

Characteristics and Radiolysis Behavior of Polyvinylchloride Under Accelerated Proton and γ -Irradiation

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Abstract

The effect of high energy protons and γ -irradiation on the structural properties, surface-energies, and toxicological properties of polyvinyl chloride (PVC) were studied due to the role PVC products play in many technologies including the nuclear industry. Accelerated 1-4 MeV protons impacting on PVC in vacuum lead to the formation of polyenyl radicals as shown by EPR and to an increase in free surface energy due to functionalization of the surface of the irradiated polymer. γ -irradiation leads to the formation of unsaturated bonds, carbonyl and hydroxyl groups as shown by IR and to the release of HCl. Correlated molecular orbital theory calculations of reaction thermodynamics were used to aid in the development of a mechanism in the absence of oxygen. The formation and accumulation of chromophores and auxochromic groups during γ -radiolysis of PVC leads to a gradual change of the initial white color of the polymer to yellow and then to brown and black with high sensitivity. A mixture of powdered PVC and silicate glue was used to determine the profile of a ^{60}Co γ -radiation beam on targets with a complex relief. γ -irradiated polymer does not have a local irritating effect due to a single application to the skin of mice in an adhesive mixture at a concentration of up to 5000 mg/kg. γ -radiolysis of PVC powder in air with a dose of up to 1400 kGy does not affect its acute toxicity when administered intragastrically to BDF1 mice. PVC and its γ -irradiated analogs are non-toxic at doses ≤ 5000 mg/kg.

Key words: polyvinyl chloride, MeV protons, γ -rays of ^{60}Co , radiolysis, EPR, free surface energy, acute toxicity, radiolysis mechanism.

This article is dedicated to the memory of Alexander Alexandrovich Potapov, a neurosurgeon, academician, and director of the National Medical Research Center for Neurosurgery named after academician N. N. Burdenko.

1. Introduction

Polyvinyl chloride (PVC) is one of the most used polymers due to its unique properties including resistance to oxidation and good compatibility with other materials. PVC is insoluble in water and resistant to acids, alkalis, alcohols, and mineral oils. [1,2] PVC has been used in the production of hydraulic pipes, cable insulators, fire retardants, packaging materials, and even artificial leather [3,4,5] due to its low production and processing costs, good tensile strength, and high compatibility with additives. PVC is susceptible to degradation with release of HCl under the influence of external factors [1,2], for example high-energy irradiation such as γ -rays [6,7], neutrons [8], accelerated electrons [7], protons [9,10], and plasma. [11,12] However, the ease of cleavage of HCl from the polymer leading to the formation of a more carbonized polymer chain containing conjugated and cumulated double bonds makes it possible to improve the electrical conductivity of PVC. [13,14] After significant dehydrochlorination of PVC, a carbonized polymer similar to polyacetylene with semiconducting properties can be obtained. [15] In addition, methods of slowing down the dehydrochlorination process by using various additives are being developed [1,2] to lengthen the life of PVC containing products.

Knowledge of the impact of radiation on PVC is important in a number of applications., For example, insulated wires and cables are widely used in the monitoring and control systems of nuclear power plants, so the radiation safety of cable products is of significant concern to this industry. During operation, even small changes in the chemical composition of the insulating material or its physical state and structure under the influence of ionizing radiation can lead to irreversible changes in the electrical and mechanical properties of the insulating material leading to degradation of the insulator. [16,17] Due to its low toxicity, PVC is used in a range of medical applications. [18,19,20,21,22] Sterilization of products containing PVC can be performed by an

electron beam or γ -irradiation. It is important to know if there is a change in the toxicity of γ -irradiated PVC after sterilization by irradiation and if there is a dosage dependence.

Another potential application of PVC is for dosimetry due to the sensitivity of PVC to ionizing radiation which is manifested by the color change of the polymer and is dependent on the radiation dose. Radiochromic films made of pure PVC polymer [23,24,25,26] or PVC composites containing various dyes [27,28,29,30] can change color under the influence of ionizing radiation. This can be used to characterize the exposure level and beam profile. Unlike X-ray films, radiochromic PVC films do not require a development process and results can be obtained almost instantly; they are also insensitive to visible light. Radiation discoloration of PVC films containing dyes (malachite green [28], bromocresol purple [29], methyl red [30], or dimethyl yellow [27]) have been used for dosimetry of γ -radiation from a ^{60}Co source with a dose, respectively up to 30 [27], 50 [29], 125 [28], and 150 kGy. [30] PVC films without additives can be used for dosimetry of radiation from 1 to 1000 kGy. [26] In addition, in radiation therapy, it is important for it to be nontoxic and to be able to use a dosimeter on surfaces with complex structures, for example those associated with anatomical features. Thus, to determine the dose field and beam direction on such a surface, an easily applied and washable, non-toxic dosimetry system is required.

In order for irradiated PVC to be used in the example applications described above, the role of dehydrochlorination on the properties of the polymer, including toxicity, need to be understood. It is known [31] that dehydrochlorination continues in irradiated PVC samples even after irradiation of the sample is stopped. This is clearly shown by the enhanced EPR signal of polyenyl radicals formed due to PVC dehydrochlorination during storage of the irradiated polymer at room temperature. [32] Any HCl released during polymer dehydrochlorination is

highly toxic. [33] With a single oral administration to rats, the LD₅₀ of HCl is 238–277 mg/kg, so it is classified as a third hazard class [34], and, in high concentrations, it is an asphyxiant. [35]

The current work provides a study of the effects of accelerated proton and γ -irradiation on the structural, surface-energy, and toxicological properties of PVC to address issues in terms of its use as an insulator under radiation conditions and its use in biological applications, for example as a dosimeter. A key aspect of the study is to understand the types of structures that are generated in PVC under irradiation conditions and how this could affect the use of this material for a range of applications.

2. Methods

2.1. Experimental

2.1.1. Materials

Industrial PVC plates with a thickness of 1.56 mm, PVC Type I Sheet (MacMaster Carr Supply Company (Atlanta, Georgia, USA), reference number 8747 K134) were used to study the effect of proton and γ -ray irradiation. Fourier transform infrared (FTIR) spectroscopy studies of the effect of γ -irradiation on the polymer and its acute toxicity were carried out using industrial PVC powder of the SSI-70 brand. These samples of industrial PVC brands were used without additional purification.

To study the effects of irradiation on the surface energy properties of PVC, polymer sheets were used. A polymer powder cannot be used for this task because the irradiated powder has to be transformed into a sheet, plate, or film to determine the free surface energy. The process to transform the powder into a plate involves heating and pressure which can lead to the destruction of the functionalized groups obtained by radiolysis of primary polymer powder.

As PVC is insoluble in water, we used a mixture of fine PVC powder with a 1% starch solution in distilled water for oral intragastric administration to mice to study its toxicity after γ -irradiation. An objective of the current work was the development of a non-toxic dosimetry system that can be easily applied to and washed off the human body, so we used a mixture of the same fine PVC powder in an adhesive mixture. The use of PVC sheets for this purpose is not suitable.

2.1.2. Proton irradiation

Proton bombardment of the PVC was carried out on a particle accelerator at the Howard J. Foster Center for Irradiation of Materials at Alabama A&M University (Alabama, USA). A polymer target $20 \times 20 \times 1.56$ mm in size was bombarded with protons with energies of 1 and 4 MeV at a fluence of 2×10^{15} protons/cm². The feed current was maintained in the region of 300 nA to avoid overheating of the polymer surface under the proton beam. The residual pressure of the evolved gases in the irradiator was maintained within 0.13 mPa.

2.1.3. γ -irradiation

Radiolysis of PVC with γ -rays of ⁶⁰Co was carried out on the UNU “Gammatok-100” device of the IPCP RAS at a γ -irradiation dose rate of 3 Gy/s in air and in vacuum. For irradiation in vacuum, the polymer sample in a glass ampoule was first pumped out in a vacuum setup to a residual pressure of 0.13 mPa; then the ampoule was sealed off for irradiation in vacuum. The radiation dose was determined with a Fricke ferrous sulfate dosimeter. The polymer samples were in powder form and were γ -irradiated in air with doses of 4, 10, 30, 100, 400, 800, 1400, and 2000 kGy.

Irradiation of the PVC plates in air will only oxidize an up to 11 μ m thick portion of the plate [36]. The irradiation of the interior of the plate in air will be similar to that irradiated under

vacuum as oxygen will not penetrate that far. The experimental limitation of a thin radio-oxidized layer on the PVC plate does not change the results of either the attenuated total reflectance (ATR)-FTIR spectroscopy or the free surface energy experiments because ATR only measures the first $\sim 2 \mu\text{m}$ of the sample in contact with the crystal and free surface energy experiments only measure the surface itself.

2.1.4. FTIR spectroscopy

IR spectra of PVC before and after γ -irradiation were recorded in the frequency range 400-4000 cm^{-1} on a Bruker ALPHA Fourier spectrometer equipped with a detached total internal reflection attachment with a single reflection diamond prism (ATR, FTIR-ATR). The spectra were measured at 23 $^{\circ}\text{C}$ for a total of 25 scans at 4 cm^{-1} resolution using an uncooled DLATGS detector. All vibrational spectra were obtained under the same spectrometer operating conditions including purging.

2.1.5. EPR

The EPR spectra were measured on a standard Varian radio spectrometer E-12, operating in the 3 cm range. EPR spectra were recorded at room temperature and at liquid nitrogen temperature. The PVC samples irradiated with protons at room temperature were stored at -78.5 $^{\circ}\text{C}$ for 24 hours before the EPR measurements. Polymer samples, including PVC, can acquire induced radioactivity by irradiation with 4 MeV protons with fairly short half-lives. To ensure the safety of the personnel, the PVC samples irradiated with protons were stored at -78.5 $^{\circ}\text{C}$ for 24 hours before the EPR measurements. In addition, the samples were bombarded at the facility at Alabama A&M University and then transported back to The University of Alabama for the EPR studies, hence the time delay.

2.1.6. Free surface energy

The free surface energy (FSE, γ_s), its acid-base (γ_s^{ab}) and dispersion (γ_s^d) components were determined from the values of contact angles of surface wetting with test liquids using the Fowkes definition of the FSE [37] and the Owens-Wendt [38] equation. Following Fowkes, the γ_s can be represented as a sum of components caused by different forces, and it is sufficient to take into account only γ_s^d and γ_s^{ab} as given in equation (i)

$$\gamma_s = \gamma_s^{ab} + \gamma_s^d \quad (i)$$

Owens and Wendt then applied equation (ii) to calculate the FSE in a solid-liquid system:

$$\gamma_{lv}(1 + \cos\theta)/2 = (\gamma_l^d \gamma_s^d)^{1/2} + (\gamma_l^{ab} \gamma_s^{ab})^{1/2} \quad (ii)$$

with γ_{lv} the surface free energy of the liquid, θ the contact angle, γ_l^d the dispersion component of the test liquid, and γ_l^{ab} the acid-base component of the test liquid. The surface tension of the liquids used in the current work and its components and the method for measuring the contact angles with the use of the KM-8 cathetometer have previously been reported. [39] The time for establishing the equilibrium value of the contact angle of wetting was initially determined for each liquid on the investigated surfaces. The relative measurement error is less than 2%. The roughness coefficient was determined from profilograms obtained on a P-203 profilograph-profilometer. The roughness coefficients were taken into account when calculating the cosine of the wetting angle using the Wenzel-Derjaguin equation (iii)

$$\cos \theta_r = R \cos \theta_0 \quad (iii)$$

where θ_r is the actual contact angle on the rough surface, R is the ratio of the real area to its projection on the horizontal plane, and θ_0 is the contact angle on a planar surface. [40,41]

2.1.7. Determination of acute toxicity.

The determination of the toxicity class was carried out in accordance with OECD 423. [42] PVC was administered to animals intragastrically (orally) at a dose of 2000 mg/kg. Male hybrid mice of the BDF1 line weighing 22 to 24 g were used to determine the hazard class. Clinically healthy animals were kept in identical conditions in the vivarium of IPCP RAS. PVC either before or after irradiation was prepared immediately before administration under aseptic conditions at a concentration of 2000 mg/kg (up to 5000 mg/kg for irradiated PVC) and was administered to animals once intragastrically. PVC was mixed with 1% starch solution in distilled water for oral administration to the animals. The individual volume of the administered dose for each animal was calculated based on the value of the body weight. The introduction of PVC solutions was carried out using a specialized atraumatic intragastric probe. The experiments used 6 mice for each group. On the first day after the introduction of the sample, the animals were monitored continuously for 4 hours. Animal deaths and the clinical picture of intoxication were assessed once a day for 14 days. The experiments were carried out following standard procedures. [43]

2.1.8. Study of the local irritating effect of PVC.

A polymer powder in an adhesive component was used to study the locally irritating effect of γ -irradiated PVC. Silicate glue ("Forum" Company, St. Petersburg, Russia) was used as the adhesive. The solution for application to the skin of animals was prepared at a dose of 5000 mg/kg. The weight content of the polymer was 40% in the used mixture of glue and PVC. In the experiment, white mice hybrids of the BDF1 line weighing 22 to 24 g were used. They were clinically healthy and were kept under standard conditions of the UNU Nursery and Vivarium of the IPCP RAS on a standard diet, and also underwent a seven day quarantine and acclimatization

before the start of the experiment. The local irritating effect of PVC before and after γ -irradiation was studied by immersing the tails of mice for 2/3 of the length in the test solution for 2 hours. During this time, the mice were placed in a special retainer to hold the animals in order to avoid licking and loss of the applied solution. Then, the residues of the applied compound were washed off with soap and water, and the animals were kept in standard cages. In the experiment, 8 mice were used for each group. Changes in the skin and in the general physiological state of the experimental animals were monitored during the experiment. The experiments were carried out according to the appropriate standards. [44]

2.2. Electronic Structure Calculations

An 8-carbon chain with CH_3 termination, $\text{CH}_3\text{CHClCH}_2\text{CHClCH}_2\text{CHClCH}_2\text{CH}_3$, was used to model PVC decomposition in vacuum. The molecular geometries were initially optimized at the density functional theory (DFT) level using the B3LYP functional [45,46] and the DZVP2 basis set. [47] Frequency calculations were performed to ensure that the geometry was an energy minimum and not a transition state. These B3LYP/DZVP2 optimized geometries were used as the initial geometries for the composite, correlated G3(MP2) [48] or G3(MP2)B3 [49] molecular orbital theory level calculations. The G3(MP2)B3 method was used when the Hartree Fock geometry optimization step used in G3(MP2) produced incorrect geometries as the B3LYP geometry optimization step in G3(MP2)B3 avoids these issues. All calculations were performed using Gaussian16. [50]

3. Results and discussion

3.1. EPR investigation of PVC bombarded with MeV protons

The EPR spectra of PVC irradiated with accelerated protons (Figure 1) contains a single

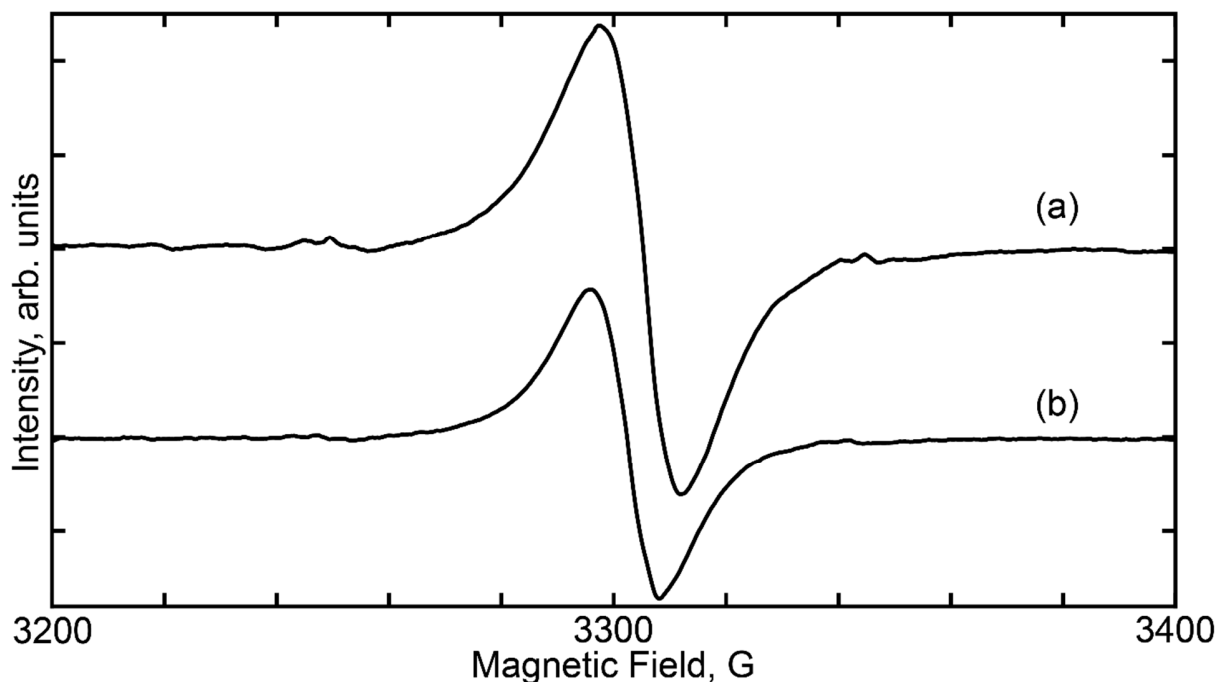


Figure 1. EPR spectra of PVC irradiated with 1 MeV protons. The irradiation dose is 2×10^{15} protons / cm^2 . (a) -196°C and (b) 23°C .

structureless line. The line widths are 1.5 and 1.3 mT, respectively, for spectra obtained at -196°C (Figure 1(a)) and 23°C (Figure 1(b)). Similar narrow singlet lines are recorded in the EPR spectra of PVC irradiated with accelerated electrons [32, 51, 52] and PVC heated after chemical treatment. [53] The lines are assigned to polyenyl radicals formed during PVC dehydrochlorination. These cannot be assigned simply to allyl radicals as the shape of the allyl radical EPR spectrum is known to be temperature dependent. [54,55]

The appearance of polyenyl radicals is due to loss of H and Cl atoms leading to the formation of polyenyl radicals of the form $-\text{CHCl}-\text{C}^*\text{H}-(\text{CH}=\text{CH})_n-\text{CHCl}-$, with $n > 1$. The formation of delocalized π systems starting with the smallest one, the allyl radical, leads to

stabilization of the radical. Irradiation with accelerated protons leads to the formation of polyenes and carbonization of the PVC chain. The formation of polyenes is especially characteristic of the thermal and photochemical destruction of PVC. [1,56] This process has been used to obtain nano- and pico-sized structures (including quasi one-dimensional ones) for electronics following the similar dehydrofluorination process of polyvinylidene fluoride. [57,58]

Proton bombardment of PVC can be used as an efficient method to produce a thin carbon rich surface on PVC. The depth of the radiation-chemical modifications of the polymer surface can be controlled using the dependence of the penetration depth of accelerated protons on their initial energy. Increasing the energies of 2×10^{15} protons to 1, 2, and 4 MeV gives maximum penetration depths of 1-2, 5-6, and 16-18 nm respectively. The dependence of the number of accelerated protons penetrating into the thickness of the PVC plate on the initial energies is given in Figure 2. The effects of proton bombardment will not be the same over the depth of the

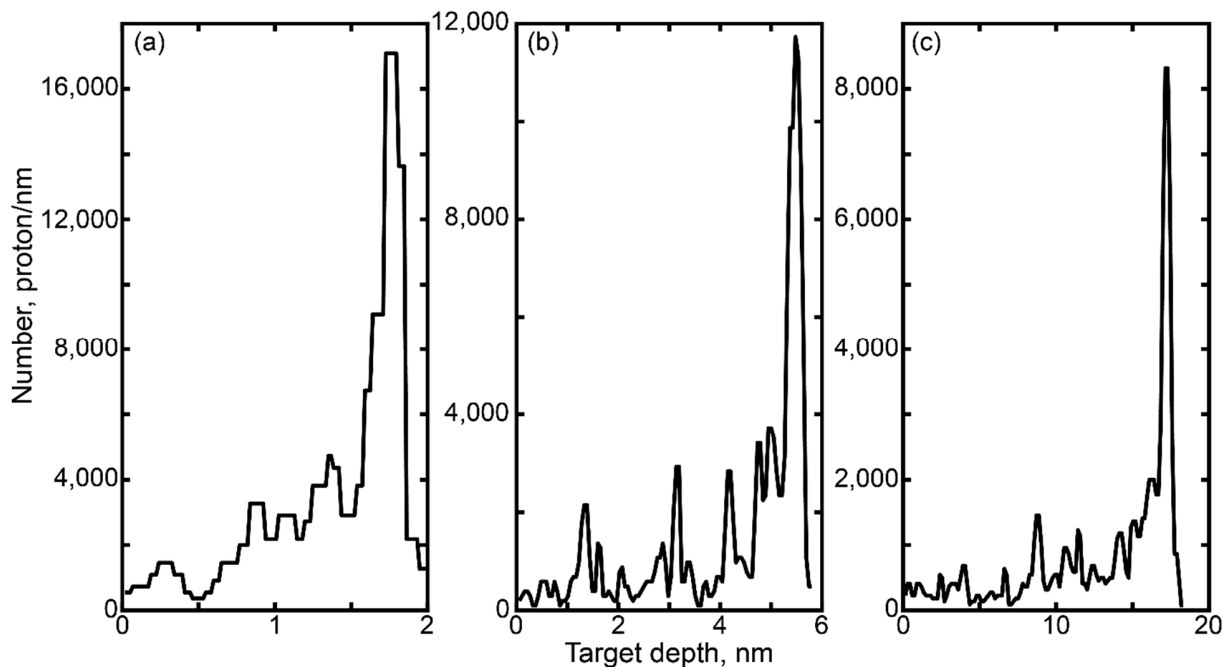


Figure 2. Number of accelerated protons penetrating into the thickness of the PVC plate, depending on the initial proton energies (MeV): (a) 1, (b) 2, (c) 4.

irradiated surface as the protons undergo inelastic and reactive scattering events. The thickness of the layer where the primary radiation-chemical processes take place is dependent on the proton energy.

3.2. The free surface energy of PVC bombarded with MeV protons.

The change in the surface properties of PVC as a result of proton bombardment can be described in terms of the free surface energy and its components, as well as the surface polarity. The surface energy characteristics were determined by measuring the contact angles of wetting of the initial and irradiated surfaces with test liquids. The data was analyzed by examining the graphical dependence in Fowkes coordinates (equation (iv))

$$x = (\gamma_l^{ab}/\gamma_l^d)^{0.5} \quad (\text{iva})$$

$$y = 0.5\gamma_l(1+\cos\theta)/(\gamma_l^d)^{0.5} \quad (\text{ivb})$$

The segment cut off on the ordinate is equal to the value $(\gamma_s^d)^{0.5}$, and the slope is responsible for the acid-base component of the FSE and corresponds to the value $(\gamma_s^{ab})^{0.5}$. According to Fowkes' concept, the value of FSE can be represented as a sum of components caused by forces of different nature, and it is sufficient to take into account only two of them, dispersion and acid-base.

The results for the surface free energies are given in Figure 3 and Table.1. Comparison of the data on the initial PVC with prior data for polyethylene [39] shows that the presence of chlorine in the PVC polymer increases the polarity of the surface, consistent with the literature. [59] A significant increase in the acid/base component of the FSE and an increasing of the surface polarity by more than a factor of 2 is observed after bombardment of PVC with

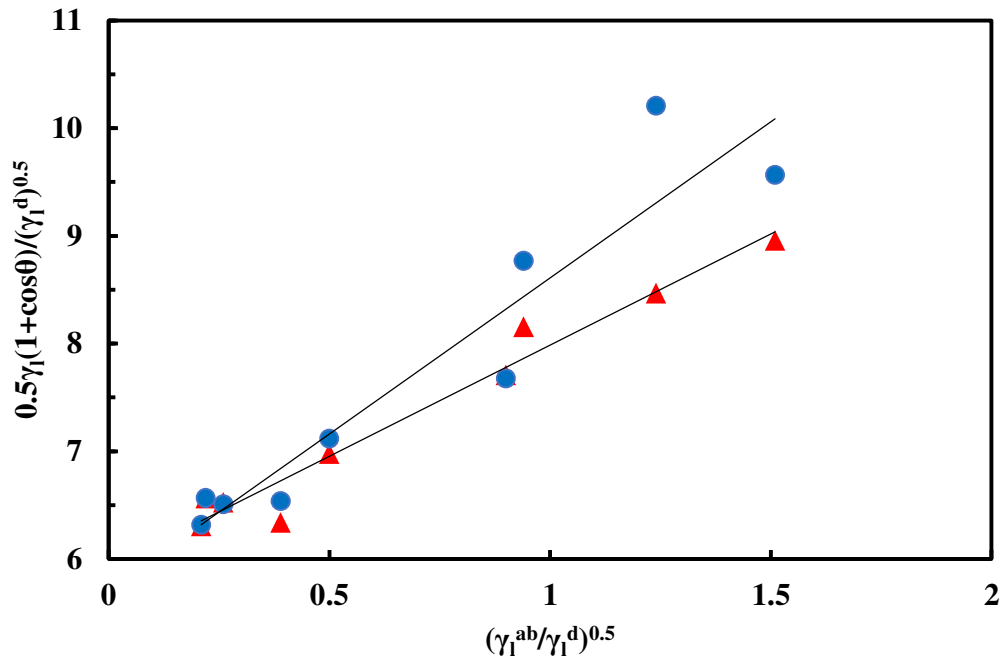


Figure 3. Calculation of the total free surface energy for ten test liquids in Fowke`s coordinates for: unirradiated PVC (blue dots; $y = 2.8968x + 5.713$ ($R^2 = 0.90$)), and PVC irradiated with 4 MeV protons with a dose of 2×10^{15} proton/cm² (red triangles; $y=2.0641x + 5.9216$ ($R^2 = 0.96$)).

Table 1. Surface energy characteristics of samples of PVC plates irradiated with accelerated 1 and 4 MeV protons with a dose of 2×10^{15} proton/cm².^a

Surface	MeV	γ_s^d , mN/m	γ_s^{ab} , mN/m	γ_s , mN/m	$x^p 10^2$	D, (mN/m) ^{0.5}
Native polymer		32.5	5.2	37.7	14.0	0.4
Irradiated polymer	1	29.7	14.5	44.2	32.8	2.96
	4	28.1	14.9	43.0	34.7	4.32

^a The relative measurement error of the contact angle of wetting is 1.7%. The error of the method for determining the FSE is no more than 2%.

accelerated 1 MeV protons. This is due to the appearance of functional polar groups containing oxygen in the irradiated surface layer. Oxidation of surface radicals can occur during bombardment with accelerated protons and become stabilized on the surface of the irradiated polymer. The oxygen is most likely introduced due to the removal of the irradiated PVC sheets from the proton accelerator cell leading to the sheets being in contact with air for a short time (5–10 s) during the removal of the sample. Similar functionalization of the polymer surface after bombardment with accelerated protons was observed in the case of irradiation of polyethylene [39], polytetrafluoroethylene, [60], and a tetrafluoroethylene–hexafluoropropylene copolymer. [61]

The results are associated with different densities of radiation-chemical transformations at different surface depths depending on the proton energy (Figure 2). In a polymer sample irradiated with 2×10^{15} protons at 1 MeV, the entire radiolysis process is carried out in the sample surface with a thickness of up to 2 nm, i.e., there is a very high density of radiation-chemical transformations in a very thin polymer layer. As a result, a large number of active centers are formed on the surface, with a depth < 2 nm and these sites are accessible due to diffusion of atmospheric oxygen. The oxidation of radicals leads to the formation of oxygen containing functional groups and an increase in the value of the acid/base component of the FSE and the polarity of the surface. The data in Table 1 indicate an increase in the functional activity of PVC as a result of proton bombardment. Fowkes [37] established the multicomponent nature of the FSE of any material. The acid-base component of the FSE includes the components in equation (v):

$$\gamma_s^{ab} = \gamma_s^h + \gamma_s^\pi + \gamma_s^{ad} + \gamma_s^e \quad (v)$$

where the index h refers to hydrogen interaction, π to π -bonds or interaction through the formation of π -complexes, ad to donor-acceptor interaction, and e to electrostatic. As a result of chemical modification with oxygen and the appearance of polar functional groups in the surface layer, the γ_s^{ab} components change and polymer chain fragments acquire permanent dipole moments, which leads to an increase in the concentration of polar fractions [59].

Bombardment with 2×10^{15} protons at 4 MeV leads to deeper dehydrochlorination of the polymer with the formation of a highly carbonized surface layer; as a result, an additional increase in polarity does not occur. The dispersion component of FSE of the polymer surface irradiated with 4 MeV protons decreases, indicative of supramolecular structural changes as a result of carbonization.

Information about the nature of the functional groups formed as a result of radiation oxidation of the PVC surface can be obtained by analyzing the change in the acidity parameter D, which was determined by the Berger method [62] based on the analysis of measurement data for contact angles of wetting with test liquids. The 2 pairs of liquids are: Lewis acid (phenol solution and glycerol) and Lewis base (aniline and formamide). In this case, the condition must be met that the pairs should be close to each other in the values of the acid-base and dispersion components, and two bipolar liquids, i.e. water and dimethylformamide. For each liquid, the value of the acid-base component of the adhesion work, W_{ab} (equation (v)), is calculated and then the quantitative characteristic of the acidity of the surface D (equation (vi)) is determined

$$W_{ab} = [\gamma_{lv}^s(1 + \cos\theta) - 2(\gamma_{lv}^d)^{0.5}(\gamma_s^d)^{0.5}] / (\gamma_{lv}^{ab})^{0.5} \quad (v)$$

$$D = W_{ab}(\text{aniline}) + W_{ab}(\text{formamide}) - W_{ab}(\text{phenol}) - W_{ab}(\text{glycerin}) \quad (vi)$$

where γ_{lv}^s is the FSE of the liquid, $\cos\theta$ is the contact angle of wetting, γ_{lv}^{ab} and γ_{lv}^d are the acid-base and dispersion components of the FSE of the liquid, γ_s^d is the dispersion component of the FSE of the solid surface.

For surfaces containing predominantly acid groups (proton donor), the acid-base coefficient $D > 0$, and for surfaces containing proton acceptors $D < 0$. The values of the acidity parameters of the unirradiated and irradiated with accelerated protons PVC surfaces are presented in Table 1. The surface of unirradiated PVC is weakly acidic as electron withdrawing groups such as Cl are present. Because the surface of PVC contains Cl atoms with electron-donor properties as well as basic properties, the PVC surface has a more complex nature and cannot be considered monopolar.

Irradiation of PVC with accelerated protons leads to an increase in the acidity parameter, which indicates an increase in the content of acidic functional groups in the surface layer. The parameter D increases by factors of 7 and 10 compared to the native sample for samples irradiated with 1 MeV and 4 MeV protons respectively. On the basis of the IR spectra discussed below, there is evidence for the formation of hydroxyl, carboxyl, and other active electron withdrawing groups on radiation oxidation of the PVC surface. In addition, as a result of carbonation the content of chlorine atoms is decreased further increasing the acidity of the surface.

3.3. IR spectroscopy of native and irradiated PVC.

The IR spectrum of the initial, unirradiated, polymer in the range of 400 to 4000 cm^{-1} (Figure 4a) shows a number of peaks with the positions of the maxima listed in Table 2. The interpretation of the position of the maxima in the spectra is based on comparison with known literature values. [63,64,65,66,67,68,69,70,71,72,73,74] The absorption bands corresponding to

the stretching vibrations of the C–Cl bond in the CHCl group are in the range 530 to 800 cm^{-1} . The intense absorption bands with peaks at 606, 636, 691, 1251 and 1424 cm^{-1} are associated with bending vibrations of the CH_2 and CHCl groups as well as the C–Cl stretches. In the high frequency region of the IR spectrum, peaks with an average intensity in the range of 2800 to 3050 cm^{-1} are assigned to symmetric (2907 cm^{-1}) and asymmetric (2971 cm^{-1}) stretching vibrations of the CH_2 group (Figure 4a). In addition, the IR spectrum of the polymer contains peaks with relatively low intensity assigned to other CH and CHCl fragment motions.

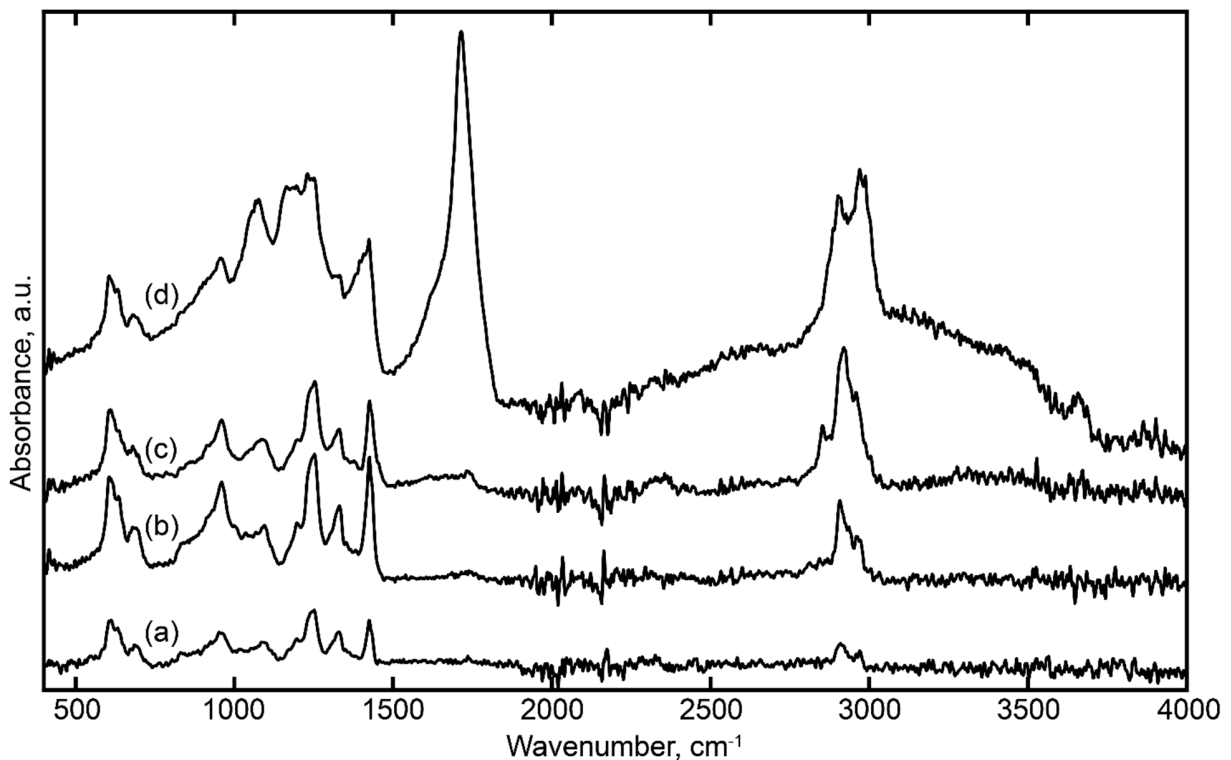


Figure 4. IR spectra of PV samples depending on the dose of γ -irradiation. Dose γ -irradiation (kGy): (a) 0 (vacuum), (b) 670 (vacuum), (c) 3000 (vacuum), (d) 3000 (air).

Table 2. Assignment of the bands of the experimental IR spectrum^a in cm⁻¹ of the PVC before and after radiolysis with γ -rays of ⁶⁰Co in air.

0 kGy	670 kGy	3000 kGy	3000 kGy ^b	Lit ν	Assignment ^c [63-73]
2971 m	2971 sl	2973 m	2972 s	2971 m	$\nu(\text{CH})$
2936 vw	2936 w	2936 sl		2930	$\nu_{\text{as}}(\text{CH}_2)$
2919 sl	2917 sl	2919 vs		2914	$\nu_{\text{as}}(\text{CH}_2)$
2907 m	2907 m	2907 sl	2907 m	2907	$\nu_{\text{s}}(\text{CH}_2)$
		2852 w		2872 \pm 10	$\nu_{\text{s}}(\text{CH}_2)$
	1950 vw	1950 w		1970-1950	$\nu_{\text{as}}(\text{C}=\text{C}=\text{C})$, $\nu(\text{CC})$
			1714 vs	1725-1705	$\nu(\text{C}=\text{O})$
1434 sl	1434 sl	1434 sl		1431	$\delta(\text{CH}_2)$
1424 vs	1424 vs	1424 vs	1424 vs	1424	$\delta(\text{CH}_2)$
1329 s	1331 m	1331 m	1331 m	1328	$\delta(\text{CH}_2)$
1251 vs	1251 vs	1251 vs	1251 vs	1249	$\gamma_{\text{r}}(\text{CH})$ in a group CHCl
1240 sl	1240 sl	1240 sl	1231 w	1249	$\gamma_{\text{r}}(\text{CH})$ in a group CHCl
1197 w	1196 w	1196 w	1196 vw	1196	$\delta(\text{CH}_2)$
1095 m	1095 m	1097 m	1076 m	1093	$\gamma_{\text{w}}(\text{CH})$
960 m	960 m	960 m	960 m	958	$\gamma_{\text{w}}(\text{CH})$
691 m	691 m	691 w	691 w	691	$\nu(\text{C}-\text{Cl})$
636 m	636 m	636 w	634 w	638	$\nu(\text{C}-\text{Cl})$
606 s	609 m	608 m	609 m	611	$\nu(\text{C}-\text{Cl})$

^a Intensity of bands: vs = very strong, s = strong, m = medium, w = weak, vw = very weak,

sl = shoulder. ^b Irradiation in air. ^c ν = stretching, ν_{s} = symmetric stretching, ν_{as} = asymmetric stretching, δ = bending, γ_{w} = wagging, and γ_{r} = rocking.

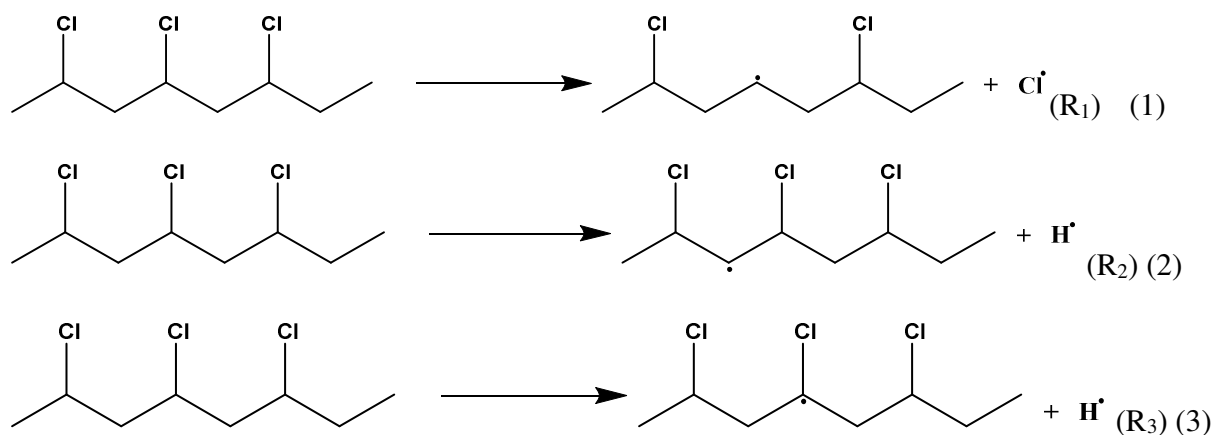
γ -irradiation of PVC in vacuum leads to changes in the IR spectrum of PVC (Figure 4b,c) consistent with prior work. [18,19,75] In the spectrum of the irradiated polymer, the intensity of the band at 2907 cm⁻¹ and the relative intensity of the band at 2971 cm⁻¹ increases. The change in the integrated intensity of absorption bands at 2971 cm⁻¹ and 2907 cm⁻¹ depends on the dose of γ -irradiation of PVC. As the irradiation dose increases, the relative intensity of absorption bands of CH fragments of the polymer relative to the intensity of the absorption band of its CH₂ fragments also increases. During radiolysis of PVC, there is a decrease in the relative intensity of absorption bands in the frequency range 530 to 800 cm⁻¹ corresponding to C-Cl stretching

vibrations [76,77,78]. In this case, the dependence on the irradiation dose for the intensity of the C–Cl absorption is similar to the dependence of the C–H bonds in the methylene fragments of the polymer. This is due to loss of HCl leading to a simultaneous decrease in the content of chlorine and hydrogen atoms in the irradiated PVC, similar to when PVC is heated. [79,80,81] These results show that radiolysis of PVC in a vacuum lead to dehydrochlorination and the formation of unsaturated bonds.

As the proposed method of dosimetry described below is carried out in the presence of air, we also studied the IR spectrum of PVC irradiated in air (Figure 4d). γ -irradiation of PVC in air leads to significant changes in the IR spectrum of PVC compared to both the unirradiated and vacuum irradiated materials. Changes in the relative intensities of absorption bands associated with C–H and C–Cl vibrations and the appearance of new bands attributed to fragments of macromolecules containing oxygen and unsaturated bonds (Table 2) are observed. The spectrum of the irradiated polymer retains absorption bands in the IR region characteristic of PVC. Thus, both in vacuum and in air, exposure to γ -radiation does not lead to complete destruction of the molecular chain of the polymer. A new broad vibrational band appears around 3570 cm^{-1} in the IR spectrum of PVC irradiated in air (Figure 4d). This band may be assigned to hydroxyl groups generated by interaction with air during radiolysis. A characteristic feature of the IR spectrum of γ -irradiated PVC in air is the appearance of peak with very high intensities in 1714 cm^{-1} , corresponding to the absorption bands of the carbonyl group (Table 2). The results show that the radiolysis of PVC in air is dehydrochlorination which leads to the formation of unsaturated bonds and the appearance of carbonyl, and possibly, hydroxyl groups.

3.4 Computational reaction thermodynamics

Different mechanisms have been proposed for the destruction of PVC [2,82,83,84,85] For example, the process of thermal dehydrochlorination of PVC is hypothesized to proceed in two stages, first single double bonds are formed, and then polyconjugated systems are formed. [82] In this case, there is no destruction of the polymer backbone. Semi-empirical calculations at the MINDO/3, AM1, and MNDO-PM3 levels examined heterolytic and homolytic cleavage in models of PVC. [86] In order to develop insights into the thermodynamics relevant to these mechanisms in vacuum, composite correlated molecular orbital theory at the G3(MP2) level was used to predict the thermodynamics of a range of reactions. The energy results are in Table 3. High-energy radiation, such as γ -irradiation, can break, with almost the same probability, the C–H and C–Cl bonds of the PVC macromolecule as shown by reactions (1) to (3).



The high probability of these processes occurring during the radiolysis of PVC is associated with the ability of the H and Cl atoms produced by bond cleavage to leave the cage of the two radicals. EPR spectroscopic studies showed [87] that in low temperature radiolysis of PVC, radical products can be formed by dissociative electron capture by chlorine (reaction (4)).

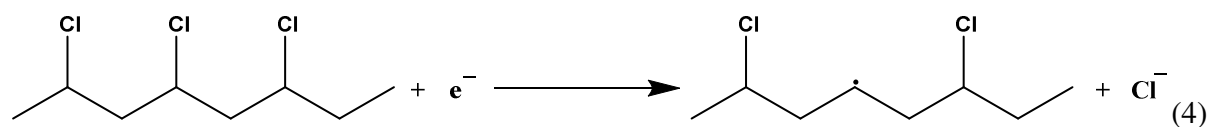


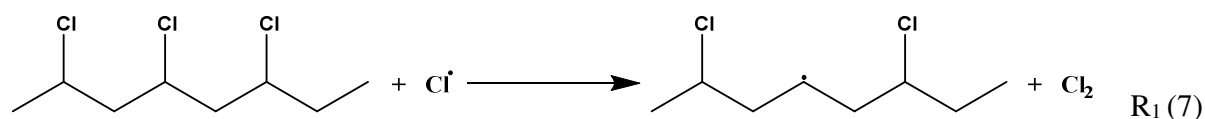
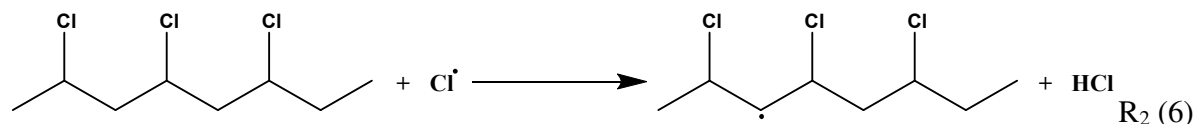
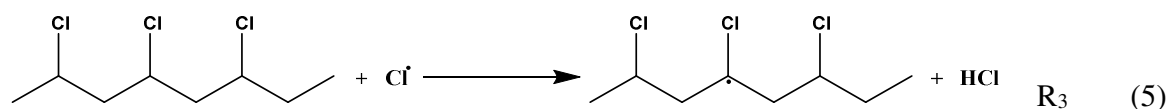
Table 3. PVC decomposition reaction enthalpy (ΔH , kcal/mol) and free energy (ΔG , kcal/mol), calculated at G3(MP2).

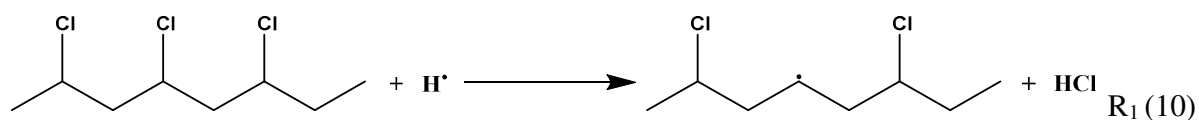
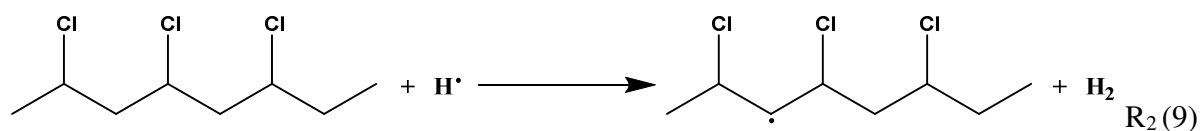
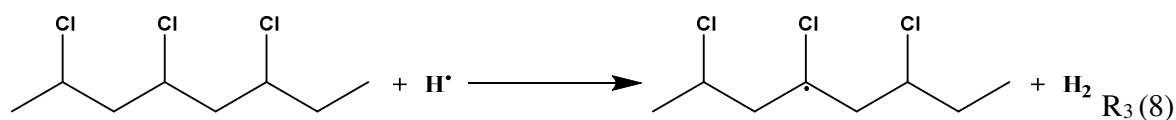
Rxn # ^a	ΔH	ΔG	Rxn #	ΔH	ΔG
1	88.1	77.0	32	42.3	35.8
2	99.3	89.5	33	29.7	21.9
3	98.8	89.4	34	46.6	39.5
4	3.3	-7.3	35	43.2	36.5
5	-4.6	-7.9	36	-61.1	-61.5
6	-4.2	-7.7	37	-63.0	-62.5
7	30.6	26.3	38	-27.9	-28.9
8	-6.5	-8.9	39	-73.8	-75.4
9	-6.1	-8.8	40	-56.8	-57.7
10	-15.3	-20.2	41	-58.7	-58.8
11	22.0	14.4	42	-60.2	-60.7
12	35.4	28.8	43	-62.1	-61.7
13	-70.3	-70.4	44	12.1	1.5
14	-72.2	-71.4	45	-29.7	-21.9
15	-68.1	-68.4	46	-42.9	-36.3
16	-70.0	-69.4	47	-16.0	-9.1
17	-35.5	-36.4	48	-28.1	-22.0
18	-81.5	-82.8	49	-29.0	-21.1
19	-68.4	-68.9	50	-43.2	-36.5
20	-70.3	-70.0	51	-17.0	-10.0
21	17.8	6.7	52	-30.3	-24.2
22	85.9	76.9	53	89.4	76.5
23	71.7	61.7	54	89.3	76.1
24	83.9	75.0	55	89.9	75.3
25	-17.6	-20.3	56	90.6	76.1
26	-19.5	-21.4	57	97.6	85.7
27	-19.6	-22.2	58	91.3	79.0
28	-21.5	-23.3	59	98.1	85.8
29	14.2	11.0	60	100.5	87.7
30	-31.7	-35.5	61	87.1	74.5
31	4.7	-5.7			

^a Reaction numbers given in the text.

The EPR spectra of the low temperature radiolysis of PVC has a total width of -17 mT. As noted above, the room temperature EPR spectrum of these radicals has a single peak showing that as the temperature increases, polyenyl radicals are formed. We hypothesize that a similar process is operating at room temperature as at low temperatures given the energetics of the process. This type of electron capture reaction was also found for low temperature PVC radiolysis in a methyltetrahydrofuran matrix. [88] The predominance of this electron capture process in the process of PVC radiolysis is due to the high electron affinity of Cl (3.612709 ± 0.000087 eV = 348.6 kJ/mol), [89] which is essentially the same as the dissociation of the C-Cl bond. (354 ± 6.3 kJ/mol for CH₃CHClCH₃). [90] Therefore, in the case of low temperature radiolysis of PVC, the heterolytic cleavage of the C-Cl bond with the formation of a free macroradical and a chlorine anion is energetically more favorable. [91] The reaction of chlorine loss with the formation of macroradicals R₁ from reaction (1) is supported by experimental studies. [92] Loss of H as shown in reactions (2) and (3) leading to the formation of macroradicals R₂ and R₃ during PVC radiolysis is not supported by our experiments.

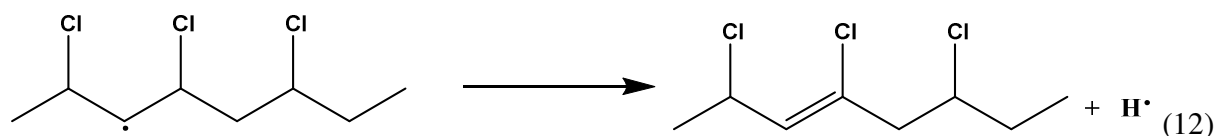
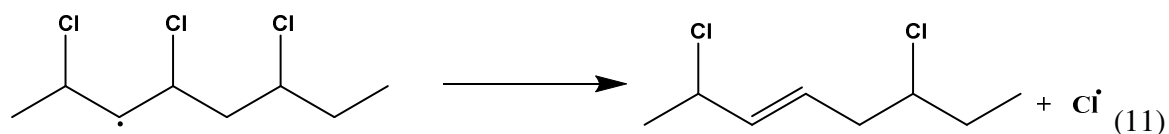
A secondary mechanism for PVC backbone radical product is H abstraction (reactions (5) and (6)) or Cl abstraction (reaction (7)) by Cl. H atoms can abstract H or Cl as shown by reactions (8) to (10).



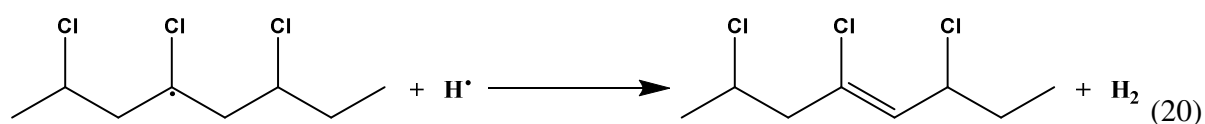
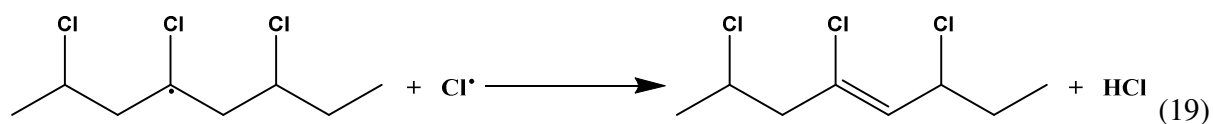
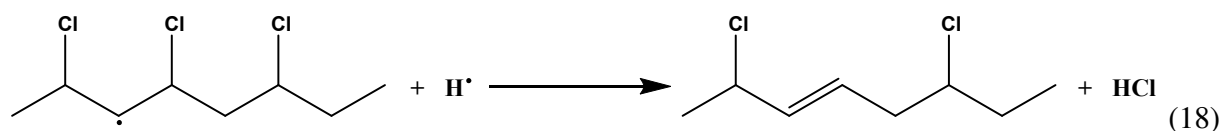
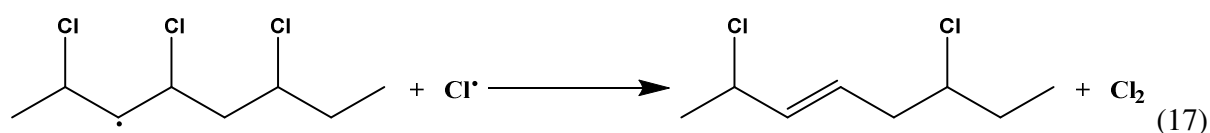
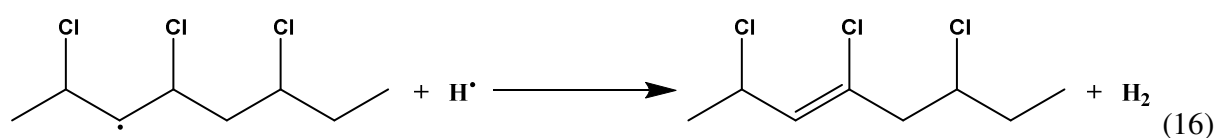
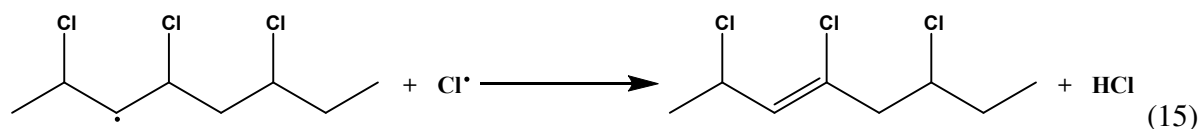
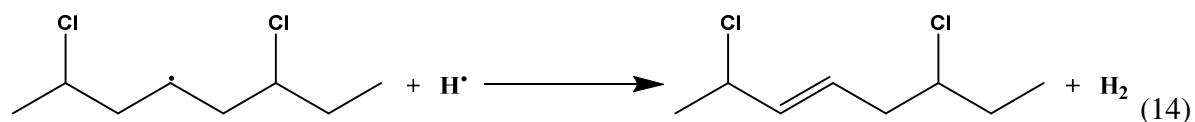
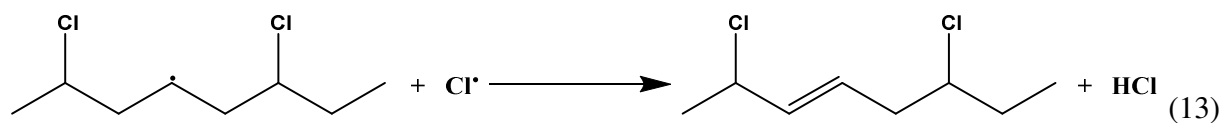


Reactions producing either HCl or H₂ are more exothermic than the reaction producing Cl₂, with hydrogen radical abstraction of a chlorine to produce HCl, reaction (10), being the most exothermic. Once initial hydrogen and chlorine radicals are present in the system, it is thermodynamically favorable for backbone radical formation to proceed through radical abstraction, but bond cleavage will still be occurring due to the presence of high energy γ -radiation.

The dehydrochlorination process proceeds predominantly according to reaction (6) in the direct chlorination of aliphatic chlorides. [93] The resulting radical from reaction (6) is unstable and can decompose with release of Cl or H as shown in reactions (11) and (12).



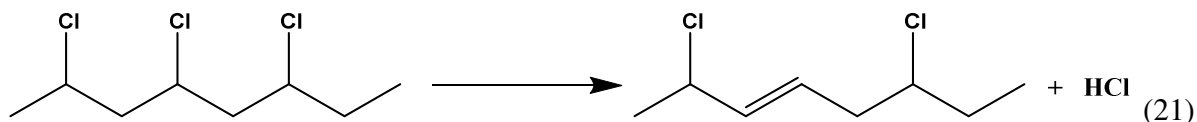
The loss of H from the product of reaction (6), reaction (12), is a higher energy reaction than loss of Cl in reaction (11). The radicals formed in reactions (1)-(3), R₁, R₂, and R₃, can all proceed to form unsaturated species by further radical abstraction reactions, (13)-(20).



The radical abstraction reactions starting with backbone radical species are exothermic. These results are similar to the initial radical abstraction to produce the backbone radicals with reactions that produce HCl and H₂ being more exothermic than the reaction that produces Cl₂; the most exothermic reaction is hydrogen radical abstraction from R₂ to produce HCl, reaction (18). Similar to the initial backbone radical formation, although radical abstraction reactions are

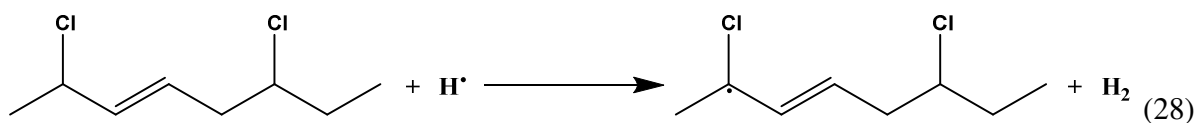
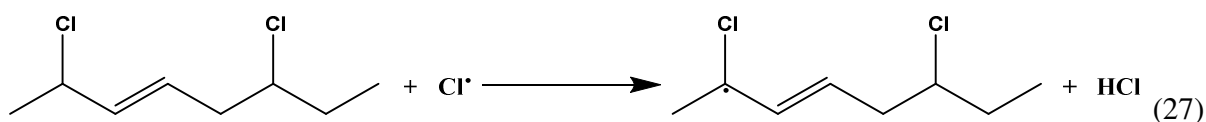
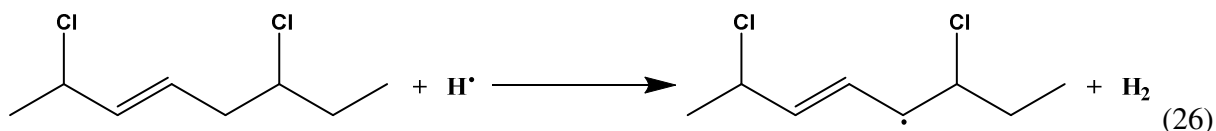
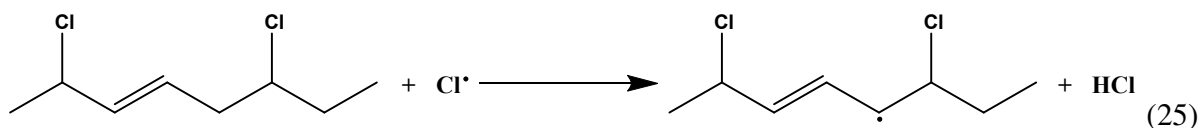
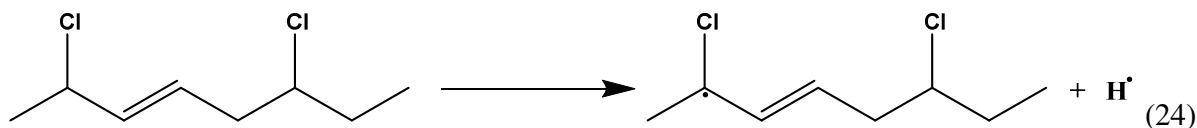
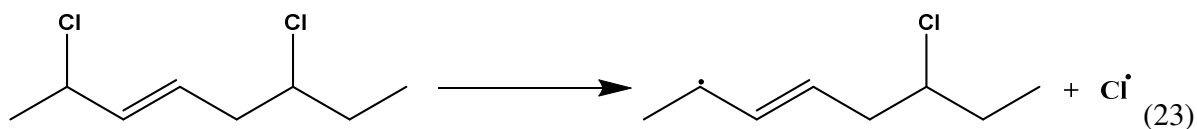
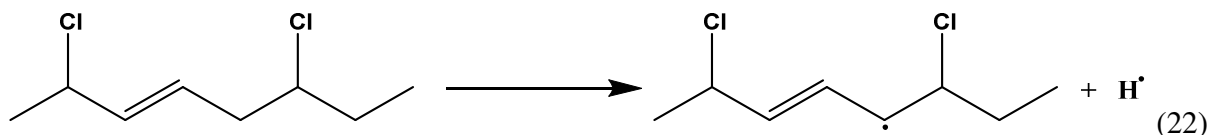
more thermodynamically favorable, bond cleavage will still continue to occur during γ -irradiation.

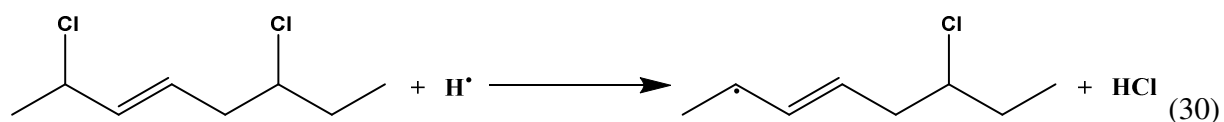
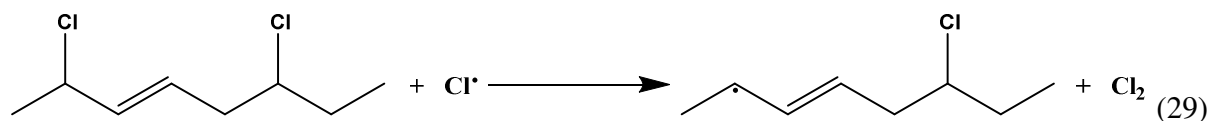
Unsaturation in the chain can also arise by the unimolecular loss of HCl, reaction (21),



However, reaction (21) is expected to have a large unimolecular reaction barrier (on the order of 210 kJ/mol for HCl loss from $\text{CH}_3\text{CHClCH}_3$) which reduces its likelihood. [94]

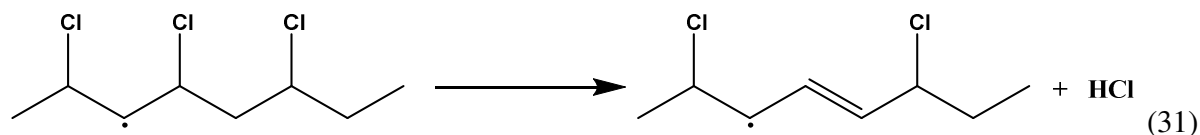
Polyenyl radical formation can occur via various pathways (reactions (22) to (30)).





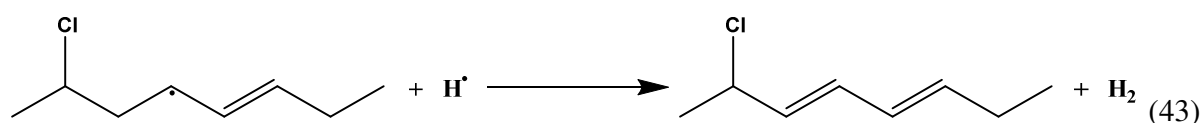
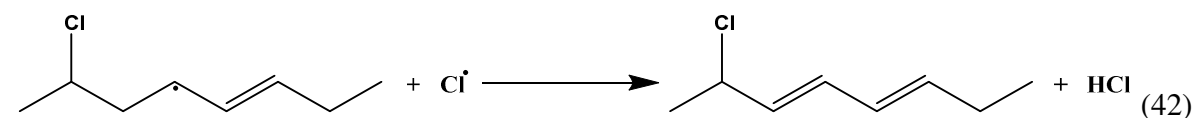
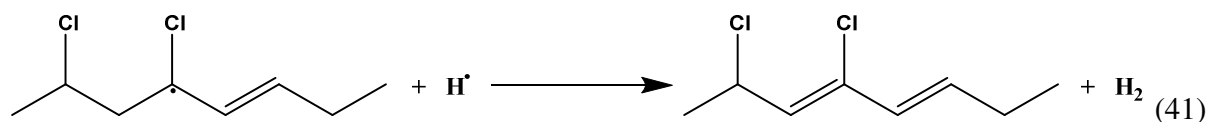
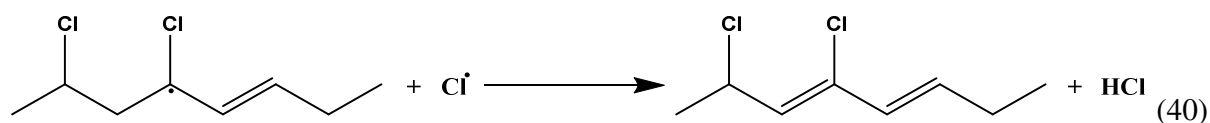
Similar to the trends described above, radical abstraction reactions (25)-(30) are much more exothermic than the pure bond cleavage reactions, reactions (22)-(24). The exception to this is reaction (29) which produces Cl₂; this radical abstraction reaction is endothermic.

It is also possible for polyenyl radicals to form directly from a radical based on a saturated system, reaction (31).

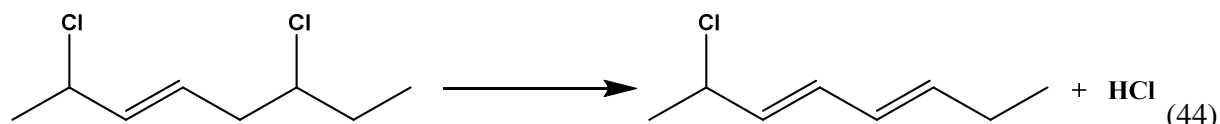


This direct formation of a polyenyl radical has a negative free energy with a positive enthalpy and there is likely to be a substantial activation energy barrier, similar to direct unsaturation by loss of HCl. The energetic benefit of polyenyl radical formation, due to radical delocalization, is clear when reaction (31) is compared to direct loss of HCl from a saturated backbone, reaction (21).

Some of these reactions likely contribute to the formation of polyenyl radicals observed in the EPR spectra of PVC irradiated with both MeV protons (Figure 1) and with γ -rays. [51,52] The single step dehydrochlorination to produce a polyenyl radical [31] can be a chain process and continue until chain termination. [91,92] Undoubtedly, both during radiolysis [91,92] and under the influence of heat and light, [1,2], polyene radicals are formed in PVC as a result of the chain cleavage due to loss of HCl. Their generation is facilitated by the presence of a double

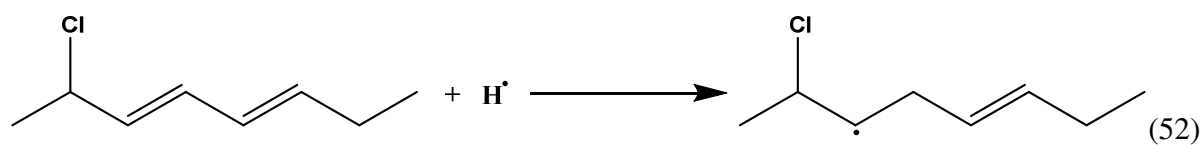


Single step loss of HCl to produce conjugated double bonds can occur, reaction (44).



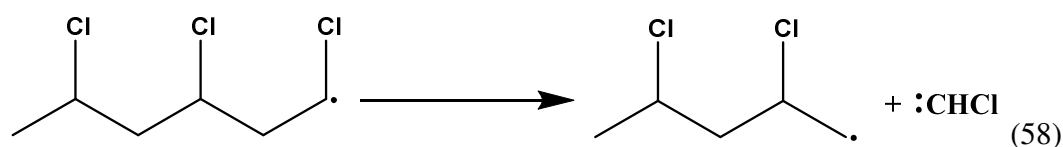
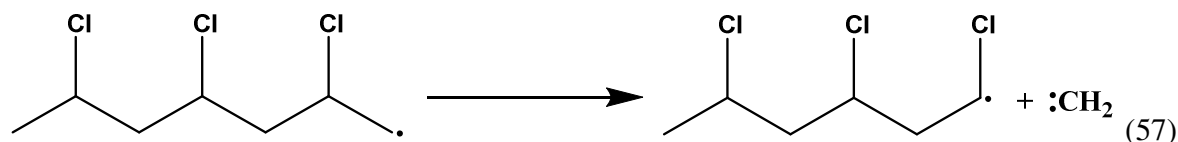
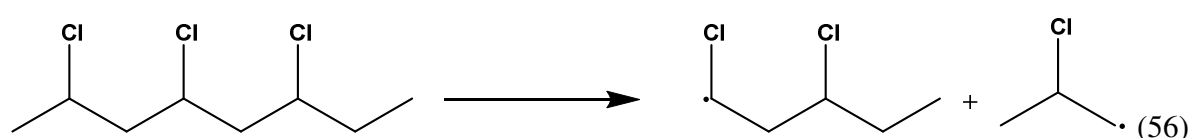
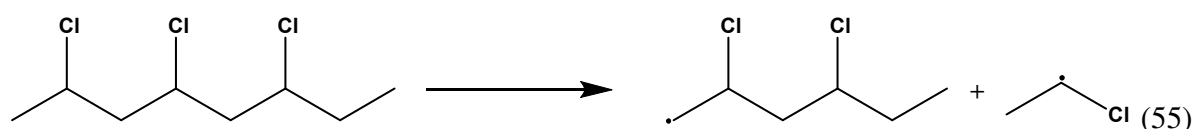
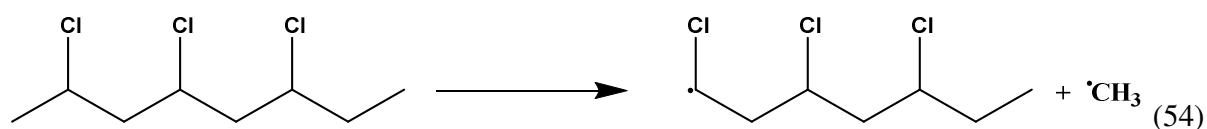
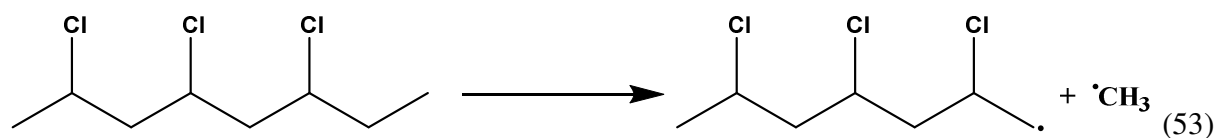
The most favorable of these reactions are the abstraction reactions; reaction (39) is the most thermodynamically favorable and reaction (38) is the least favorable with the most favorable non-abstraction reaction being reaction (33). The single step dehydrochlorination via loss of HCl, reaction (44), is thermodynamically unfavorable compared to the abstraction reactions and likely has a high activation energy barrier.

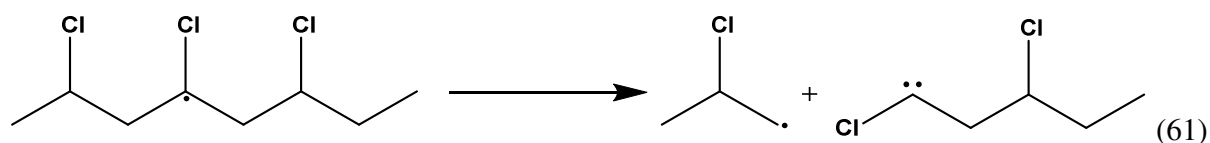
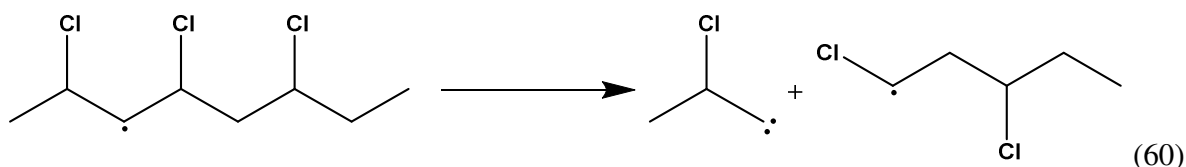
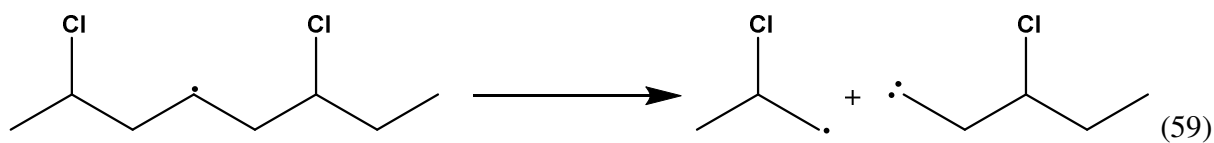
The presence of conjugated double bonds is shown by the FTIR data (Table 2). The process of PVC dehydrochlorination by the above mechanism leads to a decrease in the proportion of C–H bonds of methylene groups due to detachment of a hydrogen atom from these groups during the formation of HCl. As a result, a decrease in the relative intensity of the absorption band of these groups in the frequency range of 2907 cm^{-1} is observed in the IR spectrum. At the same time, an increase in the intensity of the band at 2971 cm^{-1} is observed,



These radical addition reactions are exothermic due to the stabilization and delocalization of the radical on the backbone. The likelihood of this process increases with the lengthening of the conjugation chain of unsaturated bonds and is unlikely to be observed during the initial stages of PVC irradiation.

One of the expected PVC radiolysis channels is the rupture of the polymer backbone C–C bond, reactions (53)–(61).





These backbone cleavage reactions, both to produce radicals (reactions (53)-(56)) and to produce carbenes (reactions (57)-(61)), are energetically similar to breaking C-Cl and C-H bonds, reactions (1)-(3); such reactions are likely to occur during high energy γ -irradiation. However, the limited mobility in the solid polymer matrix of the resulting radicals and carbenes, which are in the cage of the macroradical's pairs, does not allow them to leave the cage, so they are likely to recombine with each other or disproportionate. This cage effect involving radical recombination due to low mobility has been hypothesized in many different polymer degradation processes. [95,96] Free terminal radicals, $\sim\text{CH}_2\dot{\text{C}}\text{HCl}$ and $\sim\text{CHCl}\dot{\text{C}}\text{H}_2$, can be produced but are likely to be of such low concentration as not to be detected in the EPR spectra of irradiated PVC. A detailed computational study of the inclusion of O_2 in the reaction mechanism would generate a very large number of reactions [69] so this was not pursued in the current work.

3.5 The use of polyvinyl chloride as a dosimeter on complex surface reliefs.

The accumulation in the polymer structure of various chromophore groups (C=C, C=O) as shown by their presence in the IR spectra is consistent with a gradual change in the initial white color of the polymer during the radiolysis of PVC first to yellow, and then to brown and black with increasing radiation dose. In the case of PVC radiolysis in air, cross-linking between

adjacent macromolecules can occur, but apparently it is not dominant. The formation and accumulation of carbonyl fragments and unsaturated bonds during PVC irradiation indicates that radiative oxidation and dehydrochlorination are the dominant processes of PVC radiolysis in air. This is confirmed by the change in the initial white color of the surface of the irradiated polymer to black due to the accumulation of chromophore fragments (unsaturated bonds, carbonyl groups) in the structure of the irradiated polymer. The predominance of the degradation process over the crosslinking of the polymer chain was also observed during the radiolysis of PVC by accelerated electrons. [87] Thus, the auxochromic OH group potentially formed by radiolysis of PVC in air as suggested by the IR spectrum enhances the effect of chromophore groups and causes deeper color intensity. Such a color change from white to black with an increase in the γ -irradiation dose of PVC is consistent with carbonization of the polymer chain. Although it is possible that the dark color could be due to extended conjugation of double bonds, the amount of conjugation would have to be large, certainly greater than 6 to 10 double bonds.

We tested the possibility of using the high sensitivity of PVC color to the radiation dose to visually determine the dose field and the direction of the ^{60}Co γ -radiation beam on the surface of a target with a complex relief. The dosimetric mixture was prepared from PVC powder by mechanical mixing with an adhesive base made of silicate glue used to bond the mixture to the surface of the irradiated target. Then the finished mixture was applied to the surface of items made of ordinary window glass or polymethylmethacrylate. The color of targets irradiated in air with various doses of γ -radiation was visually assessed to determine the degree of change. Preliminary experiments have shown that such a dosimetric system can be successfully used to visually determine the dose of γ -irradiation above 2 kGy. In this case, on the surface of the

radiolysis dosimetry system, the color of the polymer component changes from white to black, depending on the radiation dose (Figure 5).

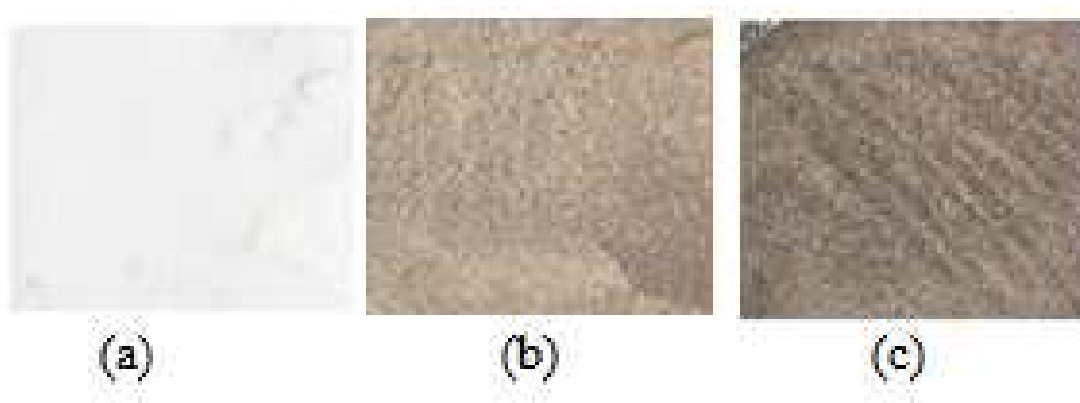


Figure 5. The Color of PVC γ -irradiated with a dose (kGy): (a) 0, (b) 36, (c) 100.

The main advantages of the proposed dosimeter system made of a mixture of powdered PVC and silicate glue are availability, low cost, compatibility of PVC with any adhesive base, good adhesion of the system to inorganic and organic surfaces, as well as ease of preparation and removal from the target surface. Discoloration of the dosimetry system caused by radiation is easily detected visually. In the future, such dosimetric systems, when studied in detail, can provide the greatest therapeutic effect and create the most favorable distribution of the absorbed dose of radiation in the body for the patient.

3.6. Determination of toxicity class and acute toxicity of PVC before and after γ -irradiation.

In order to use PVC in dosimetric systems for radiation therapy, as well as when using radiation sterilization for materials containing PVC, it is necessary to know the effect of radiation on the toxicity of the polymer. Thus, we investigated the acute toxicity of PVC powder, pre-irradiated in air with doses of 100, 500 and 1400 kGy of ^{60}Co γ -radiation. To determine the class of acute toxicity, PVC was administered to experimental hybrid mice of the BDF1 line

once intragastrically at a dose of 2000 mg/kg of body weight to 3 animals. All of these mice survived so as a further test, PVC was administered to another group of 3 mice in accordance with the experimental design of OECD 423. [40] No animals died in the second group. In an additional study, a single oral administration of 2000 to 5000 mg/kg of animal weight to six mice was also made and again there were no deaths. During the entire observation period, there were no signs of intoxication. The dynamics of body mass was positive. During clinical observations within 14 days after oral administration of PVC, during external examination of animals of both groups, it was noted that in animals there is a smooth shiny coat, the skin is elastic and mobile, the subcutaneous tissue is moderately expressed, the visible mucous membranes are shiny, and there were no pathological discharge from the natural body orifices. Based on the study carried out, PVC for acute toxicity parameters can be classified as hazard class 5 in accordance with OECD 423. [40]

The study of acute toxicity of both the initial and γ -irradiated polymer with a dose of 100 to 1400 kGy showed that its single oral administration in doses of 1000 to 5000 mg/kg does not cause animal deaths. No clinical manifestations of toxicity and changes in behavioral responses of experimental animals were observed before the end of the experiment. Autopsy of the animals did not reveal any damage to the internal organs. According to the guideline [41], if the LD₅₀ cannot be determined due to the low toxicity of the test substance, the maximum dose that was administered to the animals should be indicated and is not less than 2000 mg/kg. Thus, the studied PVC samples, both initial and radiolyzed from 100 to 1400 kGy, in accordance with the Halle and Göres classification, can be assigned to the 5th class (Little toxicity). [34]

3.7. Study of the local irritating effect of a mixture of PVC and silicate glue.

No signs of toxicity or death of mice were found in testing the local irritating effect of mixtures of PVC and silicate glue, which were γ -irradiated in air with doses of 100, 500 and 1400 kGy of ^{60}Co γ -radiation. The experimental animals did not differ in their behavior and appearance from the control animals. After applying the samples at a concentration of 5000 mg/kg to the skin of the animals, the appearance of erythema, edema and ulceration was not observed. Differences in the dynamics of weight gain in experimental and control animals were also not revealed. Thus, no local irritating effect of PVC samples (before and after γ -irradiation) was detected in the adhesive mixture at a concentration of 5000 mg/kg.

4. Conclusions

Proton bombardment of PVC at room temperature leads to the formation of polyenyl radicals with a characteristic single structureless line of the EPR spectrum. The appearance of functional polar groups in the surface layer of the irradiated polymer due to the oxidation of macroradicals by atmospheric oxygen leads to an increase in the FSE and its dispersion component, its acid-base component, and the polarity of the surface. Proton bombardment of PVC significantly increases the number of electron-acceptor centers in the surface layer giving a predominantly acidic character. These processes intensify with an increase in the radiation dose. γ -irradiation of PVC in air leads to significant changes in its IR spectrum due to the formation of hydrogen chloride, unsaturated bonds, and carbonyl and hydroxyl groups. An increase in the radiation dose from 100 to 2000 kGy does not lead to the appearance of new absorption bands, but there is an increase in the relative band intensities of the new bands.

Decomposition thermodynamics were calculated at the G3(MP2) level based upon an 8-carbon backbone chain PVC model. Although the initial loss of either hydrogen or chlorine

radicals is thermodynamically unfavorable, it is likely to occur due to high energy γ -radiation. Radical abstraction reactions are generally exothermic and exergonic and are the thermodynamically favorable pathway to polymer backbone radical formation. Further radical abstraction to produce isolated backbone unsaturation, polyenyl radicals, and conjugated backbone unsaturation is thermodynamically favorable. Although backbone C-C bond cleavage is energetically possible, these products are not found experimentally due to radical recombination due to the “cage” effect.

A mixture of powdered PVC and silicate glue can be used for γ -radiation dosimetry due to the high sensitivity of PVC color to the absorbed radiation dose. Samples of γ -irradiated PVC with a dose of 100 to 1400 kGy PVC in an adhesive mixture do not have any local irritant effect when applied to the skin of mice. Radiolysis of PVC powder in air with γ -rays at doses up to 1400 kGy does not affect its acute toxicity when administered intragastrically to BDF1 mice. PVC and its γ -irradiated analogs are non-toxic at doses up to 5000 mg/kg and belong to the 5th class (Little toxicity) toxicity in accordance with the classification of Halle and Göres. [34]

Author statement

The project was conceived by S. R. Allayarov and D. A. Dixon. The experimental work and analysis were performed by Sadulla R. Allayarov, Svetlana A. Bogdanova, Tatyana N. Rudneva, Uguljan Yu. Allayarova, Ilgiza F. Shaimukhametova, Sergei V. Demidov, Denis V. Mishchenko, Elena N. Klimanova, Tatyana E. Sashenkova, Svetlana D. Chekalina, and Sergey M. Aldoshin. The computational work and analysis were performed by M. P. Confer and D. A. Dixon. All authors participated in writing the manuscript.

Declaration of Competing Interest

The authors declare no competing financial interest.

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γ -Radiation
Sensor

