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Betul Caliskan

bcaliskan@pau.edu.tr

Pamukkale University

Merve Taş

Pamukkale University

Research Article

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Electron paramagnetic resonance analysis of gamma irradiation damage centers in N,N'-methylenebisacrylamide single crystal

Betul Caliskan[a,b]*, Merve Taş[a]

[a] Department of Physics, Faculty of Science, Pamukkale University, 20070, Denizli, TURKEY

[b] Department of Physics, Faculty of Science, Ankara University, 06100, Beşevler, Ankara, TURKEY

Abstract: N,N'-methylenebisacrylamide (NNMBA) single crystals were obtained in the laboratory. They acquired paramagnetic properties by exposure to gamma rays. Electron Paramagnetic Resonance (EPR) Spectroscopy was used to determine the paramagnetic center. No temperature-dependent changes were observed in the EPR spectra. EPR measurements were taken at 300 K. The data obtained from the EPR spectra indicated that the paramagnetic center in the N,N'-methylenebisacrylamide (NNMBA) single crystals was the vinyl radical. The spectroscopic splitting factor, hyperfine structure constant, and their direction cosines of the radiation damage center formed in the vinyl radical were obtained. The experimentally obtained data were found to be consistent with the data obtained from the simulation study.

Keywords: EPR, N,N'-methylenebisacrylamide, Radiation damage center, Hyperfine coupling constant, Spectroscopic splitting factor.

1. Introduction

Acrylamide is a harmful and carcinogenic substance that is not naturally found in raw foods and is formed by heat treatment of foods rich in starch and carbohydrates at high temperatures above 120 °C [1,2].

** Corresponding author: Tel:+902582963742 Fax:+902582963535*

E-mail address : bcaliskan@pau.edu.tr , bcaliska@gmail.com

N,N'-methylenebisacrylamide (NNMBA), an organic compound, has the formula $(H_2C{=}CHCONH)_2CH_2$. N,N'-methylenebisacrylamide is a molecule used as a crosslinker in chemical reactions during polymer and copolymer production [3]. The acrylamide / N,N'-methylenebisacrylamide reaction is a free radical crosslinking copolymerization. NNMBA, the crosslinking agent, imparts higher strength, porosity, and elastomeric properties to polymers [4]. The crosslinked polymer structure obtained with NNMBA exhibits lower toxicity than linear chain structural polymers [5].

The copolymerization of acrylamide and NNMBA via vinyl addition polymerization allows the formation of polyacrylamide gels [6]. Polyamidoamines, a group of polymers with biomedical applications, are synthesized by the polyaddition of aliphatic primary amines or secondary diamines to bisacrylamides such as NNMBA [7]. Acrylamide gel applications in biomedical systems require the use of very clean gels.

NNMBA has biomedical applications in artificial organs, contact lenses, and controlled drug release systems [8]. They are used in analytical separation processes in column chromatography and electrophoresis. They have significant impact in the chemical industry, including wastewater treatment, gel electrophoresis, papermaking, ore processing, tertiary oil recovery, and the production of permanent press fabrics.

In this study, the detection of the radiation damage in the structure of NNMBA single crystals induced by gamma irradiation was performed using Electron Paramagnetic Resonance Spectroscopy. A comprehensive literature review revealed that no previous studies have been conducted on the detection of radicals formed by ionizing radiation in NNMBA single crystals by Electron Paramagnetic Resonance Spectroscopy.

2. Experimental

A slow evaporation technique was used to obtain single crystals of the NNMBA powder sample. A clear solution of the NNMBA powder sample was obtained using methanol solvent. Single crystals suitable for EPR studies were formed.

It was found that NNMBA shows a monoclinic structure in the space group $C2/c$, with lattice parameters $a = 17.822\ (12)$ Å , $b = 4.850\ (3)$ Å , $c = 19.783\ (14)$Å, $\beta = 102.370\ (9)°$, $V = 1670\ (2)$ Å^3 and $Z = 8$ [9].

NNMBA single crystals were irradiated with ^{60}Co-γ ray source at doses of 250 kGy at 300 K. EPR spectra were obtained with a Bruker EMX 081 EPR Spectrometer. Spectrum recordings were made at microwave power of 1 mW, modulation frequency of 100 kHz and modulation amplitude of 0.2 mT. Single crystals were recorded by rotating them around the a*-, b- and c-axes from 0° to 180° at 10° intervals using a goniometer. The Bruker temperature control unit was used for low temperature measurements and spectra were taken at 300 K.

3. Results

Irradiation of NNMBA single crystals with a ^{60}Co-γ source resulted in the formation of a radiation damage center. Ionizing radiation acted on chemical bonds, resulting in the rupture of one of these bonds. The molecular structure of NNMBA is shown in Figure 1. The rupture site of the chemical bond in a NNMBA single crystal subjected to radiolysis with ionizing radiation is shown in Figure 2. The radical structure was elucidated by EPR spectroscopy. The radical structure formed was determined to be the vinyl radical. Because there was no change in the structure of the EPR spectra with temperature, EPR analysis was performed at 300 K.

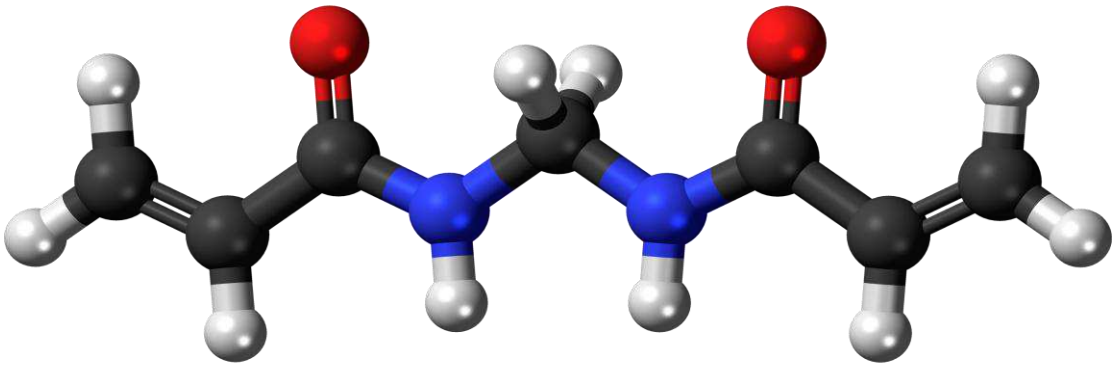


Figure 1. Molecular structure of NNMBA.

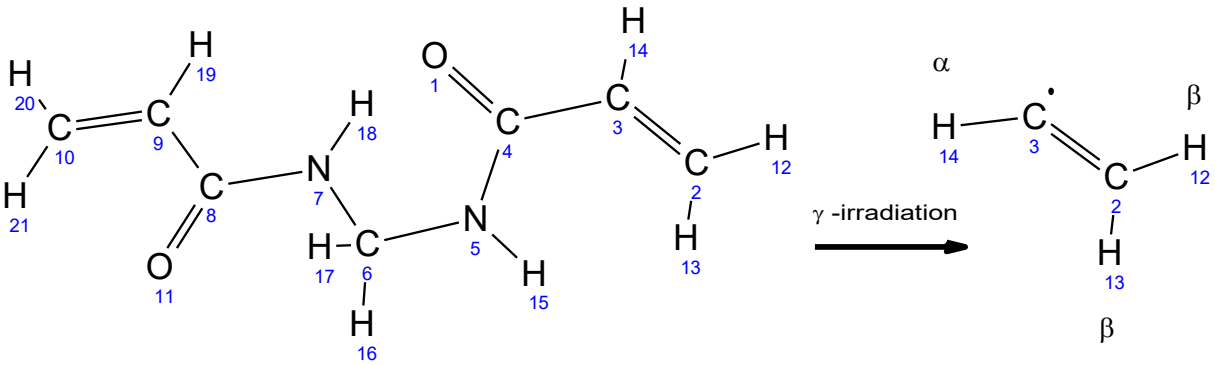


Figure 2. Structure of the vinyl radical observed in NNMBA single crystal.

Vinyl is a group with the formula ‘‘$CH_2 = CH - R$’’. The form of the ethylene molecule ($CH_2 = CH_2$) missing one hydrogen forms vinyl. The vinyl radical ($CH_2 = \dot{C}H$) is formed by the cleavage of the ‘‘R’’ group attached to vinyl and is a special radical structure.

A paramagnetic center was formed in a single crystal of NNMBA after gamma irradiation. This paramagnetic center results from the breaking of the bond between the C(3) and C(4) atoms. The radical formed by this bond breaking is called a vinyl radical. The structure of the vinyl radical contains two carbon atoms double bonded to each other and hydrogen atoms bonded to these carbon atoms. One of the carbon atoms bonds with two hydrogens. The other carbon atom bonds with a single hydrogen, and the unpaired electron is located on this carbon atom.

The atoms contributing to hyperfine structure splitting are the protons H(12), H(13), and H(14). H(14) acts as an alpha proton, while H(12) and H(13) act as beta protons. However, measurements have shown that these three protons are magnetically equivalent. The alpha proton and beta protons interact with the unpaired electron as magnetic equivalent. Therefore, only one hyperfine structure splitting constant has been calculated, denoted as A_{vinyl}.

No change was observed in the structure of the EPR spectra obtained using different temperatures. Therefore, EPR measurements were taken at 300 K. Different microwave powers were tested from 0.1 mW to 60 mW, and it was observed that the splitting in the spectrum did not change with the microwave power.

The same spectral structure, with an intensity ratio of 1:3:3:1, was observed in all spectra taken along three axes. However, the value of the hyperfine structure constant and the g-factor varied depending on the angle. EPR spectra of the sample taken along three separate axes are shown in Figure 3.

Figure 4 compares the simulated and experimental spectra. The experimental spectrum shows hyperfine structure splitting with an intensity ratio of 1:3:3:1 due to three equivalent protons.

Win-EPR software was used to obtain simulated spectra that matched the experimental spectra. Simulated spectrum were obtained using the EPR parameters obtained from experimental

measurements for the vinyl radical. Table 1 shows the EPR parameters of the simulated spectrum.

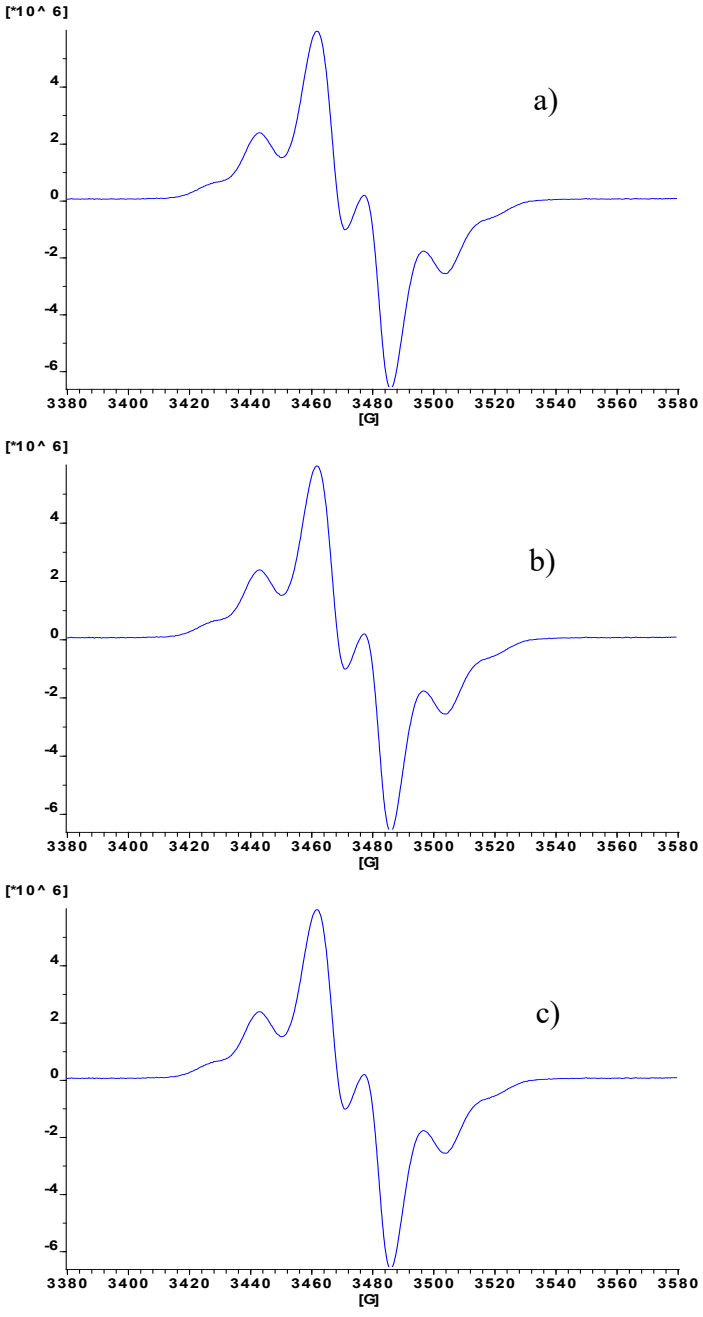


Figure 3. Experimental EPR spectra of gamma irradiated NNMBA single crystal at 300 K a) when the magnetic field is in the a*b plane at an angle 140° towards the axis; b) when the magnetic field is in the a*c plane at an angle 30° towards the axis; c) when the magnetic field is in the bc plane at an angle 80° towards the axis.

Table 1. EPR parameters of simulated spectrum.

Figure	Radical
Figure 4	$A_{(CH)_\alpha} \cong A_{(CH_2)_\beta} \cong A_{vinyl}$= 1.884 mT Center Field = 347.997 mT ν = 9.47 GHz Line Width = 1.64 mT

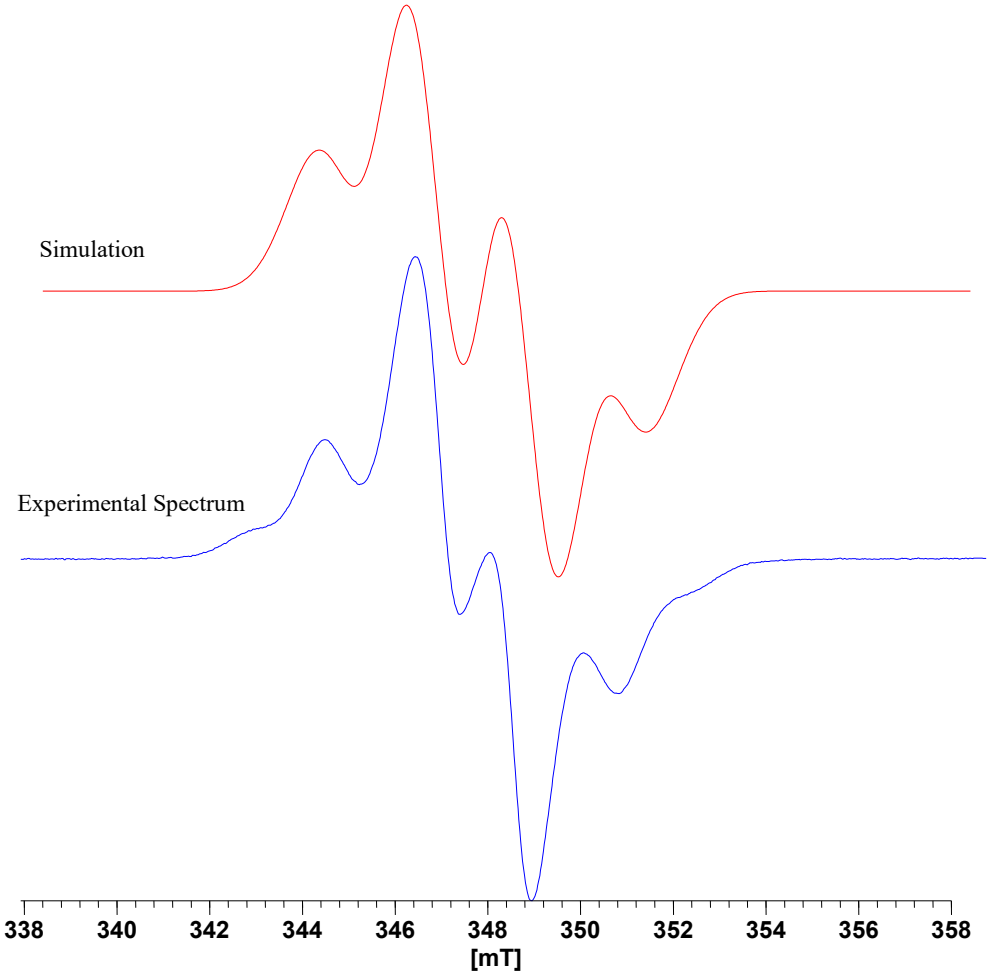


Figure 4. Experimental and simulated EPR spectra of gamma irradiated NNMBA single crystal at 300 K when the magnetic field is in the *a*b* plane at an angle 60° towards the axis.

The principal axis values of the hyperfine structure coupling tensor and g-tensor calculated for the vinyl radical formed in the NNMBA single crystal as a result of gamma irradiation and the

direction cosines of these parameters are shown in Table 2. The hyperfine structure constant and spectroscopic splitting factor of the vinyl radical are anisotropic. Angular changes of the hyperfine structure coupling tensor and g-tensor are given in Figures 5 and 6, respectively.

Table 2. The EPR parameters of the vinyl radical observed in NNMBA at 300 K. (*Note*: The errors are estimated to be ±0.00005 and ±0.005 mT for all the calculated g- and A- values, respectively.)

Radical Parameters	Principal values	Direction cosines		
A_{vinyl} (mT)	A_{aa} = 1.88 A_{bb} = 1.86 A_{cc} = 1.845 a_{av} = 1.862	0.332071399 0.374921501 0.865541711	0.537747582 0.678641126 -0.500273685	-0.774955562 0.631569545 0.023744178
g	g_{aa} = 2.00288 g_{bb} = 2.00176 g_{cc} = 2.00149 g_{av} = 2.00204	0.159261605 -0.977193491 0.140458615	0,532379255 -0,034804711 -0,845790140	0.831389241 0.209479148 0.514694489

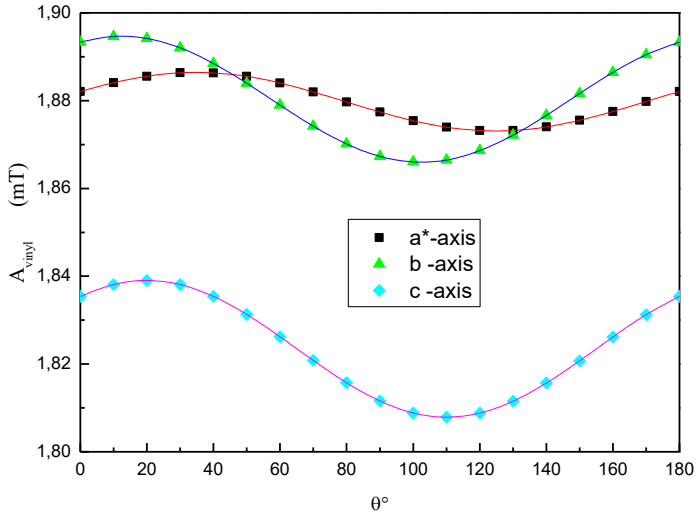


Figure 5. Angular variation of the A-tensor of the vinyl radical observed in NNMBA at 300 K.

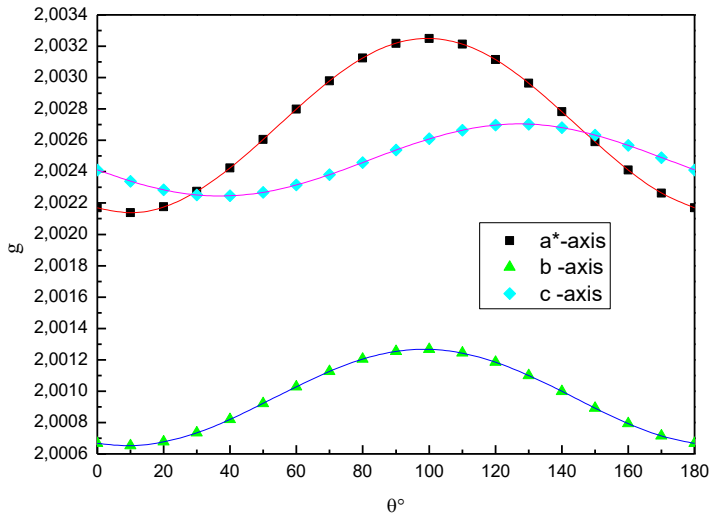


Figure 6. Angular variation of the g-tensor of the vinyl radical observed in NNMBA at 300 K.

4. Discussion

In most free radicals, the unpaired electron resides in the $p\pi$-orbitals of the radical. However, studies have also been conducted in which the unpaired electron occupies an sp hybrid σ orbital [10]. Such radicals are called σ-electron radicals. σ-electron radicals exhibit distinct properties not found in π-electron radicals. In a σ-electron radical, the unpaired electron occupies an sp-hybrid orbital rather than a p orbital. Hyperfine structure constants depend on the relative amounts of s and p character of the unpaired electron orbital. Therefore, geometric parameters such as bond angles can significantly alter the magnitude of the hyperfine structure constants. An interesting σ-electron radical that has been extensively studied by EPR techniques is the vinyl radical ($HC = \dot{C}H_2$). Experimental EPR studies of vinyl in solid argon at 4.2 K, supported by theoretical studies, revealed that the hyperfine structure constants for the three nonequivalent vinyl protons are $A_{trans,\beta} = 68$ Oe, $A_{cis,\beta} = 34$ Oe, and $A_{\propto} = 16$ Oe [11]. Here, cis and trans refer to the relative positions of the β proton and the unpaired electron orbital. CH proton is referred to as $\propto$ proton and CH_2 protons are referred to as β protons. Studies on a deuterated species, $DC = CHD$, indicated that the 68-0e splitting originates from the β proton. A separate study on the vinyl radical in liquid ethylene showed that the hyperfine structure constants of the β protons totaled 102.4 Oe, and therefore that the 34 0e splitting originates from a β proton

[12]. Theoretical work on ∝ proton splitting in vinyl and similar radicals has provided an important explanation for the different values of ∝ proton splitting in vinyl and formyl radicals [11].

In this study, irradiation of NNMBA single crystal revealed the formation of a single radical. Considering the splitting patterns, it was understood that only the vinyl radical can produce a splitting with an intensity ratio of 1:3:3:1. There are two sites in the molecular structure that will allow the formation of the vinyl radical. The single bond between C(3) and C(4) can be broken, resulting in the formation of the vinyl radical. In this study, it is assumed that the bond between C(3) and C(4) is broken.

Three protons contribute to the hyperfine structure splitting in the vinyl radical. Of these protons, the H(14) proton is an alpha proton and produces a splitting with an intensity ratio of 1:1. The H(12) and H(13) protons are magnetic equivalents and are called beta protons. These protons also produce a hyperfine structure splitting with an intensity ratio of 1:2:1. However, the hyperfine structure splittings resulting from alpha and beta protons were observed to be almost equal. Alpha and beta protons are magnetically equivalent, and the A_{vinyl} tensor was calculated instead of the $A_{(CH)_\alpha}$ and $A_{(CH_2)_\beta}$ tensors.

The spectroscopic splitting factor and hyperfine structure constant of the vinyl radical were determined. Due to the anisotropic properties of both EPR parameters, the principal axis values and direction cosines of the tensor forms of these parameters were obtained.

For the vinyl radical, the average values of the g-factor and hyperfine structure constant were obtained as $g = 2.00204$ and $a_{vinyl} = 1.862$ mT, respectively. The hyperfine structure constant and g values for the radical in the present study are consistent with previous studies [13-33].

5. Conclusions

Exposure of NNMBA single crystals to ionizing radiation led to the formation of radiation damage center in the structure. A single radical was formed. It was determined that a vinyl radical was formed in the NNMBA single crystal. The three protons in the vinyl radical created

hyperfine structure splitting as magnetic equivalent,. EPR parameters for the vinyl radical were determined. The accuracy of the experimental data was verified through simulation.

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CRediT authorship contribution statement

Betul Caliskan: Investigation, Calculation, Writing. **Merve Taş:** Investigation, Calculation, Writing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships.

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