Peculiarities of tracks formed in polycarbonate films irradiated with Kr^+ ions

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Radiation chemical transformations of polycarbonate (PC) irradiated with accelerated Kr^+ ions have been studied. The irradiation results in the cleavage of carbonate bridges accompanied by the detachment of phenyl groups to form aldehyde and ketone groups. The formation of branched and linked PC macromolecules is established. The products of etching of PC bombarded by heavy ions have been determined. It is established that the oligomers formed differ both by molecular weight distribution and chemical composition, depending on the sizes of the etched track.

Key words: membranes, heavy ions, tracks, polycarbonate.

Polycarbonate (PC) is used as a track detector for heavy charged particles[1] and is widely used in the preparation of track membranes (*e.g.*, Nuclepore membranes (Costar, USA)) because of its high stability toward irradiation. Nevertheless, irradiation (γ-beams, electrons, fast neutrons, heavy ions, and UV) results in the destruction of polymer chains to form phenyl or phenoxyl radicals and to yield CO and CO_2, respectively,[2–9] accompanied by a decrease in the molecular weight of the polymer. However, in some cases, depending on the irradiation dose, the cleavage of polymer chains is accompanied by linking.[6–8] Nevertheless, the radiation chemical transformations in PC occurring upon the irradiation with high-energy ions have not been sufficiently studied. One of the distinctive features of this type of irradiation is that the process of track formation is followed by a considerable increase in temperature along the pathway of a moving ion.[9,10] Therefore, many similarities between this process and thermal oxidation destruction of polymers are observed.[6,11] Another peculiarity of the action of heavy ions is that the ion energy is localized in the track. It has been established by electron microscopic studies of crystals that the size of a latent track is of the order of 10–20 nm.[10,12–14] For polymers, sizes of tracks measured under similar conditions vary in a very large interval: 20 to 150 nm.[15–21] In addition, it has been established that the material around the track axis is heterogeneous. For example, a study of the dependence of the pore size on the etching time for several polymers (poly(ethylene terephthalate) (PETP), polycarbonate (PC), and polyimide (PI)) shows that the region with a radius of ~5 nm is characterized by a high rate of track etching, which is related to the destruction of the polymer. Then there is a region with a lower etching rate (5–15 nm), which is explained by linking of polymer chains.[11,18]

In this work, radiation chemical processes in PC irradiated with high-energy ions are studied.

Experimental

A batch PC film based on diphenylolpropane (DPP) produced in the Scientific Industrial Plant "Zarya" (Dzerzhinsk) 10 mm in width (density 1200 kg m^{-3} and refractive index 1.5850) was studied.

The film was bombarded with accelerated Kr^+ ions with an energy of 220 MeV on a U-400 accelerator in the Laboratory of Nuclear Reactions of the United Institute of Nuclear Research (Dubna). The irradiation density varied from 10^5 to 10^{12} ion cm^{-2}.

An aqueous solution of KOH (0.3 mol L^{-1}) was used for etching of PC in a thermostat at 80 °C.

Etching in layers was used to study the products formed at different distances from the track axis.[11,20] The first etching was performed at a pore radius of 5 to 7 nm; the second etching was performed at a pore radius of 5–7 to 15 nm, and the third etching was carried out from the pore radius of 15 to 30 nm. At the fourth etching, the PC film with the irradiation density of 10^9 ion cm^{-2} dissolved completely. The etching was monitored by the change in the weight of the irradiated

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and control (nonirradiated) samples with an accuracy of ±0.1 mg.

Pore sizes were measured by the hydrodynamic Hagen—Poiseuille method and electron microscopy.[22] A Hitachi S-800 electronic microscope was used for studying the surface. The difference in pore sizes measured by both methods was not greater than ±10 %.

The concentration of dissolved PC was estimated by the loss of mass and from the concentration dependence of the intensity of the band at 280 nm in the UV region. The amount of product transported to the solution from the tracks was determined from the difference between the mass losses of the irradiated and control samples. For example, for etching a film 0.5 m^2 in surface area with an irradiation density of 10^9 ion cm^{-2}, the concentration of the etching products from the region of tracks with radii shorter than 5 nm was ~15 to 20 mg L^{-1}, and the total concentration of dissolved PC was not lower than 40 mg L^{-1}.

Chemical transformations of PC occurring both during irradiation of films with ions and upon the formation of pores were studied by UV and IR spectroscopy. UV spectra were recorded on Specord UV and Specord M 40 spectrophotometers. Before recording UV spectra, a filtered alkaline solution was neutralized by hydrochloric acid to pH 8—9.

Absorption spectra of films in the IR region were recorded on a Specord M 80 spectrophotometer using a multiple distorted full internal reflectance (MDFIR) attachment equipped with a prism of a single germanium crystal with angles of 45° and 24 reflections.

Samples for IR spectroscopy were prepared in the following way: the alkaline solution was separated from the precipitate (microgel), which was analyzed separately. Then the etching products were extracted with chloroform, the chloroform was evaporated, and the solid residue was used for the preparation of pellets based on KBr.

To estimate the parameters of molecular-weight distribution (MWD) of PC samples, a high-performance liquid chromatograph (Waters) was used, which was supplemented with a UV-detector (model 490) with a variable wavelength and three columns filled with a Micrigel sorbent with pore sizes of 10^3 and 10^4 Å and PL-gel with a pore size of 100 Å. Chloroform was used as the eluent, and the rate of feed was 1 mL min^{-1}. The wavelength of the UV-detector was 254 nm. The concentration of the initial solution was 0.1 wt. %. The volume of an injected probe was 20 mL.

Several PC samples were studied on a liquid chromatograph (Milton Roy) equipped with a small-angle laser light (SALL) detector, a KMX-100 model (Chromatix KMX), together with a refractometric detector (RD) (Milton Roy). In the GPC/RD/SALL system (GPC is gel-permeation chromatography), two chromatograms were obtained, one of which characterized the molecular-weight distribution on the basis of indications of KMX-100, and the other of which, obtained on a refractometric detector, characterized the concentration distribution. MWD parameters of the studied samples were calculated by the PCLAALS program. Chromatographic columns were filled with a Microgel sorbent with pore sizes of 10^4 and 10^6 Å, chloroform was used as the eluent, and the rate of feed was 1 mL min^{-1}.

Results and Discussion

The UV spectra of the initial PC dissolved in chloroform exhibit absorption bands at λ 267 and 272 nm caused by a π-π^*-transition due to the excitation of phenyl rings. Their intensities and shapes remain almost unchanged after irradiation of the film with heavy ions. The spectrum of the irradiated sample in the longer-wave region at 300 nm exhibits a considerable increase in the absorption of the polymer related to the formation of chromophoric and polyconjugated structures and, as a consequence, an enhancement of the yellow color of the polymer. A similar picture has been observed previously in the thermal oxidative destruction of PC[23] and in the photoirradiation of PC and model compounds.[6,24,26,27]

The IR spectra of PC bombarded with Kr^+ ions with a density of $5 \cdot 10^9$ cm^{-2} exhibit a decrease in the intensity of the absorption band at 1770 cm^{-1} assigned to the stretching vibrations of the carbonyl group of the carbonate bridge, the bands of the stretching vibrations of the C—O bonds of the carbonate group (1250, 1200, and 1170 cm^{-1}),[7,25,28,29] and the band at 1385 cm^{-1} assigned to the methyl groups.[11] In addition, the appearance of new bands at 1740 and 1660 cm^{-1} and an increase in the intensities of the bands at 1600 and 1500 cm^{-1} are observed.

When the relative optical densities D_{1770}/D_{1500} and D_{1740}/D_{1500} as a function of the irradiation density of bombardment with Kr^+ ions (Fig. 1) have been measured, the intensity of the band with D_{1500}, assigned to skeleton vibrations of the benzene ring, has been conventionally considered constant.[25] A noticeable decrease in D_{1770}/D_{1500} (curve *1*) and an increase in D_{1740}/D_{1500} (curve *2*) are observed when the irradiation density is 10^{11} cm^{-2}. The comparison of the dependences presented in Fig. 1 shows that the appearance of carbonyl groups with different structures than those in the initial polymer is related to the decomposition of the carbonate bridge and the formation of an ester bond.

The band at 1660 cm^{-1} is assigned to the appearance of a benzophenone fragment.[25] The considerable increase in the intensity of the bands is caused by the formation of monosubstituted phenyl groups.[25,28,29]. A new band at 1460 cm^{-1}, which can be assigned to the ionized carbonate CO_3^{2-} group, was additionally re-

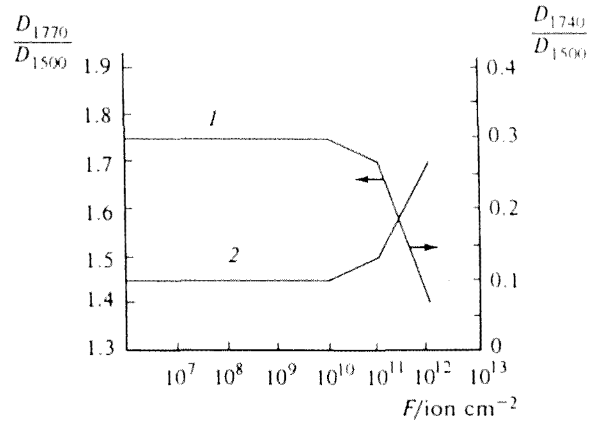

Fig. 1. Dependences of relative optical densities (*F*) on the density of irradiation of PC with Kr^+ ions: *1*, D_{1770}/D_{1500} and *2*, D_{1740}/D_{1500}.

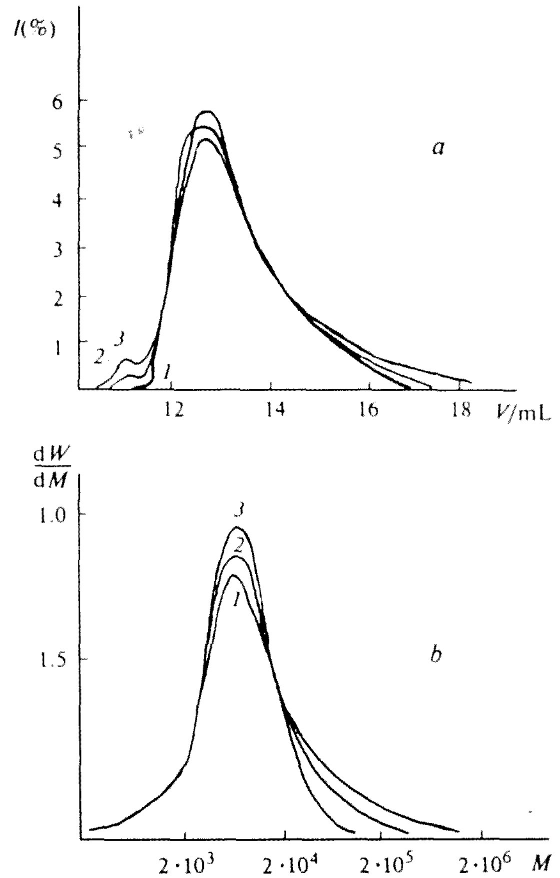

Fig. 2. Gel-chromatograms (*a*) and molecular-weight distribution curves (*b*) of PC samples: *1*, initial film; *2*, film with irradiation density 10^8 cm^{-2}; *3*, film with irradiation density 10^9 cm^{-2}. *M* is the molecular weight, *W* is the mass fraction. UV-detector (λ = 254 nm). Chloroform as the eluent. Columns: sorbent Microgel 10^3 and 10^4, PL-gel 100 Å.

corded in the IR spectra recorded by the MDFIR method.[30]

These changes in the IR spectra may be caused by processes characteristic of the thermal oxidative destruction of PC and occurring mainly *via* a chain-radical mechanism.

The GP-chromatograms of the initial sample (curve *1*) and of PC samples irradiated with densities of 10^8 cm^{-2} (curve *2*) and 10^9 cm^{-2} (curve *3*) are presented in Fig. 2 (*a*, *b*). The appearance of "shoulders" on the chromatographic peaks in the high-molecular region (Fig. 2, *a*) and of a nonmonotonic drop in the MWD curves in the same region are evidence for the existence of microgel formation in the studied solutions of PC. The appearance of these formations is associated with processes of branching and subsequent linking of macromolecules due to destruction reactions.[31—33]

The numerical-mean (M_N), weight-mean (M_W), and average (M_Z) molecular weights calculated using the Mark—Kuhn—Hawink value for linear PC in chloroform ($K = 1.2 \cdot 10^{-4}$, $a = 0.82$) are presented in Table 1.

Table 1. Average molecular weights of the initial polycarbonate sample and PC samples irradiated with different densities

Sample	$M_N \cdot 10^{-3}$	$M_W \cdot 10^{-3}$	$M_Z \cdot 10^{-3}$
PC (initial)	43.2	88.7	153.5
PC (10^8)	46.2	113.1	565.2
PC (10^9)	43.4	143.4	1620.0

The data in Table 1 and the MWD curves (Fig. 2, *b*) testify to a considerable change in the MWD parameters during irradiation. For example, the formal calculations of average molecular weights using the universal calibrating Benoit dependence[34] for linear PC and taking into account microgels show an increase in the values both of M_W and M_Z. This change in the values of molecular weight may be caused by the formation of branched structures of PC macromolecules usually accompanying destruction processes in polymers.[6,25]

To confirm the obtained results attesting to the formation of branched structures in irradiated PC, an additional series of experiments using a SALL detector was carried out.

The MWD curves of the initial PC samples and of samples irradiated with densities of 10^8 and 10^9 cm^{-2}, respectively, are shown in Fig. 3. In accordance with the requirements of the detector, the solutions were filtered immediately before entering the detector through a filter with a pore size of 0.25 mm, which prevents larger particles, including any microgel formed in polymers upon their destruction, from getting into a cell. Therefore, in this experiment, M_N, M_W, M_Z, and other parameters (Table 2) were calculated without taking microgel into account. In addition, the calibrating de-

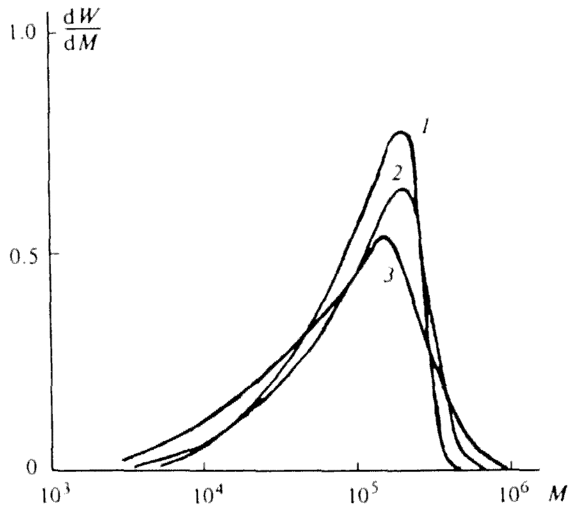

Fig. 3. Molecular-weight distribution curves of PC samples calculated from SALL data: *1*, initial film; *2*, film with irradiation density 10^8 cm^{-2}; and *3*, film with irradiation density 10^9 cm^{-2}.

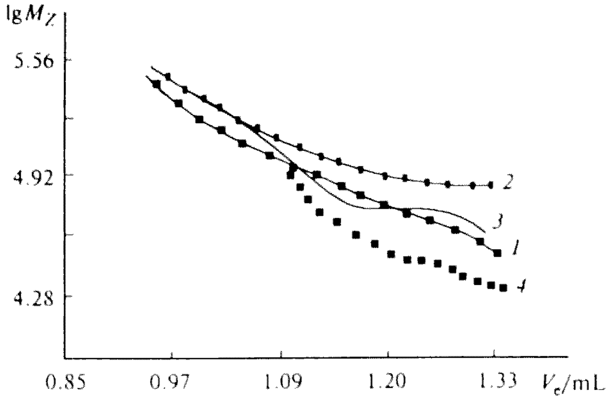

Fig. 4. Calibrating dependences log*M*—*V* of PC samples: *1*, initial film; *2*, film with irradiation density 10^8 cm^{-2}; *3*, film with irradiation density 10^9 cm^{-2}; *4*, PC of Makrolon 2800. V_e is the eluent volume.

pendence log*M* = f(*V*), (*V* is the eluting volume) differs somewhat from the similar dependence for the model PC sample (Makrolon 2800), which may be associated with the existence of branched or different structures in the initial sample. At the same hydrodynamic volume of macromolecules, the molecular weights of the irradiated samples (irradiation density 10^8 cm^{-2}, curve *2*) exceed the similar values for the initial sample (curve *1*), which is related to increased branching of the polymer. At a higher density of irradiation (10^9 cm^{-2}), a portion of the branched structures transforms to the gel fraction, their content in the sample becomes lower, destruction processes accompanied by chain cleavage increase, and the values of MW of this sample decrease (curve *3*).

The values of $M_W{}^x$ and $M_W{}^{xx}$ correspond to the fractions of the polymer in the low-molecular and high-molecular regions, which were artificially separated in the calculation and comprised 10 % of the weight of the whole sample. A decrease in $M_W{}^x$, an increase in $M_w{}^{xx}$, and an increase in the degree of polydispersity of the sample are evidence that branching processes precede the linking processes and the reactions of cleavage of macromolecules (Fig. 4, Table 2).

The UV spectrum of aqueous extracts of the products of the first etching of the irradiated films (radii of etched tracks are shorter than 5 to 7 nm) contain a broad absorption band with a maximum at λ = 315—320 nm, which is related to chromophoric and polyconjugated structures that appear, as a rule, in destructive thermal oxidation processes initiated this case by the kinetic energy of ions in place of their penetration through the film. It is likely that these compounds are derivatives of salicylates formed due to the Fries rearrangement or from dihydroxybenzophenones.[24,26,27,35]

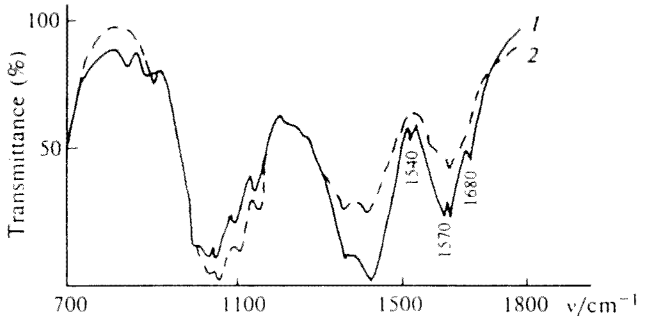

Fig. 5. IR spectra of microgel formed in the etching of PC: *1*, first etching; *2*, second etching.

This absorption band is not observed in the UV spectra of the products of the second etching (radii from 5 to 15 nm), while in the products of the third etching (radii from 15 to 30 nm) the intensity of the absorption in this region is close to that of the initial PC.

These data testify that the maximum changes in the chemical structure occur in the first region, which is the closest to the passage of high-energy ions through the film.

The distinguishing feature of the IR spectrum of the microgel of the first etching is the existence of bands at 1680, 1570, and 1540 cm^{-1} typical of compounds containing carbonyl groups (Fig. 5). The amount of the microgel decreases from the first to the third etching. This is evidence that the etching products isolated as microgel are probably high-molecular partially oxidized compounds with branched and linked structures.

The IR spectra of the products of etching in the layers (Fig. 6) isolated from a chloroform extract and molded as pellets show that the intensity of the band at 1740 cm^{-1} decreases and that of the band at 1700 cm^{-1} increases on going from the first to third etching (curves *1*, *2*, and *3*). However, at the fourth etching (curve *4*) when the PC film with the irradiation density of $5 \cdot 10^9$ cm^{-2} completely dissolves and the average radius of the etched tracks is not less than 40 nm, the bands at 1700 and 1740 cm^{-1} are more intense than those in the spectra of the initial sample. In addition, the band at 1560 cm^{-1}, which was not observed in the spectrum of the initial PC, is retained. The existence of carboxyl and carbonyl groups nonhydrolyzed with alkali is likely asso-

Table 2. Absolute values of molecular weights of the initial polycarbonate sample and samples irradiated with different densities

Sample	$M_N \cdot 10^{-3}$	$M_W \cdot 10^{-3}$	$M_Z \cdot 10^{-3}$	$M_W{}^x \cdot 10^{-3}$	$M_W{}^{xx} \cdot 10^{-3}$
PC (initial)	73.8	129.9	172.4	23.1	270.6
PC (10^8)	66.2	141.4	201.5	19.0	325.1
PC (10^9)	42.1	126.9	205.1	10.4	331.3

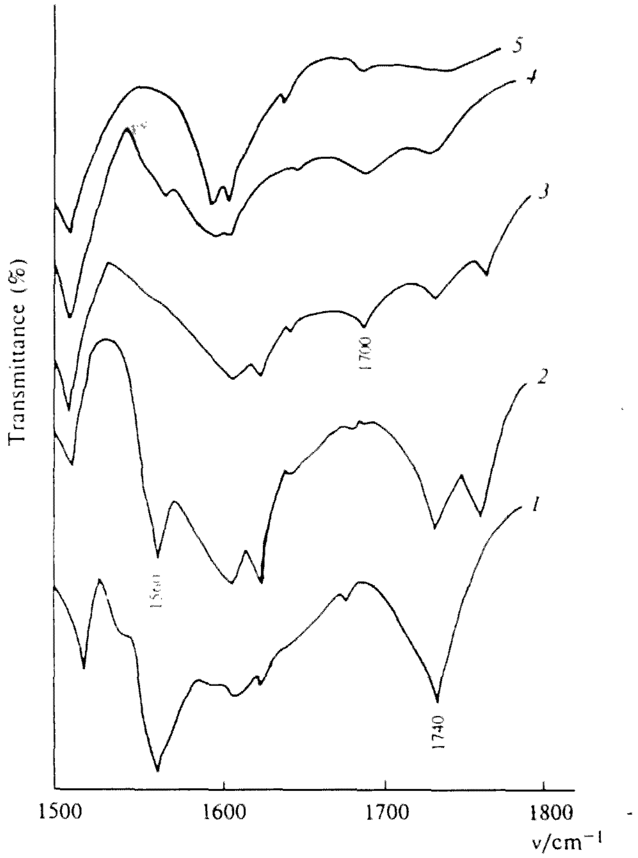

Fig. 6. IR spectra of products of PC etching in layers isolated from a chloroform extract (chloroform was evaporated, and the residue was molded with KBr): *1*, first etching; *2*, second etching; *3*, third etching; *4*, fourth etching; and *5*, initial PC.

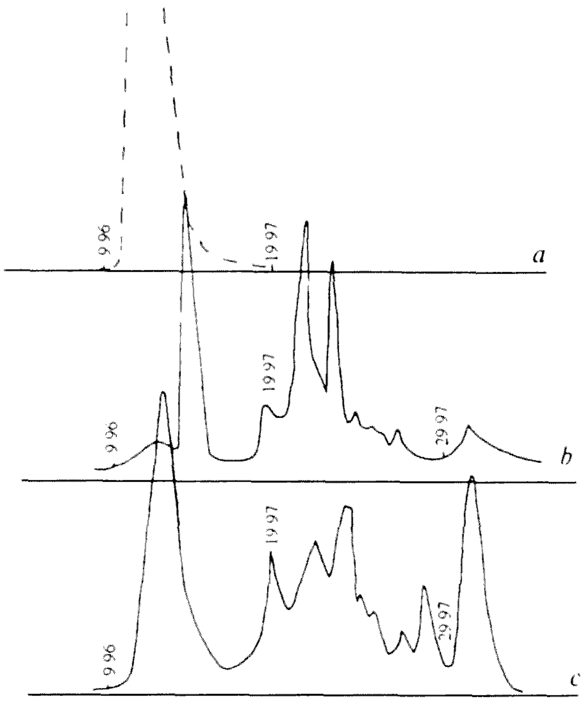

Fig. 7. Gel-chromatograms of PC (*a*) and microgel fractions (*b*, *c*). *b*, first etching; *c*, second etching. Chloroform as the eluent.

ciated with linking and branching, which prevent penetration of alkali into the polymer.

Thus, both monomeric and high-molecular compounds with carbonyl and carboxyl groups are found by UV and IR spectroscopy in the etching products of PC irradiated with high-energy ions.

The chromatograms of microgels of the first and second etching are nonmonotonic (Fig 7), which is likely caused by the existence of macromolecules of different chemical structures in the sample and probably by branched microgel formations (a high-molecular region of the peak) and destroyed linear macrochains. The sample of the second etching has a less destroyed polymeric region. Both samples contain a set of oligomers with different terminal groups, including active groups, which cause their different extents of sorption on the sorbent in the chromatographic column. The compositions of oligomers in different samples differ somewhat. The value of M_W for the polymeric region of the samples decreases from 98000 to 27000 (first etching), while for the second etching M_W = 88000. Extracts of etching products soluble in aqueous alkali contain a small amount of the destroyed polymer, a set of oligomers, and a large amount of low-molecular compounds (phenols, diphenylolpropane (DPP), ethers, esters, phenylsalicylates, and other compounds). However, alkaline hydrolysis also occurs in the case of nonirradiated PC. For example, the GP-chromatograms of the chloroform extract from an aqueous-alkaline tincture of the initial PC show the existence of polymeric and oligomeric regions of the sample in low concentrations.

The experimental data obtained in this work make it possible to present the following peculiarities of the formation of tracks. In the track region at a distance of ~5 nm from the center of the passage of the ions, fast etching of the polymer followed by a considerable change in its chemical structure occurs (according to UV and IR spectroscopy and GPC data). This is accompanied by processes of polymer destruction, including both the cleavage of macromolecules (cleavage of the carbonate bond, elimination of methyl groups, and formation of low-molecular products) and branching and linking of polymer chains involving the macroradicals formed in the isopropylidene structures of the macrochain or phenylsalicylate radicals formed due to the Fries rearrangement.

Less destruction of the polymer and a retardation of the branching and linking of molecules are observed for the track region with a radius from 5 to 15 nm. The etching products of the third region of the polymer (from 15 to 30 nm) are characterized by fewer changes than in the first and second zones, but there are some differences compared to the nonirradiated sample.

The results of this work show that the polymer structure and the surface properties of etched pores change depending on their radius up to ~40 nm, which should be taken into account in the creation and use of track membranes.

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