Study of the influence of gamma-rays on the structure and topography of the polyketone surface

M.Yu. Tashmetov, N.B. Ismatov*

Institute of Nuclear Physics of the Academy of Sciences of the Republic of Uzbekistan, 100214, Tashkent, Uzbekistan

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* Corresponding author: e-mail: normamat@inp.uz, Phone: +998 99 848 81 04

In this work, we investigated the effect of gamma-radiation of various doses on surface morphology, molecular vibrations, and polyketone structures. After irradiation of polyketone with gamma-quanta with a dose of $3.5 \times 10^8$ R, the surface roughness is smoothed, as a result, the average surface roughness decreases from $R_z = 879$ nm to $R_z = 375.4$ nm, and in the infrared spectra of the polyketone a peak with a wavenumber of $1174 \text{ cm}^{-1}$ is observed. At exposure of gamma-radiation with a dose of $3.5 \times 10^8$ R, an increase in the length of the C1–C2, C2–H1 and C2–H2 bonds is observed, which leads to an increase in the unit cell parameters of the polyketone of the orthorhombic phase (space group $Pnam$). An increase in the dose of gamma-irradiation to $2 \times 10^8$ R leads to a decrease in the content of the amorphous phase and an increase in crystallinity. Irradiation with gamma-radiation stimulates the growth of crystallinity and the degree of crystallinity increases from 45.5% to 61.7%. A further increase in the dose ($\geq 2 \times 10^8$ R) leads to a decrease in the degree of crystallinity, which is associated with the degradation of the polyketone.

Keywords: gamma rays, coherent scattering region, crystallites, X-ray diffraction, polyketone, structures, surface roughness.

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I. Introduction

Currently, one of the most pressing problems of radiation physics and chemistry of polymers is to establish the features of radiation processes occurring in polymers is exposed to various types of radiation (gamma-rays, accelerated electrons, protons, neutrons). The change in the properties of polymers under the action of radiation is due to the excitation and ionization of molecules of substances [1]. One of the
polymers are polyketones consisting of olefin and carbon monoxide units (CH₂–CH₂–C=O)ₙ [2-5] and which have high wear resistance, resistance to chemical environments, differ in viscosity, impact resistance, low gas permeability, etc. [2-6]. Considering the above properties, as well as their relatively high melting point up to 260°C [6], polyketones are used in mechanical engineering, aerospace, automobile, chemical and shipbuilding industries.

As you know, the “relief” of the surface is one of the important factors for using materials in various sectors of the economy, especially in industry [7]. Therefore, the morphology of the polyketone surface was investigated in [4, 8-12] and an increase in the surface roughness of the polyketone after treatment at a temperature of 180°C for 8 days was established, which according to [10] is associated with surface oxidation.

Infrared (IR) spectra of polyketones were studied in [9, 12-23] and it was found that the absorption band with a wave number in the region of 1700 cm⁻¹ corresponds to the groups of ketones. It was also established in [5] that the intensity of the vibration of the CH₂ bond at 1408 cm⁻¹ is less than that of the vibration of the CH₂ bond at the spectrum of 1331 cm⁻¹ due to the difference in the phase density of polymer chains in the polyketone. The presence of spectra with 1050 cm⁻¹, 1690 cm⁻¹, 1700 cm⁻¹, 1713 cm⁻¹ corresponding to the C=O valence bonds was found [9, 12, 13, 15, 18-20].

The crystal structures of polyketones were studied by X-ray diffraction after their synthesis [4, 5, 8, 11, 13, 19, 23-26] and the existence of an orthorhombic structure with a space group (sp. gr.) Pnam was established [4, 5, 23, 25] and with unit cell parameters a=7.97 Å, b=4.76 Å, c=7.57 Å [23].

The influence of external factors such as temperature, humidity, radiation and polyketone pressure leads to the production of qualitatively new materials with improved properties [10, 17]. Therefore, the structure of a polyketone molecule, crystallinity, surface roughness, binding energy of atoms, and the presence of impurities largely determine its properties. It should be noted that there is no systematic study of the effect of gamma-radiation on the above properties and characteristics of polyketone in the literature, with the exception of [27], where an increase in its mechanical properties after irradiation with gamma-radiation with a dose of 20 Mrad was found, which is associated with the formation of cross-linking of polyketone.

From the above data, it follows that the effect of radiation on the surface, crystallinity, structure, and IR spectra of polyketone has been insufficiently studied. Therefore, this work is devoted to a systematic study of the effect of gamma-radiation of various doses on surface morphology, crystallinity, molecular vibrations and on polyketone structures.

II. Object and research methods

For the study, we used polyketones (Carilon) in the form of a plate with dimensions of 20×10×3 mm³. The study of the surface morphology of the sample was carried out on a scanning probe microscope SPM 9700HT (Shimadzu). For this, a sample area with a size of 30×30 µm² was selected, in which two areas with a size of 10×10 µm² were also arbitrarily selected.

An Empyrean Series 3 X-ray diffractometer (PANalytical, Netherland) was used to determine the crystal structure of polyketone samples. The X-ray diffraction data were processed by the Rietveld method using the Fullprof program [28, 29].

Fourier transform infrared spectra were recorded on an FT-IR iS50 Nicolet spectrophotometer (Thermo Fisher Scientific, USA) in the wave number range 400–4000 cm⁻¹.

Irradiation of polyketone samples was carried out on a gamma setup with 60Co sources (Eav=1.25 MeV) at a dose rate of 75 R/s, up to an exposure dose of 4×10⁸ R.

III. Results and its discussion

Analyzes of the results of studying the polyketone surface showed that in the selected area of the sample with a size of 30×30 µm, the maximum value of the arithmetic mean deviation of the profile of the initial polyketone is Rz=96.2 nm, and the height of the average roughness is Rz=879 nm (Fig. 1). If two different sections of the mentioned profile are arbitrarily chosen, then the values of the average roughness height of this selected section differ (in section A Rz=927 nm, in section B Rz=819 nm) from the average roughness of a section measuring 30×30 µm, which is equal to Rz=879 nm. This is due to the process of making polyketone, i.e. inhomogeneity of roughness over the entire surface of the sample. Figure 2 shows the profile of the polyketone surface after gamma-irradiation with a dose of 3.5×10⁸ R.
The study of the effect of radiation on the surface roughness of the polyketone showed that when it is exposed to gamma-radiation, the roughness is smoothed out. The measurement showed that in the selected area of the polyketone sample with a size of 30×30 µm after irradiation with gamma-quanta, the maximum value of the arithmetic mean deviation of the profile and the average roughness height decrease. Figure 2 shows that after irradiation with gamma-quanta with a dose of 3.5×10^8 R, the maximum value of the arithmetic mean deviation of the profile is $R_a=59.6$ nm, the height of the average roughness $R_z=375.4$ nm. When polyketone is exposed to gamma-radiation, the surface roughness is smoothed out, and as a result, the value of the average surface roughness decreases after irradiation with a dose of 3.5×10^8 R by 2.3 times in comparison with the initial one. This is due to the fact that when polyketone is exposed to radiation, cross-linking occurs between polyketone macromolecules [27, 30].

The obtained IR spectra of the polyketone correspond to the literature data [4, 22]. Figure 3 shows the IR spectra of the initial polyketone sample with CH$_2$ stretching vibrations of about 2914 cm$^{-1}$, 1257 cm$^{-1}$ and C=O 1689 cm$^{-1}$, and CH$_2$ bending vibrations of about 1408 cm$^{-1}$ and 1332 cm$^{-1}$. However, the spectra corresponding to CH$_2$ vibrations with 1408 cm$^{-1}$, 1055 cm$^{-1}$, and 805 cm$^{-1}$ in the studied polyketone sample are shifted towards lower values, and the CH$_2$ stretching vibration at 1257 cm$^{-1}$ is shifted towards higher values as compared to [22].

After irradiation with gamma-quanta with a dose of 4×10^8 R, noticeable changes are observed in the IR spectra of the polyketone. Decreased IR spectra peaks are 1689 cm$^{-1}$, 1408 cm$^{-1}$, 1332 cm$^{-1}$ and 1055 cm$^{-1}$, which may be due to the breaking of molecular bonds. The appearance in IR spectrum the peak with a wave number of 1174 cm$^{-1}$ has been established, which is most likely associated with vibrations of the C-C bond. It should be noted that the appearance of new peaks in the IR spectra at 1378 cm$^{-1}$ and 1180 cm$^{-1}$ was found in [14], which are associated with the cross-linking of the polyketone.

The X-ray diffraction data of the initial polyketone sample were processed assuming the presence of an orthorhombic phase. The processing results...
showed that the polyketone sample has an orthorhombic structure (sp. gr. \(Pnam\)) with \(a=8.074\) Å, \(b=4.707\) Å, \(c=7.577\) Å and \(\alpha=\beta=\gamma=90^\circ\) (\(\chi^2=1.37, R_B=1.7\)) (Fig. 4).

Table 1 shows the coordinates of polyketone atoms in the orthorhombic phase (sp. gr. \(Pnam\)). The obtained values of the coordinates of the polyketone atoms do not differ greatly in comparison with the data [23]. The structure of the polyketone was investigated after irradiation up to an exposure dose of \(3.5\times10^8\) R, and X-ray diffraction patterns were calculated to determine the structure of the sample (Table 2).

Comparison of Tables 2 and 1 indicates that the coordinates of polyketone atoms after irradiation with gamma-quanta with a dose of \(3.5\times10^8\) R (orthorhombic phase (sp. gr. \(Pnam\))) do not change significantly.

![Figure 4. X-ray diffraction pattern of polyketone with orthorhombic phase (sp. gr. \(Pnam\)). I – comparison of the observed sample with the fitted sample, II – Bragg peaks, III – the difference between the observed sample and the fitted sample.](image-url)

![Figure 5. Unit cell of polyketone (orthorhombic phase (sp. gr. \(Pnam\))).](image-url)
0.927 Å, and 1.210 Å, respectively. And in a sample of polyketone irradiated with gamma-quanta with a dose of \(3.5 \times 10^8\) R, these are 1.534 Å, 1.096 Å, 1.123 Å, and 1.203 Å, respectively, i.e. the C1–O bond length decreased, while the C1–C2, C2–H1 and C2–H2 bonds increased after irradiation. An increase in the C1–C2, C2–H1, and C2–H2 bond lengths indicates that after irradiation with gamma-quanta, the unit cell parameters \((a\) and \(c)\) of the polyketone increased.

Based on the (110) reflection, calculations were performed to determine the crystallite sizes using the Scherrer formula [31]:

\[
D = \frac{K\lambda}{\beta_S \cos \theta},
\]

where \(K\) is the correction factor to take into account the grain shape (\(K \approx 0.9\)), \(\lambda\) is the radiation wavelength (for example, 0.15406 nm), \(\theta\) is the Bragg angle for the diffraction peak, \(\beta_S\) is the observed width at half maximum of the peak (in radians).

The performed calculations showed that the crystallite size in the initial polyketone sample is \(D_{(110)} = 12.03\) nm, and after irradiation with a dose of \(10^7\) R \(D_{(110)} = 11.76\) nm and a dose of \(10^8\) R \(D_{(110)} = 11.06\) nm, and after irradiation with a dose of \(3.5 \times 10^8\) R \(D_{(110)} = 10.90\) nm. It can be seen that the size of polyketone crystallites decreases with increasing dose.

To determine the numerical value of the degree of crystallinity before and after irradiation of the polyketone, the areas of the amorphous \((A_a)\) and crystalline \((A_K)\) components of the samples were calculated, as in [32–35]. The peaks were separated using the Gaussian function (Fig. 6) and under the assumption of the existence of three peaks in the angle range \(2\theta_0 = 14°–28°\) and the degree of crystallinity was determined as [32, 33]:

\[
X_K = \frac{A_K}{(A_K + A_a)} \cdot 100\%.
\]

Taking into account the nature of the distribution of the amorphous component, in the calculations the sum of the areas of the (110) and (111) reflections was taken into account as the \(A_K\).

According to the calculation, the degree of crystallinity of the initial polyketone sample is 45.5%, which is close to the degree of crystallinity (30–40%) of the carilona terpolymer [26], but lower than the degree of crystallinity of the thermoplastic material polyoxymethylene [24], which depending on temperature has a degree of crystallinity of 48–62%.

Figure 7 shows the dependence of the degree of crystallinity of a polyketone on the exposure dose of radiation. Figure 7 shows that with increasing dose the degree of crystallinity increases linearly to a dose of \(2 \times 10^8\) R. This indicates that irradiation with gamma-radiation stimulates the growth of crystallinity, which is most likely due to radiation cross linking [36].

The dependence of the degree of crystallinity of the polyketone on the dose of gamma-irradiation can be described by the following expression:
Study of the influence of gamma rays on the structure and topography of the polyketone surface

\[ K = 34.7 + 27 \exp\left(-\frac{(D - 227.4)^2}{56500}\right), \]  

(3)

where \( K \) is the degree of crystallinity, \( D \) – exposure dose, MR.

A further increase in the dose (\( \geq 2 \times 10^8 \) R) leads to a decrease in the degree of crystallinity, which is associated with the degradation of the polyketone macromolecule under radiation exposure.

IV. Conclusion

Thus, after irradiation of polyketone with gamma-quanta with a dose of \( 3.5 \times 10^8 \) R, the surface roughness is smoothed out, as a result, the value of the average surface roughness decreases from \( R_z = 879 \) nm to \( R_z = 375.4 \) nm.

It was found that after irradiation with gamma-quanta with a dose of \( 4 \times 10^8 \) R in the IR spectra of polyketone appear the peak with a wave number of \( 1174 \) cm\(^{-1}\), which is associated with its cross-linking.

It has been determined that after irradiation of polyketone with gamma-rays with a dose of \( 3.5 \times 10^8 \) R, the C1–C2, C2–H1, and C2–H2 bond lengths increase, while the C1–O bond length decreases, which contributes to an increase in the \( a \) and \( c \) parameters and decrease in the \( b \) parameter of the orthorhombic elementary cells (sp. gr. \( Pnam \)).

It has been determined that when polyketone crystallite is exposed to gamma-quanta with a dose of \( 3.5 \times 10^8 \) R, the sizes of it linearly decrease from \( 12.03 \) nm to \( 10.90 \) nm.

It has been established that an increase in exposure doses of gamma irradiation to \( 2 \times 10^8 \) R leads to a decrease in the content of the amorphous phase and an increase in crystallinity. Irradiation with gamma radiation stimulates the growth of crystallinity and the degree of crystallinity increases from 45.5% to 61.7%. A further increase in the dose (\( \geq 2 \times 10^8 \) R) leads to decrease in the degree of crystallinity, which is associated with the degradation of the polyketone macromolecule.

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54

М.Ю. Ташметов, Н.Б. Исматов
Ўзбекистон республикаси Фанлар академияси Ядро физикаси институти, Мирзо Улугбек тумани, Улугбек шахарчачи, Хуросан 1, 100214, Тошкент, Ўзбекистон

Ўшбу тадқиқот ишда поликетон юза морфологиясига, молекулалар теришишига ва структурасига гамма нурларидининг тури дозаларидаги таъсири тадқиқ этилган. Поликетоннинг гамма кванти билан 3.5×10⁸ Р дозагача нурлантирилганда кейин унинг гадир-будурлиги (дагаллик) силилкаанинг натижасида юзанинг ўрцагача гадир-будурлик киймати R₈=879 им дан R₈=375.4 им гача камайди, шу билан бирга поликетоннинг инфракизил спектрларида тўлкин сони 1174 см⁻¹ га тенг бўлган яъни чўкки (пык) пайдо бўлди. Гамма нурларининг 3.5×10⁸ Р дозадаги таъсирида C₁–C₂, C₂–H₁ ва C₂–H₂ боғлар узунлигининг ортиши кузатилди, бу эса орторомбик фаза (фазовий гуруружин Pnmt) элементар катак параметрлари қийматини оширганга олиб келди. Гамма нурлари билан нурлантириш дозасининг 2×10⁸ Р гача ошири аморф фазанинг камайишига ва кристаллликнинг ортишига олиб келди. Гамма нурлари билан нурлантириш кристаллликнинг ўсишини рабатлантиради ва бунда кристаллик даражаси 45.5% дан 61.7% гача қўр. Нурлантириш дозасининг кейинги ортиши (≥2×10⁸ Р) билан поликетон деградацияси турфайли унинг қристаллик даражаси кама бошлади.

Қалит суллар: гамма нурлари, котерент сочилли соҳаси, кристалллик, рентген нурлар дифракцияси, поликетон, структура, юза гадир-будурлариги.