S.Maiti. *J. Polem. Sci., Part A: Polym. Chem.*, **36**, 1509 (1998)
198. S.G.Kalganova. Doctoral Thesis in Technical Sciences. Saratov, Saratov State Technical University, 2009
199. Yu.A.Persidskaya, I.P.Kuzeev, V.A.Antipin. *Khim. Fizika*, **21**, 90 (2002)
200. Yu.I.Golovin. *Phys. Solid State*, **46**, 789 (2004)
201. A.I.Kitaigorodskii. *Renyxa*. (Nonsense) (Moscow: Molodaya Gvardiya, 1973)
202. E.I.Bershev, L.V.Lobova. *Pechat' Vorsom*. (Pile Printing) (Moscow: Lesprombytizdat, 1989)
203. *Photophysics of Molecular Materials*. (Ed. Lanzani). (Weinheim: Wiley-VCH, 2006)
204. M.Vaezi, H.Seitz, S.Yang. *Int. J. Adv. Manuf. Technol.*, **67**, 1721 (2013)

205. *Manufacturing Technologies for Machines of the Future 21st — Century Technologies*. (Ed. A.Dashchenko). (Berlin, Heidelberg, New York, London: Springer-Verlag, 2003)
206. I.N.Evdokimova, A.P.Losev. *Razlichnye Vidy Nanotekhnologiy – Prinuditelnaya Sborka Atomnykh i Molekulyarnykh Struktur i Samosborka Molekulyarnykh Nanoobyektov*. (Different Types of Nanotechnology — Forced Assembly of Atomic and Molecular Structures and Self Assembly of Molecular Nanoobjects). (Moscow: Gubkin Russian State University of Oil and Gas, 2008)
207. Y.Chen, X.Li, L.Zhou, Y.-W.Mai, H.Huang, in *Multifunctionality of Polymer Composites*. (Eds K.Fridrich, U.Breuer). (Amsterdam, Tokyo: Elsevier, 2015). P. 662
208. A.M.Skundin, O.N.Efimov, O.V.Yarmolenko. *Russ. Chem. Rev.*, **71**, 329 (2002)
209. A.Ponomarenko, V.Shevchenko, O.Figovsky. *Sci. Israel-Technol. Adv.*, **10**, 119 (2008)
210. M.Otake. *Electroactive Polymer Gel Robots: Modelling and Control of Artificial Muscles (Ser. Springer Tracks in Advanced Robotics*. Vol. 59). (Berlin, Heidelberg: Springer-Verlag, 2010)
211. I.P.Suzdalev. *Russ. Chem. Rev.*, **78**, 249 (2009)
212. S.Ya.Frenkel', in *Fizika Segodnya i Zavtra*. (Physics Today and Tomorrow). (Ed. V.M.Tuchkevich). (Leningrad: Nauka, 1973). P. 176
213. A.M.Muzafarov, N.G.Vasilenko. *Priroda*, (6), 3 (2011)
214. O.V.Borshchev, S.A.Ponomarenko. *Polym. Sci., Ser. C*, **56**, 32 (2014)