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STUDY OF THE EFFECT OF γ-IRRADIATION ON POLYPROPYLENE AND POLYSTYRENE WASTES BY EPR METHOD

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Abstract: This study aimed to identify and analyze the dose dependence of formed paramagnetic centers of irradiated polymer waste samples (polypropylene and polystyrene) at room temperature. EPR spectra of polystyrene polymer samples irradiated at 86.4, 174.432, and 720 kGy in a wide magnetic field are completely similar. The intensities of spectra corresponding to free radicals are increasing with the adsorbed dose within the investigated range. To discern the chemical nature of the paramagnetic centers, which are the source of free radicals, the spectra were repeatedly collected (16 scans) within a very narrow magnetic field range (30G) and using a smaller modulation amplitude (1G). As a result, the spectrum was fully detected.

Keywords: EPR spectrum, adsorbed dose, g-factor, polymer wastes.

1. Introduction

One of the effective methods for investigating the impact of ionizing radiation on polymer materials is the electron paramagnetic resonance (EPR) method. Paramagnetic centers play an important role with regard to the chemical and physicochemical properties of irradiated materials. The paramagnetic centers in irradiated polymer materials were studied in various research works [1-3]. The observation of paramagnetic centers depends on the temperature of irradiation and registration. Many studies focused on identifying paramagnetic centers at liquid nitrogen temperatures (-196^{0}C). As a result, the paramagnetic centers were not influenced at high temperatures. Therefore, the centers obtained in such conditions are not able to participate in adsorption processes.

The research aims to identify and study the dose dependence of formed paramagnetic centers in irradiated polymer waste samples (polypropylene and polystyrene) at room temperature.

2. Research method

Polypropylene and polystyrene polymer waste samples were prepared by cutting the materials into 3-4 mm^2 sizes and were subsequently exposed to ^{60}Co γ-ray radiation under vacuum conditions with a dose rate D=1.6 Gy/sec at absorbed dose ranges D=86,4-720 kGy. After irradiation, paramagnetic centers were studied by the EPR method.

EPR spectra of the samples were recorded at room temperature, in air, using the BRUKER EMX Plus EPR Radio spectrometer. The working frequency of the spectrometer is ν=9.85 GHz (wavelength λ=3.2 cm), the modulation frequency is 100 kHz, and the magnetic field variation range is within 0-6000G.

To obtain a reliable EPR spectrum, the modulation amplitude was adjusted to the width of the individual lines of the spectrum, and to avoid saturation, the power of the electromagnetic wave was taken as low as possible.

3. Experimental results

EPR spectra of annealed PP samples were first recorded over the widest possible range of magnetic field (0-6000G). Similar spectra were observed at all absorption doses. But a doublet is observed in the region of the g-factor equal to 2 (around B≈3500G of the magnetic field). A typical spectrum is shown in Figure 1.

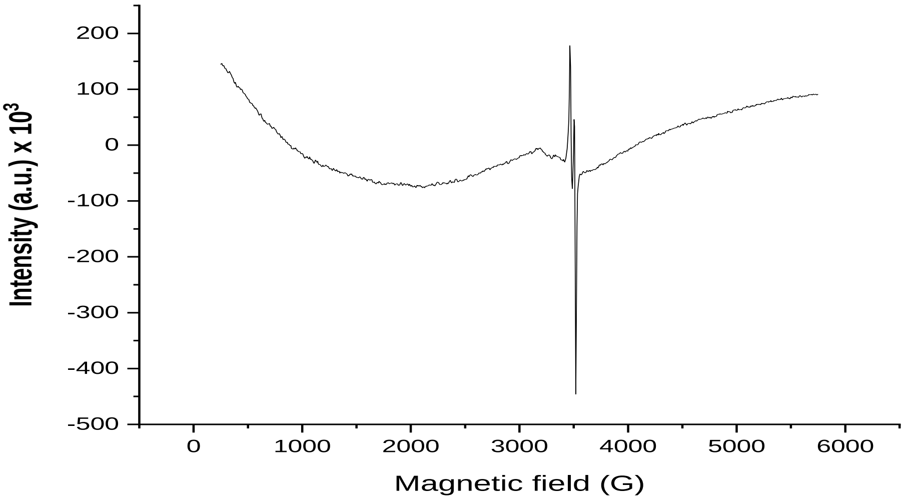
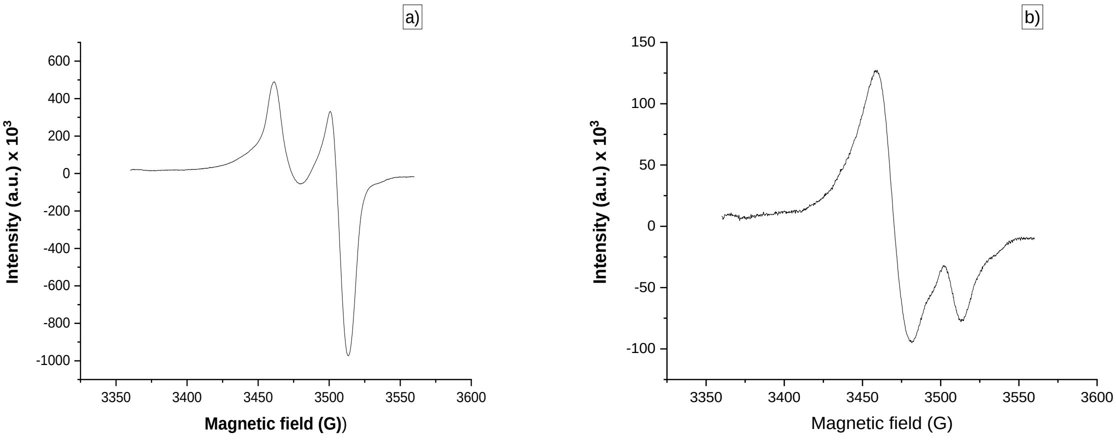


Fig. 1. Typical spectrum of PP irradiated for 432 kGy in the widest range of magnetic field variation

These spectra indicate that the studied material is quite free from other paramagnetic additives, as no appreciable lines are observed in the rest of the magnetic field. To scrutinize the doublet line in the central part of the spectrum, that part of the spectrum corresponding to all four absorption doses was expanded between 200G of the magnetic field. These doublets are shown in Figure 2.



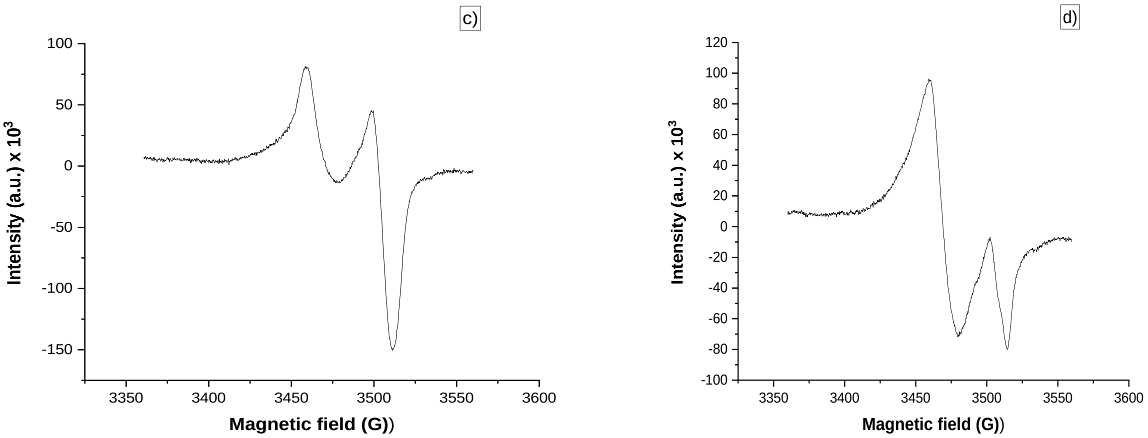


Fig. 2. The more obvious spectrum of the doublet located in the 200G range of the central part of the spectrum: a) 86,4, b) 172, c) 432, d) 720 kGy

In the spectra shown in Figure 2, the g-factor of the component of the doublets in the lower magnetic field is g=2.033, and the g-factor of the upper magnetic field is g=2.008.

The shape of the spectra indicates that the chemical paramagnetic center, responsible for such a spectrum, is located in a crystalline field with axial symmetry. In Figure 2, it is apparent that for the spectra corresponding to 86.4 and 432 kGy, the intensity of the line in the low magnetic fields is smaller than the intensity of the line in the high magnetic fields.

For comparison, EPR spectra of PP material and non-irradiated samples were also studied. Interestingly, these samples also have EPR spectra, and the EPR spectra recorded in the widest magnetic field are akin to the EPR spectra of the sample irradiated for 86.4 and 720 kGy.

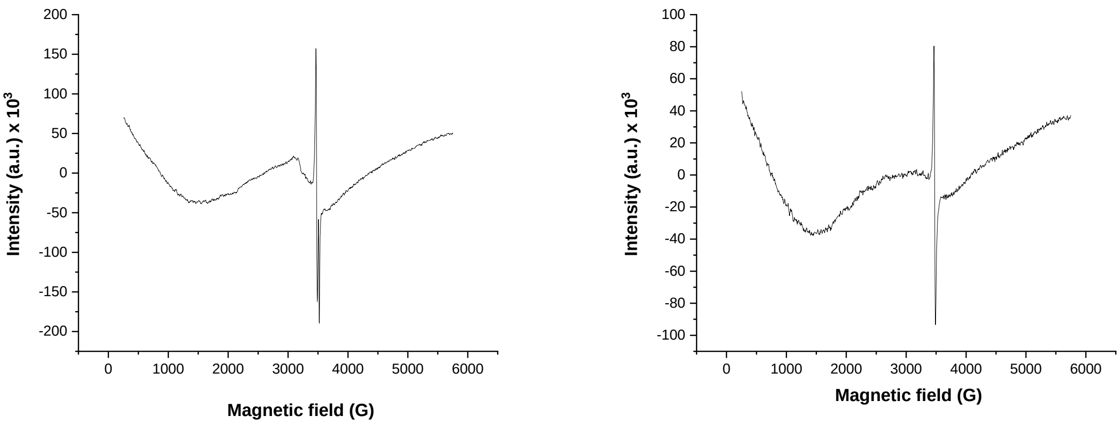


Fig. 3. EPR spectra of irradiated PP samples: a) initial spectrum, b) spectrum taken after one week

However, after a week, instead of two lines in the corresponding spectrum of that sample, only the component located in the low magnetic field appears as a singlet. This singlet line is shown separately in Figure 4.

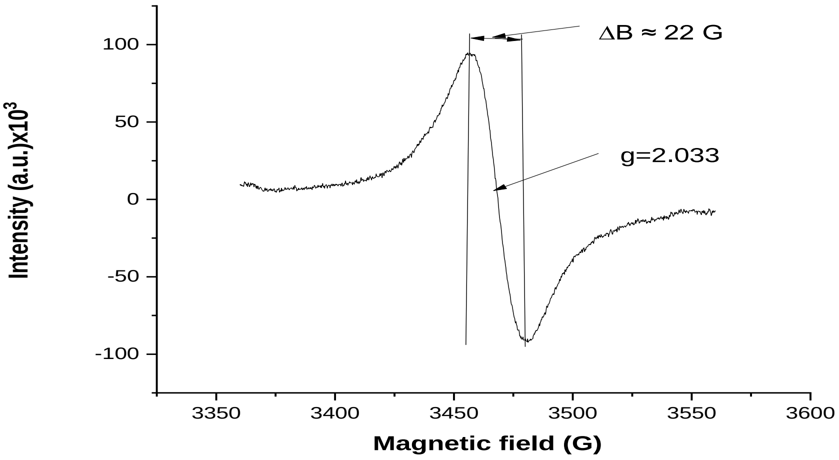
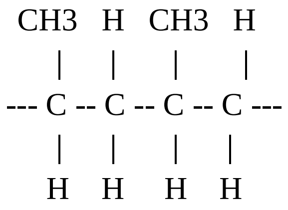


Fig. 4. Singlet EPR signal

4. Analysis of results

The molecular formula of polypropylene is as follows:



$$\begin{array}{ccccccccc} & \mathrm{CH_3} & & \mathrm{H} & & \mathrm{CH_3} & & \mathrm{H} & \\ & | & & | & & | & & | & \\ --- & \mathrm{C} & -- & \mathrm{C} & -- & \mathrm{C} & -- & \mathrm{C} & --- \\ & | & & | & & | & & | & \\ & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & \end{array}$$

As a result of the irradiation of such a molecule, the most common radicals are alkyl and allyl radicals. Alkoxyl and peroxyl radicals can also arise in such samples when they are irradiated under air conditions or in a vacuum and then stored in the open air. As the spectroscopic parameters of the spectra we observed in this work: g_1=2.033, g_2=2.008 reflect the axial structure, it can be said that macroperoxyl ROO● radicals are the chemical source of this spectrum [1]. The shape of the spectra obtained in samples cooled for 15 and 75 hours completely coincides with the spectra obtained in [1]. The line in the lower magnetic field is taken as gii=2.033 and the line in the upper magnetic field is taken as $g_\perp$=2.008. The inversion of the intensities of the parallel and perpendicular components of the spectra in the samples irradiated for 86.4 and 432 kGy shows that in this sample gii and $g_\perp$ change their places and the component of the magnetic particle along the x and y axes becomes larger than the component along the magnetic field. In addition, the presence of a stable radical in the non-irradiated samples of PP and the transformation of the crystalline electric field around this radical from axial symmetry to isotropic symmetry depending on time, that is, the transformation of a spectral line consisting of two components into a symmetrical singlet line, indicates that macro radicals inside the polymer are constantly changing and are dynamic under normal conditions.

Results of EPR studies of irradiated samples of polystyrene polymer

EPR spectra of polystyrene polymer samples irradiated at 86.4, 172, 432, and 720 kGy doses in the wide magnetic field are completely similar, and such a typical spectrum is shown in Figure 1.

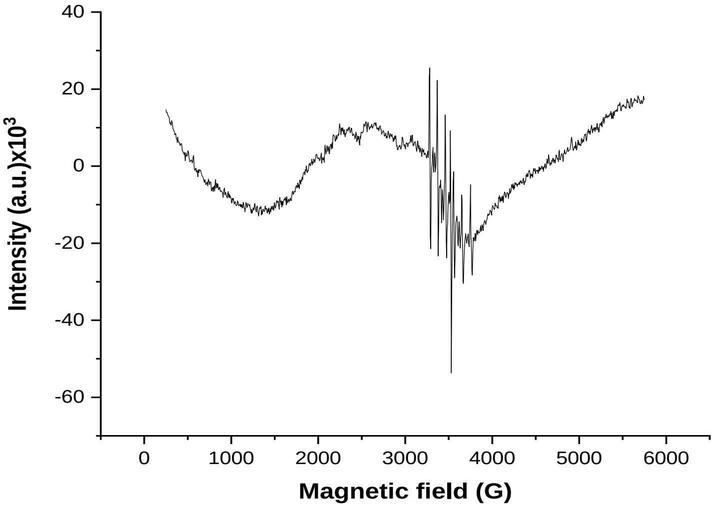


Fig. 5. EPR spectrum of a PS sample irradiated for 720 kGy in a wide (0-6000G) magnetic field interval

It can be seen from this spectrum that there are 7 thin lines in the area of values of g-factor equal to 2 (B=3500G) on a very broad line (ΔB= 1100G). To investigate the nature of those thin lines, the central part of the spectrum was taken at 1000G, and similar spectra were obtained for all samples. A typical spectrum is shown in Figure 2.

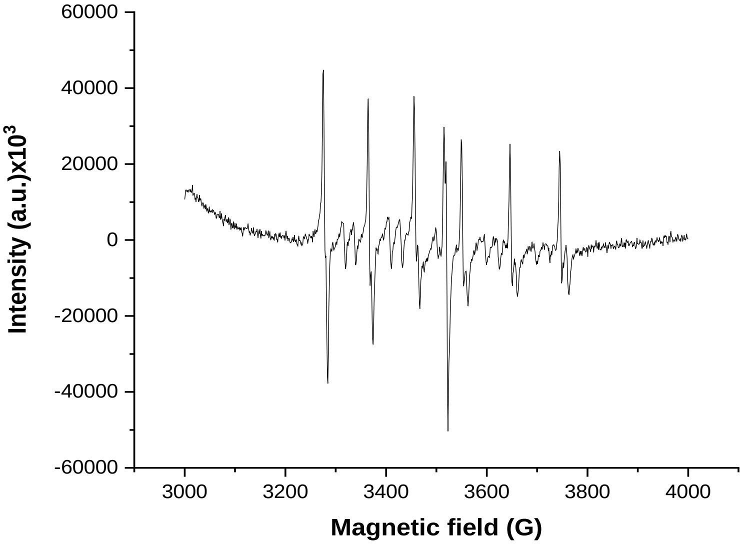


Fig. 6. EPR spectrum of a 432 kGy irradiated PS sample in a 1000G-wide range of the magnetic field

In this cross-section of the spectrum, the distance between two adjacent lines at approximately the same distance from each other (average value 95G) is a sextet consisting of 6 lines, increasing from 90G to 100G from low magnetic field to high magnetic field, and between the 3rd and 4th components of the sextet, a line can be observed. To elucidate the structure and spectroscopic parameters of the latter line and investigate it individually, that line is shown separately for all samples in the 100G range. Spectra with identical structures were obtained for all samples, although intensity levels varied. A typical spectrum in this range is shown in Figure 3.

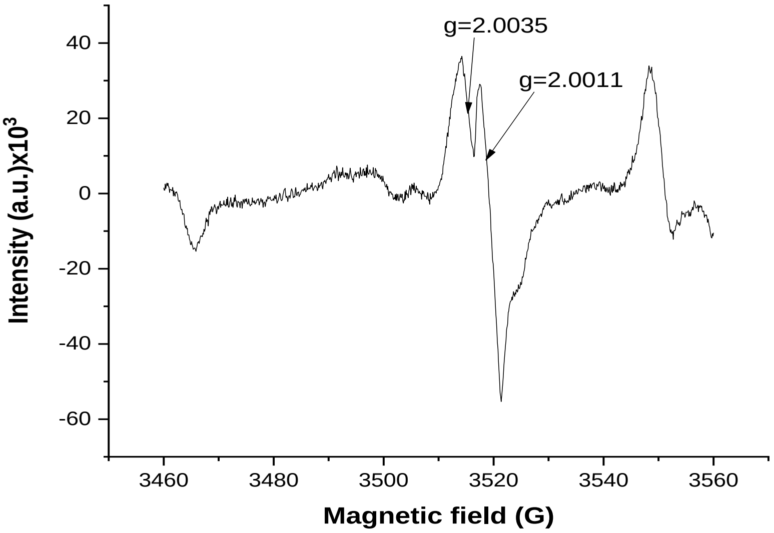


Fig. 7. Typical spectrum of PS samples taken in g≈2 region

As shown in Figure 3, this spectral line has a complex structure, and the g-factors of the two more intense lines in its central part are g_1=2.0035 (ΔB=3.9G), g_2=2.0011 (ΔB=3.9G), respectively. The g-factor values indicate that the paramagnetic center, which is the chemical source of this line, is a free radical. Depending on the radiation dose, the change in the intensity of the spectra corresponding to free radicals is presented in Table 1.

Table 1

Dependence of EPR spectrum intensity on adsorbed dose

Dose (kGy)	Intensity (a.u.)
0.00	1.00
86,4	2.70
172	2.68
432	3.17
720	2.81

To discern the chemical nature of the paramagnetic centers, which are the source of free radicals, the spectra were repeatedly collected (16 scans) within a very narrow magnetic field range (30G) and using a smaller modulation amplitude (1G). As a result, the spectrum was fully detected, and that spectrum is shown in Figure 4.

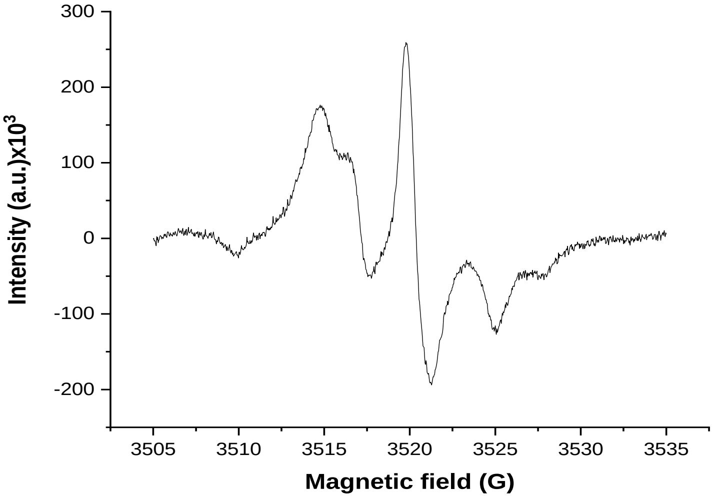


Fig. 8. The spectrum of free radicals in a sample irradiated for 432 kGy

Since the change in the number of free radicals depending on time is of some interest, the EPR spectra of the studied samples were repeated after 12 days. In non-irradiated samples, the spectrum of free radicals completely disappeared, while in irradiated samples, the intensity of the spectrum of those radicals changed almost very little.

Analysis of results

The chemical source of the very wide (1100G) spectrum observed in the EPR spectrum taken in the wide range of the magnetic field (Fig. 1) is attributed to the Fe^{+3} ion, and the spectrum consisting of six lines is attributed to the Mn^{+2} ion. The chemical feedstock used in the production of commercially produced polystyrene polymer did not need to be highly purified of these ions, and these additives probably did not compromise the consumer quality of the polymer. All the changes that occurred in the polymer due to the effect of quenching were related to the generation of free radicals. The dependence of the intensity of the EPR spectra of radicals on the absorption dose (Table 1) shows that as the dose increases, the intensity of the spectrum of radicals, in other words, the number of free radicals increases.

Benzyl and cyclohexadienyl radicals are the ones that have the largest number of radicals that occur as a result of chelation in polystyrene [2].

These radicals contain equivalent hydrogen atoms with nuclear spin ½ and should give a multicomponent fine-structured spectrum. A multi-line spectrum is indeed detected in Figure 4, but further studies are needed to correctly identify this spectrum. In addition, the disappearance of the radical spectrum as a function of time in the non-irradiated sample is of particular interest.

Acknowledgment

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ИЗУЧЕНИЕ ДЕЙСТВИЯ γ-ОБЛУЧЕНИЯ НА ОТХОДЫ ПОЛИПРОПИЛЕНА И ПОЛИСТИРОЛА МЕТОДОМ ЭПР

М.А. Гурбанов, Р.Дж. Гасымов, Е.В. Мирзазаде, У.А. Гулиева

Резюме: Исследование проведено с целью выявления и дозовой зависимости образовавшихся парамагнитных центров при облучении образцов полимерных отходов (полипропилена и полистирола) при комнатной температуре. Спектры ЭПР образцов полимера полистирола, облученных при дозах 86,4, 172, 432, 720 кГр в широком магнитном поле, полностью аналогичны. Интенсивность спектров, соответствующих свободным радикалам, увеличивается с увеличением поглощенной дозы в исследуемом диапазоне. Для выявления химической природы парамагнитных центров, являющихся источником свободных радикалов, процесс многократного сбора спектра (16 сканирований) проводился в очень узком интервале магнитного поля (30Гс) и применением меньшей модуляции амплитуды (1G).

Ключевые слова: спектр ЭПР, поглощенная доза, g-фактор, полимерные отходы.

γ-ŞÜALANMANIN POLİPROPİLEN VƏ POLİSTİROL TULLANTILARINA TƏSİRİNİN EPR METODU İLƏ ÖYRƏNİLMƏSİ

M.Ə. Qurbanov, R.C. Qasımov, E.V. Mirzəzadə, Ü.A. Quliyeva

Xülasə: Bu tədqiqat işində otaq temperaturunda şüalanmış polimer tullantılarının (polipropilen və polistirol) nümunələrində əmələ gələn paramaqnit mərkəzlərinin təyini və dozadan asılılığı öyrənilmişdir. 86,4, 172, 432, 720 kQr dozalarda şüalandırılmış polistirol polimer nümunələrinin geniş maqnit sahəsində EPR spektrləri oxşar olduğu müəyyənləşdirilmişdir. Sərbəst radikallara uyğun gələn spektrlərin intensivliyi tədqiq edilən diapazonda udulan doza artdıqca artır. Sərbəst radikalların mənbəyi olan paramaqnit mərkəzlərin kimyəvi təbiətini müəyyən etmək üçün çox dar maqnit sahəsi intervalında (30G) və daha kiçik modulyasiya tətbiq edilməklə spektrin təkrar toplanması prosesi (16 skan) amplitudada (1G) aparılmışdır.

Açar sözlər: EPR spektri, udulan doza, g-faktor, polimer tullantıları.