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HYSCORE and Davies ENDOR Study of Irradiated Ultra High Molecular Weight Polyethylene.
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Abstract
Ultra high molecular weight polyethylene (UHMWPE) has been studied with different magnetic resonance techniques to elicit information on the nature and the location of radicals generated during high energy irradiation. Field swept EPR, Pulse Davies Electron Nuclear Double Resonance (Davies-ENDOR), and Hyperfine Sublevel Correlation (HYSCORE) spectroscopic measurements allowed extracting for the first time the full $^1$H hyperfine coupling tensors of the most abundant radical, i.e. a secondary alkyl radical and to ascertain the formation of allyl radicals in the first stages of the irradiation process. The $^1$H hyperfine coupling tensors are analogous to those reported for single crystal irradiated polyethylene, suggesting that radicals generated in UHMWPE are located in the crystalline region of the polymer.

Keywords: UHMWPE, Macro-radicals, CW-EPR, ENDOR, HYSCORE

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Introduction

Ultra high molecular weight polyethylene (UHMWPE) is commonly used in medical implants. Thanks to its properties this material is particularly suitable for this purpose because of durability, high melting point, hardness, proper density and overall non-toxicity\textsuperscript{[1]}. Sterilization procedures are mandatory for materials used in medical applications, and involve the use of high energy radiation, which causes both immediate and time dependent changes in the physical and chemical properties of the material, usually ascribed to the formation of different radicals.\textsuperscript{[2-6]} A large body of work exists concerning the formation and characterization of macro-radicals in irradiated polyethylene.\textsuperscript{[7-12]}

UHMWPE is best regarded as a three-phase material which contains, in addition to the fully crystalline and fully amorphous phases, a significant intermediate “all-trans” amorphous/crystalline inter-phase\textsuperscript{[13,14]}. Being the energy of the incident radiation used for sterilization procedures some orders of magnitude higher than that of the C-H or C-C bonds, the formation of radicals can occur in all the three phases\textsuperscript{[15-17]}. Due to different mobility and migration paths different radicals lifetimes have been observed in the three different phases.

Even though a large number of studies have been devoted to irradiated polyethylene (PE) in the past, an upsurge of interest in this topic is related to the use of this material in medical implants. The formation of radicals during sterilization procedures is of particular concern as radicals are considered to be responsible of breakings and damages in prosthesis.\textsuperscript{[18]}

Knowing the location, the reactivity and the fate of radicals created during sterilization with high energy irradiation is thus of crucial importance in determining prosthesis lifetime and reliability in implantation systems. Moreover the localization of macro-radicals in different structural parts of PE (crystalline, amorphous, inter-phase) is decisive towards reactivity with oxygen that can generate damages in the final products.

The initial effect produced in solid polymers by the action of high energy radiations is the formation of different radical species (alkyl radicals, $\text{H}^*$, dangling bonds) which are involved, after their formation, in complex secondary reactions resulting in crosslinking, gas evolution and unsaturation in chemical bonding.\textsuperscript{[19-22]} In the case of UHMWPE different hypothesis on the localization and nature of the radicals formed upon high energy irradiation have been made, however no general consensus is present at the moment. In particular whether radicals are stabilized in the amorphous or crystalline phase and the nature of these radicals remains a debated question.\textsuperscript{[11,23-25]}

There are several methods to study the secondary products of irradiation (e.g. IR spectroscopy, UV-Visible), and these have yielded much information on the radiation chemistry of polymers. On the other hand, in order to clarify the reaction mechanism, it is just as important to study the
primary products of irradiation. Electron Paramagnetic Resonance (EPR) spectroscopy, due to its capability of detecting radical species, is one of the most direct and informative techniques to elicit information relative to radical species. Conventional CW-EPR techniques have been widely applied in the past to study macro-radical intermediates generated by irradiation of polyethylene.\[20-22\] EPR experiments have played a major role in this field, as they can provide a wealth of detailed structural and dynamic information. Nonetheless, establishing reliable radical models and reaction pathways is a non-trivial task, not in the least because these compounds do not contain any specific functional group and have considerable conformational freedom. In a recent work \[26\] we studied by means of conventional CW-EPR, UHMWPE samples irradiated with electron beam at different doses. Three different radical families were identified on the basis of the EPR spectra among which secondary alkyl radicals are the most abundant. Other two different radical types were identified, which were assigned to allyl and tertiary alkyl radicals. Allyl radicals were observed only after the decay of the most abundant alkyl radicals and it was verified that they were stable over a longer time with respect to secondary alkyl species. However, the CW-EPR technique, did not allow verifying if allyl species were generated directly during the irradiation process or if they were the consequence of chemical reaction of alkyl radicals.

The aim of the present work is thus to address the difficult question of radical localization within the different phases of UHMWPE and the nature of these radicals. To do so different hyperfine spectroscopic techniques (Pulse ENDOR, HYSCORE) have been used to elucidate in detail the nature of formed radicals and their evolution during time.

**Experimental**

Medical grade UHMWPE (Gur 1050, Poly Hi Solidur – MediTECH Division, Fort Wayne, USA) with a molecular mass higher than 5·10^6 a.m.u. has been used as resin powder. This material shows 75% of crystallinity (as evaluated with DSC analyses). The studied material, in accordance with standards for implant material ASTM F 648-84, was completely free from any additives.

Samples were irradiated in vacuo with electron beam at 60 kGy. A suprasil quartz tube sample holder, an inlet for the insertion of the sample and a connection with a vacuum line through a tap has been used. Before the irradiation test, the sample has been kept under dynamic vacuum (10^-4-10^-5 mbar) by turbo-molecular pump for 24 hours, in order to evacuate the EPR tube and to eliminate the oxygen diffused into the powder. During irradiation of the powder the EPR tube has been protected by a lead screen in order to avoid the formation of EPR active defects in the glass, as reported elsewhere \[27\].
E-beam irradiation was performed with a 10 MeV accelerator (Bioster, Seriate, Italy), operating at 25 kW power, with a dose rate of $6 \cdot 10^4$ kGy/h, at RT. The maximum dose given in one single passage is 30 kGy; two passages were necessary for 60 kGy dose. Each irradiation passage took about 5 minutes, so the complete irradiation procedure was completed in 10 minutes. The irradiation set up was formed by a revolving trolley equipped with an irradiation chamber shielded by a lead covering. The UHMWPE samples were sealed in quartz tubes under vacuum and irradiated in the chamber, with the EPR tube shielded out of the chamber in order to avoid the formation of paramagnetic defects in the quartz tube. The irradiation was performed at room temperature. After irradiation the samples were put in liquid nitrogen, until the beginning of EPR measurements.

X-band CW EPR spectra were detected at 77 K on a Bruker EMX spectrometer (microwave frequency 9.75 GHz) equipped with a cylindrical cavity. A microwave power of 1 mW, modulation amplitude of 0.1 mT and a modulation frequency of 100 KHz was used. Pulse EPR experiments were performed on an ELEXYS 580 Bruker spectrometer (at the microwave frequency of 9.76 GHz) equipped with a liquid-helium cryostat from Oxford Inc. All experiments were performed at 10 K. The magnetic field was measured by means of a Bruker ER035M NMR gauss-meter.

Electron-spin-echo (ESE) detected EPR experiments were carried out with the pulse sequence: $\pi/2 - \tau - \pi - \tau$-echo, with microwave pulse lengths $t_{\pi/2} = 16$ ns and $t_{\pi} = 32$ ns and a $\tau$ value of 200 ns.

Davies-ENDOR spectra were measured with the mw pulse sequence $\pi-T-\pi/2-\tau-\pi-\tau$-echo, with mw pulses of length $t_{\pi/2} = 16$ ns and $t_{\pi} = 32$ ns, and $\tau = 220$ ns. A radio frequency pulse of length 12 μs and variable frequency $v_{\text{ENDOR}}$ was applied during time $T$.

Hyperfine Sublevel Correlation (HYSCORE) experiments $^{[28]}$ were carried out with the pulse sequence $\pi/2 - \tau - \pi/2 - t_1 - \pi - t_2 - \pi/2 - \tau -$ echo with the microwave pulse length $t_{\pi/2} = 16$ ns and $t_{\pi} = 16$ ns. The time intervals $t_1$ and $t_2$ were varied in steps of 8 or 16 ns starting from 96 ns to 3296 ns. In order to avoid blind spot effects different $\tau$ values were chosen, which are specified in the figure captions. A four-step phase cycle was used for eliminating unwanted echoes. The time traces of the HYSCORE spectra were baseline corrected with a third-order polynomial, apodized with a Hamming window and zero filled. After two-dimensional Fourier transformation, the absolute value spectra were calculated. The spectra were added for the different $\tau$ values in order to eliminate blind-spot effects.

The field swept EPR spectra were simulated with the EPRSIM32 program $^{[29]}$, while ENDOR and HYSCORE spectra were simulated using the Easyspin software package $^{[30]}$.  

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Results and discussion.

The interaction of high energy radiation (X-rays, γ-rays, e-beam) with UHMWPE leads to the random scission of C-C and C-H bonds, producing H atoms together with primary and secondary radicals. Among the different radical species generated upon irradiation, secondary alkyl radicals are the most abundant products. These radicals, schematically illustrated in Scheme 1, are often referred to as macroradicals, accounting for the solid state nature of the system.[27]

Scheme 1. Schematic illustration of a secondary alkyl radical

The CW-EPR spectra recorded at 77K and electron spin echo (ESE) detected EPR spectra of irradiated UHMWPE after irradiation and upon 20 hours ageing at room temperature are shown in Figure 1 along with the corresponding computer simulations.

Due to the experimental setup irradiation is performed at room temperature and samples are frozen in liquid nitrogen after approximately 10 min from the end of irradiation. During this time a large number of the formed radicals are known to recombine[11]. The recombination process is stopped upon freezing at 77K. Both CW and electron spin echo (ESE) detected EPR spectra observed after irradiation (Figure 1A and 1B) are characterized by a 6 line powder pattern typical of an alkyl radical and extensively described elsewhere.[26,31] Despite its seemingly simplicity, a thorough understanding of the spectra reported in Figure 1A and 1B, is challenging. The simulation of the CW-EPR signal of the secondary alkyl radical indicates a weak anisotropy of the g tensor (g∥=2.0031 and g⊥=2.0020) that agrees with previous literature reports[32], and a larger anisotropy in the hyperfine coupling constant generated by the interaction of the unpaired electron with the protons of the polymer chain. The sextet structure derives from the hyperfine interaction of the unpaired electron (localized in a carbon p orbital) with 5 nearby protons. The hydrogen atom in α position is responsible for a highly rhombic hyperfine interaction[33], while two pairs of nearly magnetically equivalent β hydrogen atoms (Hβ1-3, Hβ2-4) lead to axial hyperfine coupling. It should be noted that in most of the conventional EPR studies on irradiated polyethylene, the spectra are treated as isotropic even though, large anisotropies actually characterize the 1H hyperfine constants in these solids.
The signal reported in Figures 1A and 1B can be considered (at least for practical purposes) indefinitely stable at the liquid nitrogen temperature, however the spectrum evolves fast at room temperature at the hour time scale leading to the spectrum reported in Figures 1C and 1D. The overall spectral intensity is about 30% of the intensity of the spectrum reported in Figure 1A and the spectral features are typical of an allyl radical species.[26] This time dependent study clearly indicates that the secondary alkyl radicals are unstable and that allyl radicals are also present in the irradiated sample. However it is not clear if the spectrum of the allyl radicals is buried within the more intense spectrum of the secondary alkyl radical or if allyl radicals are formed as a result of the subsequent radical reactivity. In order to answer this question and to better clarify the localization of the alkyl radicals in the UHWMPE polymer ESEEM and ENDOR methods have been applied.

The Davies ENDOR spectrum recorded at 10K at the observer position indicated by the solid arrow in Figure 1B is shown in Figure 2 along with its computer simulation. The spectrum is characterized by several sets of signals arising from hyperfine interactions with different sets of protons. Two sets of peaks characterized by a distinct axial powder pattern separated by twice the proton nuclear Larmor frequency and centered at $A/2$ (so called strong coupling condition) where $A$ is the hyperfine coupling constant. The high resolution of the ENDOR spectrum allows extracting by means of computer simulation the full hyperfine matrix for the two sets of protons (Table 1). The values agree with those reported by Tomaszewskiñ et al. [34] in the case of $\gamma$ irradiated polyethylene single crystals and assigned to $\beta$ protons.

Another set of three distinct signals is found centered at the nuclear Larmor frequency of the proton ($v_H = 14.604$ MHz at 343.0 mT) (weak coupling conditions) separated by hyperfine coupling constants $A$ ranging from 5 to 2 MHz. The full hyperfine matrix (Table 1) was obtained by means of computer simulations and corroborated by HYSCORE measurements (vide infra). These three smaller couplings represent chemically distinct protons interacting with the unpaired electron. Comparison with literature data for single crystal irradiated polyethylene, indicates these couplings as arising from more distant protons as found in $\gamma$ and $\delta$ positions. It should be noted however that protons belonging to side chains may also give rise to these small couplings.

Spectral features with lower intensity centered at the proton Larmor frequency and separated of approximately 10 MHz are also observed in the spectrum, which are due to a different set of protons. These signals are better characterized with the HYSCORE technique (vide infra). HYSCORE spectra were therefore recorded at the same field positions of the ENDOR spectrum. HYSCORE is a two-dimensional experiment where correlation of nuclear frequencies in one electron spin ($m_S$) manifold to nuclear frequencies in the other manifold is created by means of a
mixing $\pi$ pulse. The HYSCORE spectrum of the irradiated polyethylene recorded at observer position $B_0 = 343.0$ mT is reported in Figure 3a.

The spectrum contains a peak from weakly coupled $^1$H matrix nuclei located on the diagonal of the (+,+) quadrant at the proton nuclear Larmor frequency ($\nu_H = 14.604$ MHz). In addition to the diagonal peak, four pairs of cross features can be distinguished, designated as H(3), H(4), H(5) and H(6). Cross-peaks H(6) appear as extended, weak arcs along the diagonal of the (-,+), centered at about (-2.5, 30.7),(-30.7, 2.5) MHz, the two coordinates of the two cross peaks differing by close to $2\nu_H$. Two other cross features are located in the (+,+) quadrant, centered symmetrically around the diagonal point of $\nu_H$. Cross-peaks indicated as H(5) have maxima at (9.5, 20.5), (20.5, 9.5) MHz, which correspond to the side wings observed in the Davies ENDOR spectrum. Cross-peaks H(3,4) overlap with the high-intensity matrix peak forming a ridge with maximum extension of 5.2 MHz. The contour line shapes of the cross-peaks in the (+,+) quadrant, show a small shift from the ($\nu_H$, $\nu_H$) value, indicating a small dipolar coupling. This is confirmed by computer simulation (Figure 3b) where two slightly different protons have been considered as contributing to the ridge, on the basis of the splittings observed in the Davies ENODR spectrum (Figure 2). The hyperfine coupling tensors used in the simulation of both HYSCORE and ENDOR spectra are reported in Table 1 and agree with values obtained by CW-ENDOR and assigned to remote $\gamma$ and $\delta$ protons [26].

Cross peaks H(6) have no counterpart in the Davies ENDOR spectrum of Figure 2. The peaks are due to hyperfine couplings close to the cancellation condition ($A = 2\nu_H$), which explains the presence of cross peaks in the (+,+) quadrant indicated with the arrows as due to the same set of protons. This is confirmed by computer simulation, which indicates that these features can be reproduced using a single H with a rhombic hyperfine coupling (Table 1). These relatively strongly coupled protons, as well as those labeled H(5) have lower intensity with respect to the weakly coupled protons H(3,4). The reason why the contribution of the strongly coupled protons H(6) is not observed in the Davies ENDOR spectrum may be explained considering that this coupling will induce a pair of transitions centered at $\nu_H$. One such transitions will fall at very low frequency where it is difficult to be observed, while the other transition will overlap with features associated to H(1) protons.

The H hyperfine couplings labeled as H(1,2), H(3) and H(4) correlate with values reported for hyperfine couplings due to $\beta$ (H(1,2)), $\gamma$ (H(3)), and $\delta$ (H(4)) protons in alkyl radicals obtained by irradiation of polyethylene single crystals. Values for the $\alpha$ proton have also been reported (Table 1, detected by CW-EPR), which are not detected in the Davies ENDOR powder spectrum, due to the large anisotropy of this proton. The values reported in Table 1 for the alkyl
radical were used to simulate the echo detected EPR spectrum reported in Figure 1B. In the
simulation the contributions of the $\alpha$ and four $\beta$ protons where considered allowing for computer
optimization of the spectral linewidth. The simulation accounts relatively well for observed
features of the EPR spectrum, in particular the small anisotropy observed is nicely reproduced.
Small discrepancies in the reproduction of the spectrum can be understood considering that
couplings due to H(5) and H(6) are not compatible with an alkyl radical, and indicate that even
though these radicals are largely dominant, other radicals are formed in the irradiated polymer.
Comparison with H(5) and H(6) couplings with literature values indicate that these are
consistent with allyl radicals, which are assumed to be formed as a minor fraction during the
irradiation process [32]. Even though ENDOR and HYSCORE signal intensities cannot in general
be used for quantization of the number of species, the relative intensities of the allyl proton with
respect to the alkyl proton signals indicates at least an order of magnitude difference in the
number of the two species. This is in line with the fact that the allyl signal is completely
overwhelmed by the spectral features of the alkyl radical in both CW and ESE detected EPR
spectra recorded at the minimum possible time after irradiation (Figure 1). This is corroborated
by computer simulation of the CW EPR signal, which indicates that the spectral features of the
allyl radical start to become visible in the presence of the alkyl radical spectrum when the
intensity ratio of the two species is of the order of 1/10.

ENDOR and HYSCORE spectra were also recorded for the room temperature aged
time at a field position corresponding to the maximum echo intensity (arrow in Figure 1D).
The ENDOR spectrum is shown in Figure 2b, while the HYSCORE spectrum is reported in
Figure 3c. The ENDOR spectrum clearly reveals that the signals due to the strongly coupled
protons indicated by H(1) and H(2) and typical for the secondary alkyl radicals are no longer
present, in agreement with the CW and ESE detected EPR spectra. On the contrary the weak
signals flanking the $^1$H matrix line (H(5)) are still present. This is in agreement with the
HYSCORE spectrum which is substantially unchanged featuring cross peaks indicated with H(5)
and H(6) which are assigned to allyl protons. This result clearly confirms that allyl radicals are
formed in the early stages of irradiation and are far more stable than alkyl radicals, thus
surviving the annealing process.

**Conclusions**

Advanced magnetic resonance techniques (ESE-EPR, ENDOR and HYSCORE) have been used
to study the radicals formed in UHMWPE upon e-beam irradiation.
The main results obtained from this study can be summarized as follows:
i) Secondary alkyl macroradicals represent the most abundant radicals family formed during the electron beam irradiation process of UHMWPE.

ii) The full hyperfine tensors for the different protons of such secondary alkyl macroradicals have been measured for the first time in this material by means of hyperfine techniques. The spin Hamiltonian parameters are analogous to those observed in irradiated polyethylene single crystals, strongly suggesting that the macroradicals are localized within the crystalline phase of UHMWPE.

iii) HYSCORE and ENDOR spectra reveal the presence of allyl radicals identified by specific $^1$H hyperfine couplings. The time evolution of EPR, ENDOR and HYSCORE spectra shows that these radical species are formed during the irradiation process and have a longer life time with respect to the alkyl radicals.

Figure 1
Figure 2
Figure 3

![Diagram](image-url)
Scheme 1
Figures Captions

Scheme 1. Secondary alkyl radical

Figure 1 A) CW-EPR spectra of irradiated polyethylene recorded at 77K. a) experimental; b) computer simulation. B) ESE-EPR spectra of irradiated polyethylene recorded at 10K. a) experimental; b) computer simulation. C) CW-EPR spectra of allyl species appeared after the decay of secondary alkyl radicals recorded at 77K and a) experimental; b) computer simulation. D) ESE-EPR spectra of allyl species appeared after the decay of secondary alkyl radicals recorded at 77K a) experimental; b) computer simulation

Figure 2 Davies ENDOR spectra of irradiated polyethylene measured at 10 K. a) experimental and computer simulation of secondary alkyl species, b) Davies ENDOR spectra of decayed sample where H(1) is H(1.6), H(2) is H(2.6), H(3) is H(0.1.3.4), H(4) is H(1.2.3.4), H(5) is assigned to an allyl radical.

Figure 3 HYSCORE spectra a) Experimental, b) Simulated of irradiated polyethylene measured at 10 K. c) HYSCORE spectra of allyl species appeared after the decay of secondary alkyl radicals

References

Table 1 Hyperfine parameters extracted from the simulation of the CW-EPR spectra and HYSCORE and Davies ENDOR spectra for the different protons. Hyperfine coupling are given in MHz.

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