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REVIEW

Radiation Chemistry of Polymers[1]

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Abstract—Results of basic and applied research in radiation chemistry of polymers in Russia and Belarus for the last 5–10 years are presented.

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MECHANISMS OF RADIATION-CHEMICAL PROCESSES IN POLYMERS

Despite of the fact that mechanisms of radiation-chemical processes in polymers have been the subject of a great variety of experimental studies over almost fifty years, the obtained results are controversial and fragmentary in many respects. Obviously, this is caused by both an insufficient level of understanding of the early stages of radiation-chemical effects and the complexity of the structure and composition of real polymers. The analysis of early works shows that in most cases it is difficult to unequivocally differentiate between "primary" (actual radiation-chemical) effects and secondary (postradiation) processes, which sometimes can proceed even at rather low temperatures in solid polymers. As applied to radiation chemistry of polymers, an intuitive model is widely used; according to this model, the primary cleavage of chemical bonds by the action of ionizing radiation occurs in the random (nonselective) mode and the further localization of the changes is associated with the specifics of the secondary reactions of radicals (concept of "molecular baton"). Meanwhile, these concepts generally are not physically justified and are inconsistent with many experimental data. An alternative approach based on the allowance for the specific selectivity of early stages of radiation-chemical processes in polymer systems has been developed during the last 10–15 years. The results of experimental studies in which the emphasis was placed on analysis of the properties of the primary ionized states and hole and electron migration processes, formed the basis for the concept of "molecular scalpel" [1–3]. These studies were characterized by the use of the helium range of temperatures (from 10 K) for the reconstruction of the initial pattern of distribution of radiation-chemical effects and the use of the matrix isolation method for the experimental modeling of the structure and properties of the most reactive intermediates, primary positive ions (radical cations). Obtaining the first direct experimental evidence for the selective localization of primary radiation-chemical effects on the conformational defects of macromolecules was of key importance to the concept. In particular, it was shown [1, 4] that, during irradiation of oriented linear polyethylene containing extended-chain crystallites (PE with ECC) at a temperature of 15 K, ~30% of radicals were originally localized on defects (*gauche*-conformers), despite of the fact that the concentration of the latter in the sample was rather small. On the basis of simulation studies, this result was explained by hole delocalization over significant distances along segments of the extended-chain of the ionized macromolecule followed by selective deprotonation on conformational defects (the latter play the role of the effective chain ends). Note that such an effect was not observed earlier, because the experiments were carried out at higher temperatures (77 K and above), at which the ini-

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[1] The authors dedicate the review to the memory of B. L. Tsetlin and L. T. Bugaenko.

tial distribution is distorted by the processes of local migration of the radical center [4]. Thus, contrary to the adopted stereotypes, it turned out that secondary radical reactions can level off (mask) the high selectivity characteristic of the primary radiation-chemical processes above all. The effect of hole delocalization along the extended polyethylene chain also made it possible to explain the primary localization of the radical center on the block boundaries in block copolymers of acetylene with ethylene (less than 10% acethylene blocks) irradiated at low temperatures [5]. Oligomers and polymers of substituted vinylphenylenes represent another type of the systems in which hole delocalization along the chain in the ionized states produced by low-temperature irradiation was experimentally shown [6].

It is quite likely that correlation between the properties of primary radical cations of model compounds and the probability of breaking of chemical bonds during low-temperature irradiation of corresponding polymers exists for other types of macromolecules as well [7]. However, it is necessary to take into account that the characteristics of the medium can have a critical effect on the direction of transformations of ionized molecules (up to complete "switching" of reaction pathways [8, 9]).

Analysis of the hole migration and localization processes in solid disordered matrices containing a large number of traps of one type with close (but not identical) ionization energies becomes of special importance in relation to the problem of localization of primary radiation-chemical processes. Such a situation is typical of polymers characterized by the presence of various defects, conformational dispersion, and difference in the local environment of units. The simplest variant of investigation of these processes can be accomplished in terms of the so-called two-trap model [10, 11], which consists in the following. Organic molecules of two types with a relatively small difference between the ionization potentials, playing the role of hole traps (T_1 and T_2), are distributed in a rigid inert matrix (M) with a fairly high ionization potential. It is convenient to use freons, which possess a high ionization potential and a high electron affinity, as matrices. During irradiation, primary ionization occurs in the matrix, and the radical cations of isolated organic molecules are produced via the fast resonant migration of the hole along the matrix and the subsequent capture by the trap:

$$M^{+\bullet} + M \longrightarrow M + M^{+\bullet}, \quad (1)$$

$$M^{+\bullet} + T_1 \longrightarrow T_1^{+\bullet} + M, \quad (2)$$

$$M^{+\bullet} + T_2 \longrightarrow T_2^{+\bullet} + M. \quad (3)$$

Since the probabilities of hole trapping by molecules with close chemical structures in freon matrices are practically identical, the radiation-chemical yields of radical cations $T_1^{+\bullet}$ and $T_2^{+\bullet}$ (in fact, trap populations) at first sight should be proportional to the concentrations of the parent molecules T_1 and T_2. However, these yields in some cases can differ by an order of magnitude and more at identical concentrations of traps simultaneously present in the matrix [10]. This result can be explained by the secondary redistribution of the hole, namely, by transfer between the traps:

$$T_1^{+\bullet} + T_2 \longrightarrow T_2^{+\bullet} + T_1. \quad (4)$$

It is obvious that under high-dilution conditions at low temperatures, which provide the isolation of traps and preclude the diffusion of molecules T_1 and T_2, this process most likely proceeds via the tunneling mechanism.

Detailed studies of the specifics of hole migration between traps with close ionization energies ($\Delta IP_{gas} \leq$ 0.5 eV) and analysis of possible consequences for polymer systems were performed in [11–13]. It was found that the effective hole transfer to a trap with a lower ionization energy for molecules of benzene derivatives occurs even at a difference of the ionization potentials of ~0.3 eV, with the transfer distance reaching 2–3 nm (as estimated from the concentration dependence). At very small values of the difference between the ionization energies ($\Delta IP_{gas} \leq 0.2$ eV), the efficiency of the transfer sharply decreases (e.g., the hole redistribution of between the traps is practically absent for the *m*-xylene–*p*-xylene pair [13]). Meanwhile, the specific effects of "fine tuning" due to the difference in the actual ionization energy of the traps in solid matrices because of conformational effects, difference in the local environment, and intermolecular interaction can become critical under these conditions. It is obvious that it is impossible to use the IP_{gas} value as a measure of ionization energy in these cases. The most illustrative example of such an effect is given by the toluene–ethyl benzene system ($\Delta IP_{gas} = 0.06$ eV). It was shown that the direction of hole transfer in this system depends on the conformation of the ethylbenzene radical cation; the "high-energy" (vertical) conformer can transfer charge to the neutral toluene molecule, whereas the "low-energy" conformer of the ethylbenzene radical cation, in contrast, can be formed via hole transfer from the toluene radical cation [12, 13]. Effects of this sort can be observed in solid polymers, since transitions between the conformers are either complicated or impossible.

It may be assumed that the processes of hole transfer between the traps and the related "fine tuning" effects are of great importance for the localization of primary radiation-chemical effects in polymers, especially, in the case when the hole delocalization along the macromolecular chain is impossible. In particular, for polystyrene, they can result in primary localization of the hole on certain conformers or dimer associates of phenyl rings possessing a lower ionization energy, thus making it possible to explain the influence of the degree of crystallinity on the radiation sensitivity of the polymer [14].

Along with the hole migration, long-range electronic processes related both to free path of secondary electrons before thermalization and to electron transport over traps can play an important role in the localization of radiation-chemical processes in polymers. In spite of the fact that the effects of electron capture at long distances are well-known in radiation chemistry, their potential use for control of radiation-chemical processes in solid polymers has been barely considered. Meanwhile, as shown in [15], the introduction of even small amounts of electron scavengers (~0.1–0.3%) into polystyrene sharply increases the yield of paramagnetic species during the low-temperature radiolysis of the polymer. Such an approach can turn out to be more effective than the traditional methods for the regulation of radiation sensitivity based on the use of secondary radical reactions.

Analysis of the behavior of secondary electrons in organized polymer systems with typical sizes of microphases less than 100 nm is of special interest because, in this case, electrons generated in one microphase can enter into chemical reactions in another [16]. The effect of the interphase migration of electrons was first revealed upon the investigation of radiation-chemical processes in styrene–butadiene block copolymers of varying composition [17]. An analysis of the composition of paramagnetic particles showed that there is negative deviation from the additivity in the formation of both radical anions in the polystyrene phase and allyl radicals in the polybutadiene microdomains in such systems. This result was explained by the migration of electrons formed in the polystyrene microdomains across the phase boundary and their reaction with allyl radicals in the polybutadiene phase. A more pronounced non-additive effect was observed in the case of irradiation of microheterogeneous interpolymers of polytrichlorobutadiene with polystyrene [18]. In this case, the migration of electrons from the polystyrene microphase to the polytrichlorobutadiene microphase (RCl) results in the dissociative electron capture and the additional formation of radicals from polytrichlorobutadiene:

$$RCl + e^- \longrightarrow R^\bullet + Cl^-. \qquad (5)$$

Simultaneously, the yield of radicals of the benzyl type formed as a result of the deprotonation of primary polystyrene radical cations that escape recombination with electrons increases in the polystyrene domains. Thus, a positive deviation from additivity in the formation of radicals from both components of the system (mutual sensitization effect) is observed. These examples show that the processes of interphase migration of electrons during the radiolysis of two-component heterogeneous polymer systems with the phase dimensions on the order of several nanometers can either increase or decrease the yield of radicals, depending on the electronic properties of the components and the local concentration of physical and chemical (intrinsic or extrinsic) electron traps.

This opens up opportunities for the development of substantially new ways of controlling the radiation sensitivity of such systems by virtue of the long-range electronic effects.

Considering the specifics of the mechanisms of radiation-chemical processes in complex polymer systems, it is important to possess information not only about the composition of intermediate and final products of radiolysis but also about their localization and spatial distribution in the solid matrix. As shown in the studies of the radiolysis of the polycarbonate–poly(alkylene terephthalate) systems, the approach based on the combination of ESR and low-temperature IR spectroscopy [19–21] is be rather useful for tackling this problem. These systems are characterized by rather complex chemical and phase compositions. In the given case, CO molecules are formed with a significant yield during the radiation degradation of polycarbonate chains; at low temperatures (in the absence of diffusion) they are trapped in the rigid matrix at their formation sites. The position of the maximum of the intense absorption band of CO molecules in the IR spectrum is very sensitive to the local environment [19, 21], thereby making it possible to judge directly both the mechanism of radiolysis and the evolution of the composition and the microstructure of the system. Interesting information can be also obtained from detailed analysis of the ESR parameters, in particular, the values of dipole–dipole splitting in radical pairs formed in low-temperature radiolysis [20, 21]. This value is very sensitive to small changes of the center-to-center distance in a radical pair, a property that makes it possible to distinguish, e.g., the pairs formed in amorphous and crystalline regions [21]. Investigation also made it possible to substantially refine the concepts of the mechanism of radiolysis of some classes of individual polymers, in particular, to reveal that radiolysis of dialkylene terephthalates yields radicals of the cyclohexadienyl type in substantial amounts [22].

In general, the development of the concepts of selective and long-range effects at the early stages of the radiation-chemical transformations of macromolecules is not only of the fundamental scientific interest, but also forms the basis for the formulation of new principles of radiation stabilization and radiation modification of polymer systems. The case in point can be approaches that employ quite low radiation doses and small concentrations of additives or chemically modified units introduced into certain positions. The concept of "molecular scalpel" becomes of particular value for organized polymer systems with a low concentration of structural and chemical defects, as well as systems structured on the nanosized level.

RADIATION CHEMISTRY OF POLYSACCHARIDES

Cellulose (poly-1,4-β-glucopyranose) is the most abundant natural polymer, the main component of plants. Cellulose and products on its basis are widely used in a daily life. Therefore, the special interest that has been always focused on investigation into the effect of ionizing radiation on the properties of cellulose is understandable. The degradation of cellulose under natural conditions consists in its hydrolysis to oligo- and monosaccharides, and it mainly proceeds with the participation of the cellulase enzyme [23]. The irradiation of cellulose, as other polysaccharides, is also accompanied by its degradation. However, the decomposition of the glucopyranose cycle with the formation of various compounds and, first of all, gases (CO_2, CO and H_2) takes place in this case. The results of studies of the radiation-chemical transformations of cellulose are summarized in a review [24]. New data on the polymer, as well as other polysaccharides, are surveyed in [25].

The action of radiation alters the entire set of the physical and chemical properties of cellulose, the structural state, mechanical strength, solubility in various media, reactivity, and other characteristics. Experimental data on the degradation of cellulose are described fairly well by equations derived with allowance for the random character of the events of scission of the polymer chain [24, 25]. The most probable molecular-mass distribution is reached as a result of irradiation. The radiation-chemical yields of degradation estimated as the average value mainly fall in the range 6.0 ± 1.0 bond/100 eV. In this case, the yield is almost independent of the γ-radiation or electron-beam dose rate, the initial degree of polymerization, and the microcrystallinity of the initial cellulose; nor it depends on the irradiation conditions (vacuum, a noble gas atmosphere, or air). The absence of a pronounced effect of air on the degradation efficiency is most likely due to the dense crystal packing of cellulose, which complicates the diffusion of oxygen to the reaction centers. The action of oxygen only slightly affects the formation of carbonyl and carboxyl groups, a fact that should be associated with radiation-induced partial oxidation of the surface layer of the material. It was found that the mechanism of the radiation-chemical event is characterized by the local "explosion" of the pyranose cycle in the polymer chain and is accompanied by chain scission. The destruction of the glucopyranose cycle results in the formation of CO_2 (or CO) molecule and polymer compounds with the carbonyl or carboxyl end groups (RCHO and RCOOH, respectively). Experimental data on the yields of the main products [24, 25] show that the yield of carbonyl groups is close to the degradation yield and the yield of CO_2. That is, every event of scission of the cellulose polymer chain is accompanied by the formation of approximately one molecule of CO_2 and one carbonyl group.

Degradation processes similar to those for cellulose are observed for other natural polysaccharides as well [25]. Examples are structural isomers of cellulose, poly-α-D-glucopyranoses, namely, starch, xylan, glycogen and amylose, as well as chitin and chitosan, the product obtained from chitin via partial hydrolysis of acetamide groups. The formation of carbon dioxide during irradiation of polysaccharides indicates that the formation of radicals indeed not simply occurs via the cleavage of the glycoside bond but also is accompanied by the degradation of the pyranose unit. That is, there is sufficiently strong resemblance in the mechanism of the radiation degradation of the saccharides and cellulose. The degradation yields for xylan and starch are on the level of 5–7 bond/100 eV. Starch, like cellulose, consists of D-glucose units. However, these units are linked by 1,4-α-glycoside bonds in starch and 1,4-β-glycoside bonds in cellulose. It may be concluded that this circumstance has no significant effect on the efficiency of radiation degradation. On passing to chitin in which the OH group in the C(2) position is replaced with the CH_3CONH group, unlike the case of cellulose, the degradation yield decreases by a factor of 4–5 and deacetylation, not degradation, becomes the prevailing process. The same effect is observed when the NH_2 group is substituted for the OH group in the case of chitosan. Thus, the presence of NH_2 and $NHCOCH_3$ groups in the case of chitosan and chitin, respectively, substantially enhances the radiation resistance of these materials as compared to cellulose. A significant influence of the absorbed-dose rate on the degradation efficiency was reported for chitosan [26]. As the dose rate decreases, the yield increases. The degree of deacetylation at an absorbed dose of 37 kGy sharply decreases from 54% to 27% and, then, remains practically unchanged. It was also found that the calculated polymer flexibility parameter was not affected by irradiation.

The protective role of substituents in the degradation of cellulose clearly manifests itself in the case of various cellulose ethers (nitrates, acetates, sulfates, and others) [25]. Like cellulose, they undergo degradation. The efficiency of polymer-chain scission is determined by the nature of the substituent and the degree of substitution. Apparently, the protective action of the substituents is due to their ability to localize on themselves the excitation energy or the primary radical ion products of radiolysis. As should be expected, the presence of aromatic groups (benzyl, benzoyl, naphthoyl, etc.) in cellulose is especially effective. They substantially increase the tear strength of cellulose fiber exposed to ionizing radiation.

The degradation of cellulose obviously does not rule out the possibility that the generated primary radicals will decay via the disproportionation mechanism only. They can recombine to some extent, resulting in partial crosslinking in the polymer. This case was considered by Kovalev and Bugaenko [27], who studied the buildup of macroradicals in irradiated cellulose and their degradation upon plasticization by water during the postradiation period. The revealed complex dependences were explained in terms of the influence of radiation crosslinking on the mobility of radicals and on submicroscopic capillarity of the structure of cellulose fibers.

The mechanisms of the formation of molecular products of radiolysis of polysaccharides involving intermediate radicals of various types were surveyed by Sharpatyi [28]. Among the products of radiolysis of starches of various natural origins, citric, dicarboxylic (succinic, malic, fumaric, tartaric, and malonic), pyruvic, and glyoxalic acids were detected. Mechanisms of their formation including transformations of peroxide radicals, as well as the dehydration of radicals with β-elimination of water molecules and appearance of allyl-type radicals, were proposed [29]. The sequence of elementary events and time intervals of transformations of radicals up to the formation of molecular products were revealed for cellulose [30]. This finding also made it possible to correlate the results of the analysis with the mechanism of the formation of carboxylic acids in irradiated starches [31]. On the basis of analysis of mass spectrometric and ESR data for irradiated glucose and polysaccharides and computer simulation data, it was concluded [32] that the site of the initial localization of the unpaired electron in the glucopyranose cycle is the C(3) position. The elimination of water occurs as a result of two consecutive acts of β-elimination from this radical. A study of radicals after γ-irradiation at 77 K and during their thermal annealing to 420 K has shown [33] that their consecutive transformation into alkyl; allyl; and, ultimately, polyenyl radicals takes place. The mechanism of methane formation during γ-irradiation of cellulose, starch, and dextran was discussed in [34]. It was assumed that the degradation of the primary radical localized in the C(6) position yields the methyl radical, which further dehydrogenates monomer units of the polymer (thereby resulting in methane). The presence of water inhibits this process.

Cellulose is the main component of paper and, in particular, paper insulation used in electric power industry. It was found [35] that paper insulation of power transformers also degrades while in service. The development of partial discharges, which are diffused streams of accelerated low-energy electrons, is one of the major factors responsible for the damage to paper insulation of high-voltage devices [36]. That is, there is very close resemblance with radiation-chemical processes. Therefore, the radiation-chemical degradation of paper insulation in a transformer oil medium and the change in its strength characteristics were studied [37]. Under the action of γ-radiation, which models the action of partial discharges (accelerated electrons with energy of 50 keV and higher), cellulose degrades in the random fashion with the efficiency inherent in other celluloses [24, 25]. Neither the immersion in the transformer oil nor the presence of impurities (first of all, lignin) in the paper has a substantial effect on the degradation process. The radiation-chemical yield of the degradation of cellulose is 6.5 ± 1.0 scission/100 eV. This value coincides with the one measured in many other works for celluloses of various origins. The mechanical strength of paper decreases upon its γ-irradiation. The number of the bends of paper before its tearing n decreases with an increase in the absorbed dose. In this case, the dependence expressed by the equation $n = n_0 \times \exp(-\beta D)$ (n_0 is a number of bends for the initial papers; which is 1.2×10^4; D is the absorbed dose, kGy; and β is a factor that makes 0.23 ± 0.03).

A substantial difference in the degradation processes between pure cellulose and the cellulose of paper insulation plasticized with transformer oil was detected at elevated temperatures [38]. There are two regions of the radiation degradation of cellulose, the one up to 380 K in which the yields substantially do not change and the other above this temperature in which the yields substantially increase upon further increase in temperature [25, 39]. The calculated critical activation energy in the temperature region above 380 K is 6.2 ± 0.4 kcal/mol (23.4 ± 1.6 kJ/mol). Most likely, the activation energy corresponds to the diffusion of radical states in the polymer. An increase in temperature initiates transfer to the nearest polymer chain and causes its degradation. For the transformer oil–plasticized cellulose, no increase in the rate of radiation degradation with temperature is observed. Obviously, this is due to the scavenging of “cellulose” radicals by oil and, hence, the suppression of the chain process of degradation. The electron-beam induced degradation of cellulose was studied in [39]. The irradiation conditions under which the polymer experiences destructive decomposition in the high-temperature mode without the use of additional heating devices were revealed. Cellulose is heated to 430 K at a dose rate of ≥9.0 kGy/s and an absorbed dose of 300 kGy. In this case, the radiation-chemical yield of degradation reaches a value of 29 bond/100 eV and is 4–5 times that at ambient temperature. It was shown [40] that intense heating of cellulose modified by salts of iron or other transition metals takes place during its electron-beam irradiation. At an absorbed dose of 400 kGy, the temperature is 650 K. Under these conditions, the pyrolysis of cellulose occurs and ultrafine particles of metals and nonstoichiometric oxides in the pyrophoric state are formed.

The results of studies of the degradation of the paper insulation of power transformers under their operation conditions were discussed in [41–46]. It was shown that the deterioration rate of the cellulose insulation for long-run operated transformers depends on the initial polymerization rate of the wound paper, other conditions being equal. Rate equations that adequately describe the process of the degradation of cellulose insulation were obtained, and methods for calculation of the state and the trouble-free service life of power transformers on their long run were proposed.

Recent years have seen an outbreak of attention given to investigation into the degradation of polysaccharides in aqueous solutions. The specific character of the relevant processes, in contrast to those in dry materials, is associated with the fact that the degradation is mainly caused by the indirect action of ionizing radiation. The primary radical ion products of water radiolysis, hydrated electrons, H atoms, and OH radicals interact with macromolecules of polysaccharides, resulting in their chemical transformations. The character of change in the molecular-mass distribution of dextran (20 g/1) up to an absorbed dose of 0.26 MGy was studied in [47–49]; it was found that the change is caused by the simultaneous occurrence of the degradation and crosslinking of macrochains. As the concentration of the polymer in a solution increases, the role of crosslinking increases relative to degradation upon γ-radiolysis. This effect is less pronounced when the initial molecular weight of dextran is lower. It was shown that acidification of the solution first results in an increase of the role of crosslinking of macromolecules and further acidification (above 0.01 M H^+ ions), on the contrary, enhances the degradation. At a low concentration of protons in the solution, hydrated electrons transform into H atoms, which dehydrogenate polysaccharide macromolecules, and the arising radicals preferably recombine. The enhancement of degradation at a high concentration is explained by the catalytic action of protons on the unimolecular degradation of the primary macroradicals.

Thus, the interest in the use of ionizing radiation for the modification of cellulose, chitin, and other natural polysaccharides is obvious. It is caused by the feasibility of implementation of quite a simple process flow sheet for changing the initial molecular-mass distribution of these materials and, hence, the set of their physicochemical properties without the use of additional reagents. The use of the radiation methods makes it possible to simplify or even abandon environmentally unfriendly traditional chemical methods of processing of cellulose raw materials.

RADIATION MODIFICATION OF POLYMERS

Radiation modification of polymers is usually carried out by the radiation graft polymerization (RGP) and radiation crosslinking of polymers (RCL). There various lines of research concerning the radiation modification of polymers.

Investigations on the modification of polymers by radiation grafting of "smart" (stimuli-responsive) macromolecules have been performed. Known as smart (stimuli-responsive) polymers are usually polymers whose macromolecules in solutions undergo conformational and phase transformations via the "unfolded coil–compact globule" mechanism. The conformational changes follow the cooperative mechanism and are quite sensitive to the environment (temperature, pH, ionic strength, etc.). Macromolecules with phase transitions in the range of ambient temperatures (32–36°C), such as poly-*N*-isopropylacrylamide and poly-*N*-vinylcaprolactam, are of particular practical interest. These conformational transformations are close to denaturation of proteins in their nature. The self-organization ability determines a high practical potential of smart polymers; in the last few years, these polymers have become a subject of intensive research. The radiation chemistry of smart polymers is also developing now [50, 51]. The modification of polymer track membranes (PTMs) by RGP of *N*-isopropylacrylamide was studied in detail. Polymer track membranes based on poly(ethylene terephthalate) (PET) and polypropylene (PP) with a pore size of 0.03 μm or smaller and a thickness of 10–20 μm have been used. The direct grafting technique and the method with pre-irradiation were applied to carry out RGP. The influence of various factors (solvent nature, a dose, dose rate, monomer concentration, etc.) on RGP was studied [52–54]. The surface of modified PTMs was investigated by means of scanning electron microscopy and atomic-force microscopy. Water permeability and electric conductivity of modified PTMs were investigated. It was shown that water permeability and electric conductivity of modified PTMs substantially increase near the phase transition temperature of the grafted layer. Thus, the temperature-controllable permeability of modified PTMs (thermoresponsive membranes) was reached [52–54]. It is possible to change the thermal sensitivity of membranes by selecting the RGP conditions. Such modified PTMs (with controllable pore size) are of substantial interest for the separation of various, mainly, biologically active substances (in pharmaceutics, medicine, biotechnology, etc.)

The radiation grafting of another smart (stimuli-responsive) polymer, poly-*N*-vinylcaprolactam, on PP and PETF was pioneered by the Kabanov group [55–58]. The new, modified polymer was studied with the use of various instrumental techniques [56, 58]. It was shown that the graft layer is localized mainly on the surface of the polymer and the limiting value grafting ratio reaches 15–18%. It was found that RGP takes place only from a monomer emulsion in water. The grafted layer exhibits the temperature-responsive properties [55].

Polymer track membranes were modified by the RGP of 2-methyl-5-vinylpyridine [59] and methacrylic acid [60]. Various processes for the modification of PTMs are discussed in a review [61].

Works on the radiation modification of gas-separation membranes based on polyvinyltrimethylsilane (PVTMS) have been performed. PVTMS membranes with grafted chains of poly(acrylic acid), polyacrylamide, polyacrolein, and other polymers were synthesized [62, 63].

Radiation crosslinking of PVTMS with the use of a special crosslinking agent was carried out. This made it possible to substantially improve the stability of PVTMS in hydrocarbon media [64].

Works on the use of RGP for the manufacturing of haemocompatible (compatible with blood) polymers for use in medicine have been developed.

The process for the modification of various polymers by the RGP of acryloyl chloride (AAC) with the subsequent bonding of various physiologically active substances (PAS) to the polymer surface via the acylation reaction with the use of the reactive acid chloride group has been developed in detail [65]. A process for the manufacture of macromonomers by the introduction of active double bond into PAS via the acylation reaction with AAC was developed. Radiation graft polymerization of the heparin macromonomer together with other hydrophilic monomers on the surface of various polymers makes it possible to obtain polymeric materials with a high haemocompatibility. Catheters, artificial blood vessels, artificial heart details, etc. were modified with the use of these methods [66].

Radiation graft polymerization was applied to prepare haemocompatible polymeric materials by coating the surface of polymers with physiologically active substances evolved from medical leeches (the “Piyavit” preparation) [67–69].

A method for the modification of polymers by RGP from the gas phase of a monomer was proposed. The method made it possible to perform modification with the minimal formation of the homopolymer. It was shown that two-layer composites combining properties of the starting material (substrate) and the grafted component could be prepared by the RGP from the gas phase of the monomer [70]. Processes for the manufacture of the Katiolan® ion-exchange fiber and the Vitlan® thromboresistant and biocompatible thread were designed as a result of research-and-development works by the Tsetlin group [70–72]. The Vitlan manufacture process comprises two stages, the radiation graft polymerization of vinylidene chloride (VDC) on a polypropylene multifilament thread and subsequent dehydrochlorination of the graft polymer. Owing to the unique combination of properties, such as thromboresistance, biocompatibi1ity, and processability on the textile equipment, in the Vitlan® thread produced on the pilot scale, textiles for cardiovascular surgery (artificial blood vessels, knitted cups of artificial heart valves), orthopaedy and traumatology (artificial limbs of tendons and ligaments) were made from the obtained complex threads. In experiments on animals, as well as in clinical tests of these products, it was found that they have substantially higher thromboresistivity and biocompatibility than other textiles designed for this purpose. There is a long-term positive experience of use of the Vitlan® thread for knitted cups of serially produced artificial heart valves. No cases of lethal outcome because of dysfunction of the valve have been ever reported. The cup of the valve quickly is sprouted with fibrin, reliably fixes the case of the valve and is characterized by enhanced thromboresistivity due to the carbon component of the thread [70].

Being based on the positive results the researches on manufacture of seam surgical monofilament threads, pre-production models of such threads equipped with atraumatic needles have been made. Medical and biological tests and the preliminary clinical testing of the samples in various areas of surgery (dentistry, traumatology, microsurgery, etc.) have shown that atraumatic Vitlan monofilament threads are much superior to the currently used materials [70].

The feasibility of preparation of seam surgical threads combining the aforementioned properties with the bactericidal activity was shown. The method of imparting a biological activity to Vitlan filaments consists in the inclusion of fragments of poly(acrylic acid) into the structure of Vitlan carbon layers. The carboxyl groups of the acid are capable to bind silver in the form salt, which then can be transformed to the metal form. In preliminary studies, it was found that the seam thread possessing bacteriostatic properties prevents the accumulation of bacteria in puncture channels upon the superposition of surgical junctures [70].

In addition to applied studies, investigations dealing with the search for new areas of application of radiation graft polymerization from the gas phase were carried out. For example, based on the fact that polymerization from the gas phase possesses matrix and oriented character, VDC copolymers with acrylic acid (AA) were synthesized on a polyamide substrate with the subsequent dehydrochlorination of VDC fragments and formation of metallic silver of nanometer sizes in AA units of the particles. The quantity and size of silver particles were controlled via salt formation–reduction cycling. The obtained samples contained fragments with conjugated bonds and metallic clusters alternating in certain sequence in the grafted polymer chain. The conductivity of the film specimens was 10^{-3} to 10^{-2} Ω^{-1} cm^{-1} with a positive temperature coefficient, a signature of the semiconductor character of conductivity [71].

Proceeding from the assumption that carbon coatings should improve medical and biological performance of metal surfaces, works on the formation of chemically bonded carbon structures on the surface of titanium were performed. Graft polymerization was conducted with the use of a ^{60}Co γ-radiation source from unsaturated VDC vapor with the subsequent dehydrochlorination of the polymer. The titanium surface was preliminarily subjected to electrochemical or chemical oxidation. It was shown that the thickness of the polymer coating increases with the thickness of the oxide layer, a behavior that is consistent with the hypothesis of the formation and migration of active sites during graft polymerization [72]. The results can be of interest for the areas of medicine related to cardiovascular surgery (biocompatible coating for cardiostimulators, details of heart valves, stents), as well as traumatology and orthopedy.

In the Republic of Belarus, works on the use of RGP with the purpose of manufacturing of polymeric sorbents are developed. The technology for the production of fibrous sorbents based on polyolefins has been developed in detail.

Long-term research works on the liquid-phase radiation polymerization of vinyl monomers on polyolefins formed the basis for the technology of manufacture of ion-exchange materials, the fibrous cation exchangers FIBAN K-l and FIBAN K-4 [73, 74].

FIBAN K-l is a sulfonated polypropylene (PP) fiber with a grafted styrene copolymer with divinylbenzene (DVB) (graft ratio, 100–110%; styrene conversion, 95–98%, DVB content of the copolymer, 1%) obtained via the direct irradiation of PP fibers in a solution of the monomers with ^{60}Co γ-rays on an UGU-420 γ-ray facility.

The FIBAN K-4 fibrous cation exchanger is produced by the method of preirradiation of PP fibers in air on the UGU-420 facility at a dose of 70 kGy with the subsequent aging (6 days without heating) of the irradiated fiber in aqueous solutions of acrylic acid in glass-lined reactors of 160-1 capacity [75]. To provide the processability of FIBAN K-4 into bonded fabrics, the grafting ratio is limited to 50–80% (exchange capacity, 4–6 mg-equiv/g).

FIBAN K-l and FIBAN K-4 are purchased by enterprises in Germany and Austria to equip purification filters for removal of ammonia from air and of heavy metal ions from water [76, 77].

Many original studies on the RCL of polymers have been performed in Russia. A technology for the production of radiation-modified products from polymers has been developed. Radplast T heat-shrinkable tubes, Radlen heat-shrinkable tapes for protecting cable splices, and the Radeva adhesive tape for the manufacture of solar cells are produced. Irradiations are carried out on an universal radiation-chemical facility based on the ILU-6 accelerator. As a result of radiation treatment, the thermal and shape stability of products increases. A valuable property of the products is the so-called memory effect [78].

The radiation crosslinking of ultrahigh-molecular-weight polyethylene substantially enhances its thermal stability [79].

A radiation technology for the modification of polytetrafluoroethylene (PTFE) has been developed, which makes it possible to obtain radiation-modified PTFE with very high performance characteristics. This PTFE has a 100–150 times lower tensile creep, a 10 times lower value of the compression set, a 10000 times higher wear resistance, 100–200 times higher radiation resistance, and 3–5 times higher transparency in the visible spectral range [80]. It was shown that a substantial improvement in the tribological behavior and physical–mechanical properties as compared to the initial PTFE is observed as a result of the radiation modification of PTFE in the temperature range 330–340°C. A scheme of the radiation-chemical transformations of PTFE near the phase transition temperatures was proposed [81].

Radiation crosslinking was used for the manufacture of new sorbents based of *N*-carboxyethylchitosan. The radiation crosslinking of *N*-carboxyethylchitosan was effects by irradiation with nanosecond electron beams. The sorption of Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+} ions was examined. The obtained sorbents possessed a high selectivity for Cu^{2+} ions [82].

Works on the RCL of polyolefins with the use of organosilicon compounds (vinyltrimethoxysilane, vinyltriethoxysilane, allyltrimethoxysilane, etc.) were performed. The mechanism of radiation crosslinking was investigated. It was shown that a mixture of vinyltriethoxysilane and maleic anhydride is an effective crosslinking agent [83, 84].

The wasteless and environmentally appropriate radiation technology was used for designing heat-resistant composites capable to work under extreme conditions [85].

Studies of radiation effects in polyorganosiloxanes, including siloxane block copolymers, were carried out. It was found that the radiation-chemical yield of crosslinking depends on the number of phenyl groups only. In the case of block copolymers, the protective action of phenyl groups is manifested to a lesser degree, and the radiation-chemical yield of the crosslinking increases. The influence of the supermolecular structure of siloxane block copolymers on their radiation modification was investigated in [86, 87].

The action of space flight factors on various polymers was investigated. Experiments were carried out at the Mir orbital station. Films based on a tetrafluoroethylene–hexafluoropropylene copolymer and fluorinated polyimide were studied. Hydrophilization of the films, caused by the formation of oxygen-containing groups, and the formation of spatially oriented structures take place upon the exposure of the films on the external surface of the space vehicle. The mechanisms of processes occurring in polymers under the action of outer space factors were discussed [88, 89].

RADIATION POLYMERIZATION

The characteristic feature of the radiation method of initiation is the possibility of creation of high (and easily controlled) concentrations of active sites, which are distributed almost evenly throughout the entire volume of the sample and initiate polymerization irrespective of the temperature and the phase state of the reaction medium. This makes it possible to carry out the process in the solid or viscous supermodel state at substantially lower temperatures than in the case of traditional, chemical initiators. Such specific conditions of the reaction, resulting in a substantial increase in the contact time of the reagents, substantially alters the concept of monomer reactivity [90].

Traveling-wave and self-oscillatory modes of cryopolymerization of monomers in the crystalline and vitreous states were revealed and investigated in detail in studies of the mechanism of chemical reactions occurring near the absolute zero of temperature [91, 92]. The main results of the investigation of cryopolymerization in traveling-wave modes were discussed on the examples of polymerization and copolymerization of acetaldehyde, hydrogen cyanide, cyclopentadiene, ethylene oxide, epichlorohydrin and other monomers [91]. The traveling-wave cryopolymerization processes show the feasibility of the formation of macromolecules under conditions close to those in outer space, at low temperatures and weak radiation fields. It is reasonable to attract the ideas advanced for explanation of processes of the “cold” chemical evolution of matter in the Universe. The achievement of the record rates of chemical transformation at low temperatures in the traveling-wave mode is attractive. It is supposed that traveling-wave modes of transformation will turn useful for the development of new unconventional chemical technologies.

Experimental and theoretical studies of thermokinetic self-oscillations of the rate in cryochemical solid-state chain reactions initiated by radiation were carried out [92]. Self-oscillation modes have the general character and have been observed for various reactions (including polymerization and copolymerization) in the crystalline and glassy states both directly in a γ-radiation field and as the posteffect during heating the samples. The modes of occurrence of chemical transformations (stationary mode, thermal explosion, and oscillation mode) were analyzed. The obtained data are of significant interest in relation to the opportunity of enhancing the selectivity of complex processes and extending the range of technological means of controlling the cryochemical synthesis.

A comparative study of the radiation postpolymerization of a number of dienes (butadiene, isoprene, etc.) and α-olefins (ethylene, butene-1, cyclopentene, 2-methylpentene-l, etc.) with sulfur dioxide proceeding both upon heating of samples radiolyzed at 77 K and spontaneously during their mutual dissolution was carried out [93, 94]. It was shown that the reaction at low temperatures is accompanied by specific features that are inconsistent with the conventional concepts of liquid-phase processes. A complex phase state of solid multicomponent systems, as a rule, determines the course of cryochemical reactions. For example, during copolymerization of isoprene with SO_2, not only the 1 : 1 donor–acceptor complex but also an excess of the monomer enter the reaction; therefore, a not strictly alternating copolymer can be formed. The formation of the donor–acceptor complexes of SO_2 with monomers is not a sufficient condition; it is essential that the structure and composition of the formed complex be favorable for the subsequent polymerization.

From the molecular structure of ketene $H_2C=C=O$ containing the cumulated heterochain double bonds, it follows that the process of its linear polymerization can occur in three directions, namely, the formation of polyketone, polyacetal, or polyester. The feasibility of both anionic and cationic mechanisms of the reaction, depending on the conditions of the process, was shown in studies of the low-temperature postradiation polymerization of ketene [90, 95]. The reaction can proceed with the opening of either C=O– or C=C– bonds. The use of solvents relevant to cationic (butyl chloride) or anionic (diethyl ether) polymerization as a vitrifiable matrix makes it possible to select the preferred route of the reaction.

Low-temperature polymerization of divinylsulfone in the crystalline state and in glassy solutions of dimethyl formamide and acetone was investigated in [96]. It was shown that the polymerization reaction effectively proceeds in a viscous supercooled liquid. The specifics of the reaction in a viscous supercooled liquid make it possible to prepare both highly branched or ladder soluble polymers and crosslinked three-dimensional network structures. The crosslinking process is affected by the nature of the solvent and the initial monomer concentration.

The specifics of radiation copolymerization of *N*-vinylpyrrolidone (VP) with triethylene glycol dimethacrylate (TGM-3) was investigated at ambient temperature [97]. The optimum conditions of the process of VP copolymerization with TGM-3 were determined via the monitoring the amount of the VP homopolymer, the content of VP units in the crosslinked copolymer, and the conversion of double bonds in the entire course of the process. The obtained products can be used as foodstuff purification sorbents.

The specific features of radiation-initiated copolymerization of various monomers (*N*-vinylpyrrolidone, acrylic and crotonic acids, acrylamide, methyl acrylate, divinylsulfone, etc.) at low temperatures in glassy solutions were investigated in [98, 99]. The mechanism of the formation and the conditions of preparation of random and alternating copolymers with various functional groups (–OH, –COOH, $–NH_2$, $–SO_2$) were determined. The obtained products can be applied in medicine and biology as polymer carriers of biologically active substances, medicines, sorbents, hydrogels, etc. Polymers and copolymers based on fluoro(meth)acrylates and α-fluoroacrylates (2,2,3,3,4,4,5,5-octafluoroamyl acrylate, 2,2,3,3-tetrafluoropropyl 2-fluoroacrylate, 2,2,3,3,4,4,5,5-octafluoropentyl metacrylate, etc.) were synthesized by the radiation method. The radiation crosslinking and degradation processes in the obtained polymers were studied [100]. The polymers are of interest in relation to the creation of a radiation-chemical technology for the manufacture of polymer optical fibers (synthesis of the core and shell from corresponding compositions, or the formation of a light-reflecting layer on a prefabricated core) in a continuous process with the use of electron accelerators. In addition, high-energy radiation can be used for modification and improvement of prefabricated polymer optical fibers, e.g., for the crosslinking of the shell or core. Results are also of interest in connection with the problem of radiation resistance of the materials used under different conditions.

Works on the radiation polymerization of phosphorus have been performed. The methods of high energy chemistry are widely used for the synthesis, study of the formation mechanisms, and modification of organic polymers of various structures. However, the discussed methods of synthesis have been little used for the synthesis of inorganic polymers.

An analysis of the structure and properties of polymers of elemental phosphorus (red phosphorus) made it possible to reveal features characteristic of high polymers and to formulate the main trends in the synthesis and control of the properties of phosphorus-containing polymers (PCP) [101–104].

The use of tools of chemistry of macromolecular compounds and radiation chemistry methods provided an understanding how phosphorus-containing polymers are formed under various conditions of the radiation polymerization of white phosphorus (in solution, heterogeneous systems, and in bulk).

The main products are insoluble and refractory polymers of orange and red color. The phosphorus content of the samples depends on the synthesis conditions and varies from 65 to 100 wt %.

The main characteristics of the single-step synthesis of modified PCPs, which consists in the action of ionizing radiation on multicomponent systems containing white phosphorus, were determined, and the principles of designing PCP materials with organic or inorganic fillers were developed [102, 103].

It studies of the radiation-initiated graft polymerization of white phosphorus to organic macromolecules, it was found that the process involves the routes of both grafting inorganic polymer chains to organic high-molecular compounds and the formation of a red phosphorus homopolymer. The nature and structure of the macromolecular matrix substantially influence the properties of PCP.

Phosphorus–sulfur containing polymers are formed under the action of ionizing radiation on solutions containing two inorganic monomers (white phosphorus and elemental sulfur S_8). Theoretical concepts of copolymerization processes were used to describe the reactions of their synthesis.

A topochemical model of a contracting (growing) sphere was used for the first time for the description of the PCP formation reactions in heterogeneous systems and during bulk polymerization; values for the kinetic parameters of the emulsion and bulk polymerization of white phosphorus were obtained on the basis of the model [102].

The formation of PCPs with a wide range of performance characteristics occurs under the action of initiating factors on systems with varying polarity, aqueous heterogeneous systems, and systems based on white phosphorus in the presence of Lewis acids and the ionic liquid $EMIM(CF_3SO_2)_2N$. For example, the introduction of fragments of various solvents into the structure of a polymer of elemental phosphorus forms its major physical and chemical properties, the stability to self-ignition and phosphine evolution and the reactivity. The nature of a solvent determines the kinetic behavior of the formation of the inorganic polymer.

The developed method of synthesis made it possible to introduce various polymer-stabilizing components (zinc and titanium oxides, aluminum hydroxide, talc, and graphite) into the matrix of the inorganic polymer, a development that reduced the phosphine evolution from the finished product under heating by a factor of 2–5 and increased the self-ignition temperature by 20–60 K as compared to the self-ignition point of commercial red phosphorus [103].

A series of research works on the formation of polyelectrolyte hydrogels (HG) under the action of ionizing radiation on aqueous or water–salt solutions of copolymers of acrylamide (AAm) with sodium acrylate were performed at the Belarus State University [105–110]. The copolymers were obtained via the base hydrolysis of polyacrylamide (PAAm) [105, 106] or polyacrylonitrile (PAN) fibers [107, 108]. The ratio of acrylamide to acrylate units in copolymer macromolecules, the length of the polymer chain, the concentration of aqueous copolymer solution, the chemical nature of low-molecular-weight ions in the aqueous copolymer solution, and their concentration were varied. It was found that these factors have a substantial effect both on the dose that provides the formation of a hydrogel with the maximum water uptake and on the value of water absorption. The dose corresponding to the maximum in the water uptake decreases with an increase in the molecular weight of the copolymer, its concentration in the aqueous solution, and the content of acrylamide groups in copolymer macromolecules. The value of the maximum water absorption increases with an increase in the molecular weight of the copolymer; however, its dependence on the ratio of acrylamide to acrylate units in copolymer macromolecules is nonmonotonic in character. Extrinsic ions, which can present in aqueous solutions of a copolymer, reduce the value of the dose corresponding to the maximum in water absorption, as well as the degree of water absorption.

Hydrogels based on the products of base hydrolysis of the PAN fibers obtained by the radiation-chemical method were used as for the production of the Gisinar preparation implemented in the Republic of Belarus as a component of protective-stimulating compositions for the presowing treatment of seeds of agricultural crops [110].

A series of studies on the deposition of thin polymer films and nanostructures by means of electron-beam polymerization of monomers from the vapor phase (E-VDP process) were carried out. The electron energy in the beam was 10–100 keV and the monomer vapor pressure was from 10^{-2} to 10^2 torr.

Continuous films of vinyl polymers (PMMA, polystyrene, polybutadiene, PTFE, etc.) with a thickness of 0.1–10 μm on various substrates (single-crystal silicon wafers, silicon with an oxidized surface, gold layer on silicon, etc.) were obtained [111]. It is supposed that the film formation process proceeds mainly via the adsorption radical chain mechanism. It was found that the properties of the films can be varied over a wide range by changing their deposition conditions, in particular, the electron-beam current density [112].

It was shown that the PTFE films obtained at incident electron-beam current densities on the order of 1 μA/cm^2 consist of a low-molecular-mass polymer (with a degree of polymerization of ~30) in the mesomorphic liquid crystalline state with the orientation of the axes of macromolecules normal to the substrate surface [113]. These films are characterized by the dichroism of IR spectra and by structural transformation in an electric field. An increase in the beam current density to 10^2–10^3μA/cm^2 makes it possible to obtain crosslinked PTFE films with the thermal resistance of 450–500°C [112].

The proposed "dry" process for the deposition of thin polymer films can be considered an alternative to the solvent-based processes, which are applied, in particular, in microelectronics (e.g., so-called spin-coating technologies). The deposited films can have various functional purposes: polymer resists; dielectric, optical, and protective layers; etc.

It has been shown that the E-VDP method with the use of a sharply focused electron beam can be used with a high resolution for the deposition of nanostructures of various functional purposes. Images of nanostructures with a typical size of 100 nm based on PTFE, PMMA, etc. with various film thickness in the range of 5–200 nm were obtained. Films with quite a high continuity are formed already at a thickness of 5–7 nm. At high current densities (10^4 μA/cm^2 and above), similar nanostructures were also obtained from precursors incapable of polymerizing, in particular, from saturated hydrocarbons. With the use of metallic precursors, it is possible to obtain metal-containing conducting nanostructures [114].

Works on the radiation polymerization and copolymerization of hardly polymerized monomers, which do not enter into copolymerization reactions in the case of chemical initiation, were performed [115]. The radiation copolymerization of acryloylmorpholine with 4-methylpentenoic and undecenoic acids, as well as *N*-vinylcaprolactam with acrylic, 4-pentenoic, and undecenoic acids was studied. The content of units of hardly polymerized monomers did not exceed 6–7% in all cases. A mechanism of the radiation polymerization was proposed.

The synthesized copolymers possess unique biocompatibility and can be used as plasma substitutes in the manufacture of synthetic vaccines and drug vehicles. The possibility of manufacturing high-purity copolymers uncontaminated with initiators is an advantage of radiation polymerization [115, 116].

THE ACTION OF FAST HEAVY IONS ON POLYMERS AND POLYMER TRACK MEMBRANES

The studies of the action of heavy ions with energies on the order of 1 MeV/amu on polymers were motivated mainly by practical tasks, in particular, by the development of the technology of track membranes [117]. The shift of emphasis to the area of nanotechnologies stimulated more detailed investigation into the nature of the track of a heavy ion. First of all, it was necessary to understand the character of radiation-chemical transformations occurring at different distances from the trajectory of an energetic charged heavy particle, to reveal the dependence of the dimensions of radiation damage on the linear energy transfer (LET) of the ion, and to elucidate the main features of the formation of nanosized pores upon the chemical etching of ion-irradiated polymers. Along with PET and bisphenol A–based polycarbonate, traditional materials in the track membrane technology, other advanced polymers also became the objects of research.

Powerful accelerators of multiply charged ions are used as radiation sources in research in this area. Most works on the ion track modification of polymers were performed on accelerators at the Flerov Laboratory of Nuclear Reactions (JINR, Dubna) [117] with the use of beams of accelerated ions of various elements (O, Ar, Kr, Xe, Bi, etc.) with energies in the range of 1–5 MeV/amu and intensities of 10^{11}–10^{12} s^{-1}. The range of the ions in polymers is tens of micrometers, the linear energy transfer lies within the limits of 1–25 keV/nm, and the dose rate upon the irradiation of thin polymer films reaches 1–50 kGy/s.

The investigation of macroscopic characteristics of the irradiated polymers (PET, PC, PP, PE, and fluoropolymers) showed that the action of heavy ions causes effects that are qualitatively similar in many respects to those caused by low-LET radiation [118–122]. This finding is the direct consequence of the fact that a substantial fraction of the ion energy is transferred to the stopping medium through a cascade of secondary electrons forming the track penumbra. The same radiation-chemical reactions as in the case of electrons or γ-rays occur in the penumbra of a heavy-ion track. At the same time, some differences are observed at high LET, for example, a substantial shift in the balance between the degradation and crosslinking processes in favor of the latter and a substantial increase in the yield of unsaturated bonds in hydrogen-containing polymers. The increase in the crosslinking probability is presumably due to a high local concentration of radicals on small distances from the trajectory of the heavy ion. A high yield of unsaturated bonds is a consequence of specific conditions in the core of the heavy-ion track. As is known, an extremely high ionization density in the track core results in the formation of the short-lived, positively charged string in which electrostatic forces initiate a short-term collision cascade. In this case, the displacement of the lightest atoms and ions, H and H^+, occurs. Thus, the formation of unsaturated structures in tracks of heavy ions can occur via special mechanisms that substantially differ from usual radiation-chemical reactions. The "cloud" of highly labile H radicals can, supposedly, also initiate the crosslinking of polymer chains around the core of the ion [119, 121].

The specifics of the processes occurring in the core of a heavy-ion track determine its capacity for selective chemical etching. Even in a typical crosslinked polymer, such as polyethylene, heavy ions leave tracks, which are visualized by the action of chromic acid [121]. This indicates that the core is formed according to the aforementioned physical mechanism. The important property of the track core is its increased free volume. The free volume facilitates the transport of an etching agent along the track axis and an increase in the rate of the chemical reaction of etching in a narrow area around the ion trajectory. One cannot but infer that there is a duality of the properties of the track core; its cross sectional area is determined by a fast physical process [119, 124] and is almost unaffected by secondary reactions that follow the process, whereas the state of the substance in the core substantially depends on the secondary reactions of radiolysis products. This manifests itself in the dependence of the rate of the chemical etching of tracks on the oxidation in air, the irradiation temperature [123], and the presence of an antioxidant in the polymer [121].

Traditional methods for the investigation of radiation-chemical processes in polymers often cannot provide information on the spatial distribution of various radiation-induced effects. The method of chemical etching, proposed initially for track visualization only, has appeared rather useful for revealing the spatial structure of the tracks of heavy ions. Chemical etching in combination with the technique of conductometric measurements of micro- and nanopores was applied to the investigation of the structure of the tracks of multiply charged ions with atomic numbers from 18 up to 92 [119, 124–126]. The dependence of the local etching rate V_r on the distance from the track axis is shown in Fig. la. In the region with a radius of several nanometers, the local rate of the dissolution of the material exceeds the rate of etching of the intact material by several orders. The V_r value rapidly decreases with an increase in the radius; passes through a minimum; and, then, slowly grows approaching in the asymptotic mode a constant value V_∞. The diameter of the channel formed by the time when the local etching rate reaches its minimum is a parameter convenient for use as a typical size of the central part of the track. This size corresponds to the maximum crosslinking density. The core of the track is surrounded by a diffuse penumbra in which crosslinking prevails over degradation. The radius of the penumbra is at least an order of magnitude higher than the radius of the selectively etched central part of the track. The dependence of the parameter d^* on the LET is shown in Fig. lb. Using PET as an example, it was shown that the sizes of the core and penumbra are approximately proportional to the square root of the LET in its interval of 3–25 keV/nm [124, 125]. Thus, it may be concluded that the LET is proportional to the volume of the radiation-modified area around the ion trajectory.

The prevalence of crosslinking and related delayed chemical etching in the track shell is observed in other polymers (PP, polycarbonate, poly(ethylene naphthalate), polyimide) as well, which is supposedly a general trend for tracks of energetic ions of a sufficiently high mass [118, 121, 126]. Another interesting feature consists in the fact that the penumbra radius is substantially larger than it may be expected from the radial distribution of the absorbed dose created by secondary electrons on the track periphery [119, 124]. It seems that the diffusion of short-lived products of radiolysis and their reactions with polymer molecules result in track smearing. Completing the discussion of the structure of heavy-ion tracks, we should emphasize once again that the track formation process is very complicated and cannot be rationalized in terms of the traditional radiation-chemical processes. In addition to the excitation and ionization of atoms and the subsequent secondary reactions between charged and neutral products of radiolysis, it is necessary to take into account the Coulomb explosion, thermal shock, generation of shock waves, and other effects. The effect of orientation of macrochain segments detected in PTFE, whose exact mechanism remains unclear, also may be related to these processes [127].

Another important aspect of the track membrane technology is the formation of a porous structure by chemical treatment of ion-irradiated polymer films. Different formulas and procedures of chemical treatment are required for polymers of different classes. The chemical nature of the polymer is the starting point for

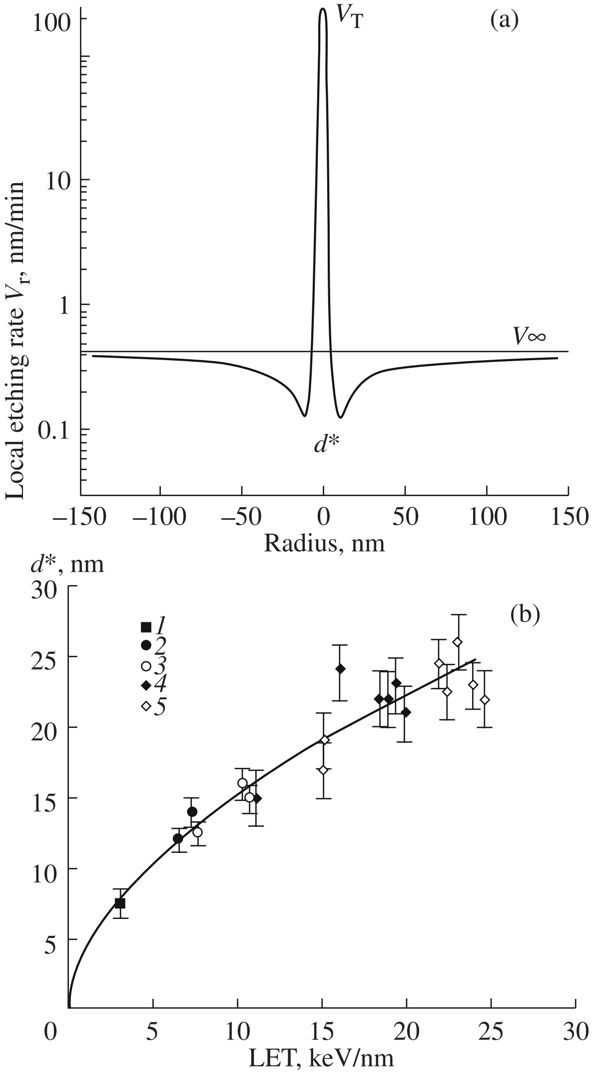

Fig. 1. (a) The local etching rate of the substance in a track as a function of the radius by the example of the track of an uranium ion in PET [124]; (b) a typical track diameter *d* in PET as a function of the LET for fast ions with different masses and energies [125]: (*1*) ^{40}Ar, (*2*) ^{84}Kr, (*3*) ^{132}Xe, (*4*) ^{97}Au, and (*5*) ^{238}U. The solid line is an approximation of the power function A• (LET)$^{0.55}$, where A is a constant.

the choice of processing conditions, although the determination of the optimum etchant formula in each specific case remains a problem of the empirical character. Methods for highly selective etching of tracks in poly(ethylene naphthalate) [126], poly(vinylidene fluoride) [122], polyimide [128], and polypropylene [129] have been found. In highly selective etching, the ratio of the track core dissolution rate to the etching rate of the initial polymer reaches 2–4 orders of magnitude, a condition that is compulsory for obtaining homogeneous pores of submicron size. The ion track technique remains the unique method for the manufacture of polymer membranes with pores of the regular cylindrical shape (Fig. 2a). At the same time, the cylindrical shape of pores is not always favorable. The structure with a thin selective layer, in which pores have a smaller diameter than in the bulk of the membrane, is more preferable for micro- and ultrafiltration membranes. A new method for the chemical treatment of heavy-ion tracks, which makes it possible to obtain pores of a complex profile, has been developed recently [130]. This method is based on the use of the effect of self-organization of supramolecular structures in the "track" pores during chemical etching. The chemical treatment of the ion-irradiated polymer is carried out in a solution containing additives of amphiphilic molecules. The latter are sorbed on the surface of the polymer and form aggregates in the mouths of the etched nanopores. The difference in the track penetration rate between different components of the etching solution results in the formation of channels converging to the surface. Asymmetric ultrafiltration membranes distin-

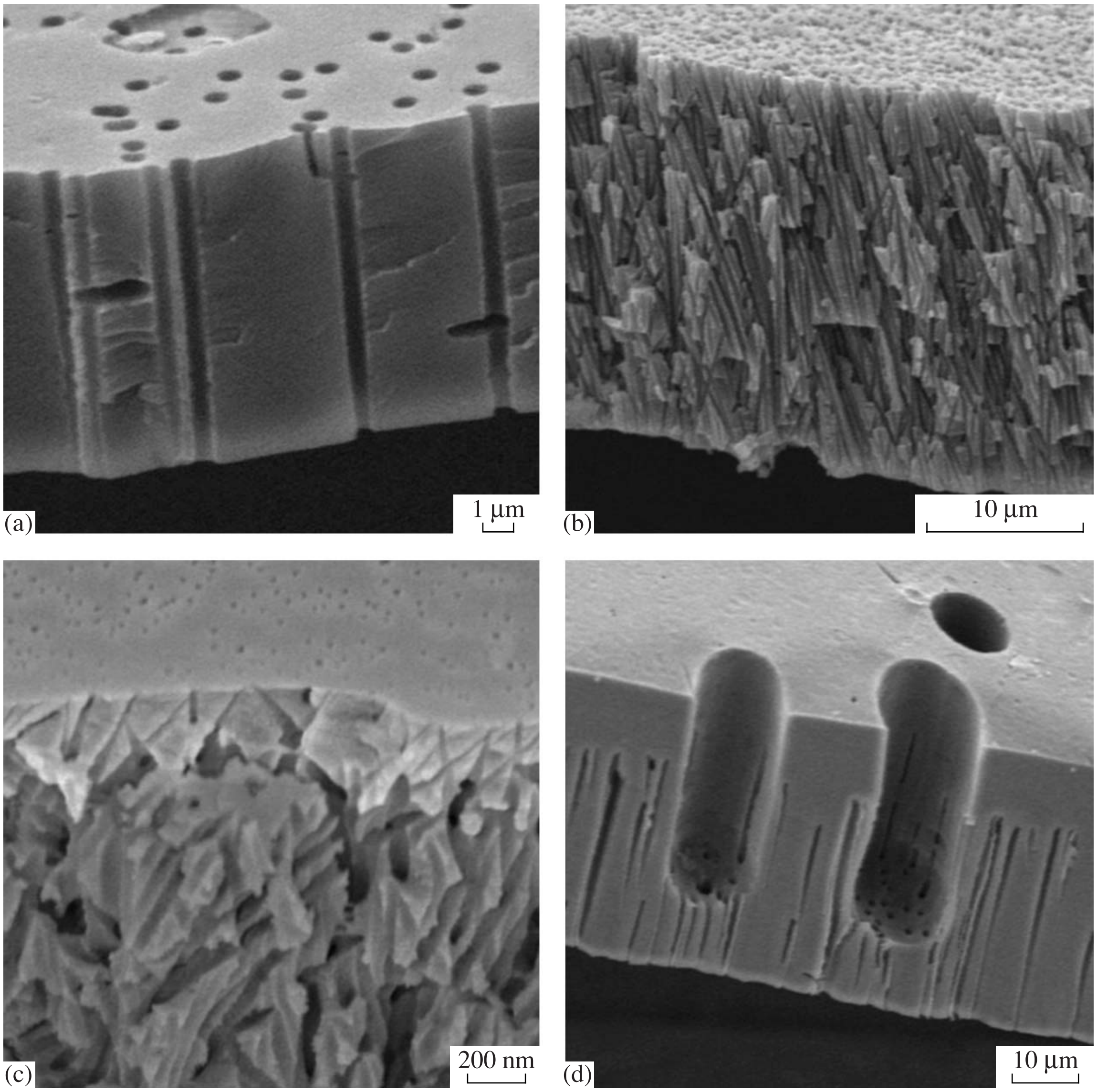

Fig. 2. SEM images of track membranes of various structures: (a) a low-porosity membrane with cylindrical parallel channels, used as a model capillary porous solid; (b) a microfiltration track membrane with pores of 0.2 μm in diameter; (c) an asymmetric ultrafiltration membrane obtained with the use of a special etching technique [130]; and (d) microwells with a porous bottom [131].

guished by a high specific capacity were obtained by this method [130]. The structure of the selective layer of such a membrane is shown in Fig. 2c. The diameter of pores on the surface of the selective layer is 20 nm, and the thickness of the selective layer does not exceed 500 nm. The diameter of pores in the bulk of the membrane is 70–80 nm. Owing to the nonparallel arrangement of the tracks, they form a united porous system in the support matrix. A high bulk porosity and a relatively large pore diameter in the substrate in combination with small thickness of the selective layer provide low hydraulic resistance of the membrane as a whole.

The traditional track membranes used in microfiltration processes possess the structure shown in Fig. 2b. The ion bombardment of the film is conducted under different angles in order to prevent superposition of closely located pore channels [117]. Using two-stage ion bombardment and two-stage etching, it is possible to obtain the structure shown in Fig. 2d. The system of microwells with a porous bottom can be used as a porous substrate when operating with cell cultures [131]. A wealth of various scientific problems is tackled with the use of track membranes as model porous solids with exactly defined characteristics. The potential of this approach is far from being exhausted, despite the use of this idea in a wide diversity of areas of physics, physical chemistry, colloid chemistry, instrument making industry, biology, and medicine. In addition, the ion-track technique finds a progressively increasing use for “nonmembrane” applications, ranging from surface modification to the manufacture of protective signs [131].

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