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# Nitroso labeling in electron-irradiated LDPE

**Andreas Petr and Lothar Dunsch***

Institut für Technologie der Polymere, Akademie der Wissenschaften, O-8010 Dresden, Federal Republic of Germany

## Summary

The nitroso labeling method (1) has been used to demonstrate its possibilities for the characterization of irradiated polyethylene (LDPE) with respect to its crosslinkings and oxygen functionalities.
ESR spectra of nitroso labeled LDPE consist of the superposition of the signals resulting from three different radicals.
It has been shown that a relative estimation of the ketone content is possible in irradiated LDPE samples even at low concentrations thus giving a sensitive method for this functional group in polyethylene.

## Introduction

The formation and decay of radicals as that of peroxides in electron-irradiated polyethylene was studied in great detail (for a review see 2) to understand the chemical reactions at the polymer chains initiated by irradiation.
The mechanical properties of plastics are altered by chemical changes in the polymer structures as a result of radical reactions even at a small extent. Such low concentrations are hardly to be detected by conventional spectroscopic techniques.
The high sensitivity of ESR-spectroscopy can be used only in the case of radicals but not with diamagnetic structures. Its application is possible for such purposes if a specific labeling of chemical structures in polyethylene is available.
A convenient way in ESR-spectroscopy is the study of nitroxyl radicals which can be formed by the application of spin probes, by spin trapping or nitroso labeling.
We prefered to use the method of nitroso labeling in the manner described in (1).
In nitroso labeling radicals were produced as well as trapped by one and the same nitroso compound.
It is the advantage of this method that the polyethylene under study can be labeled after any special treatment like crosslinking, irradiation, oxidation or something else.
For the labeling of polymers only a slightly elevated temperature is needed but gaseous oxygen must be carefully removed before the polyethylene is labeled to avoid oxidation during the labeling procedure.

*To whom offprint requests should be sent

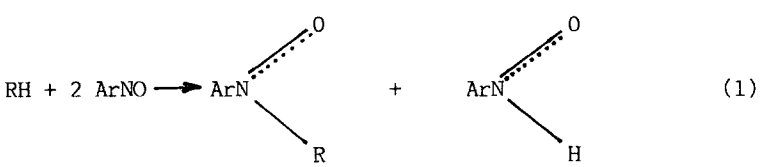
## Experimental

Foils of low density polyethylene (Orbitaplast GDR, AL 23 FA, 30 µm thick) were electron irradiated in air, in nitrogen and under vacuum.
The irradiation was carried out with an electron accelarator ELT-1.5 from the Nuclear Research Institute of the Soviet Academy of Science (installed in our institute).
Three days after irradiation and storage at room temperature when the concentration of the radiation induced radicals was neglectable, the foils were swollen in a 5 x $10^{-2}$ M solution of 2,4,6-tribromonitrosobenzene (3) in benzene at room temperature for about 10 hours.
After swelling no radicals are detectable by ESR-spectroscopy but after storing the foils at 80 °C for 30 minutes under vacuum intensive ESR spectra were obtained.
For the detailed ESR study the LDPE foils were swollen for 2 hours in pure benzene to improve the resolution of the spectrum.
The ESR measurements were performed at 70 °C. At this temperature the intensity of the spectra didn't change for several hours.
The x-band ESR spectrometer ERS 221 (Centre of Scientific Instruments of the Academy of Science of GDR) was used in this study which is equipped with an variable temperature accessory of an accuracy of ± 1 degree.

We performed the measurements in a x-band rectangular cavity containing the quartz dewar using a 100 kHz field modulation.
The gel content of LDPE was determined by an extraction with xylene in an Soxhlet apparatus for 16 hours.
The IR measurements were made at a FT IR spectrometer IRF 180 (Centre of Scientific Instruments of the Academy of Science of GDR) the resolution of which was 4 $cm^{-1}$.

## Results and discussion

The nitrosobenzene reacts with polyethylene according to the following equation (4).




(1)

The instability of the second product is the reason that only spectra of trapped polyethylene radicals can be observed.
ESR spectra of irradiated LDPE treated with 2,4,6-tribromonitrosobenzene consist of two six-line patterns (radical A: g = 2.0066, $a_N$ = 1.26 mT, $a_H$ = 0.61 mT; radical B: g = 2.0066, $a_N$ = 1.32 mT, $a_H$ = 0.84 mT) and one three line pattern (radical C: $a_N$ = 1.44 mT).
According to (5) we used the quotient (cf. Fig. 1)

$$Q = I_B / I_A \qquad (2)$$

for characterizing the irradiated polymer with respect to chemical changes.

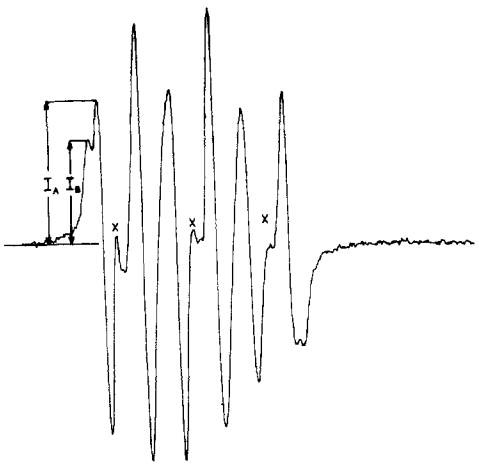



Fig. 1
ESR-spectrum of nitroso labeled polyethylene (x-trapped alkoxy radical)

Q correlates quite well with the radiation dose at samples irradiated in air (Fig. 2).

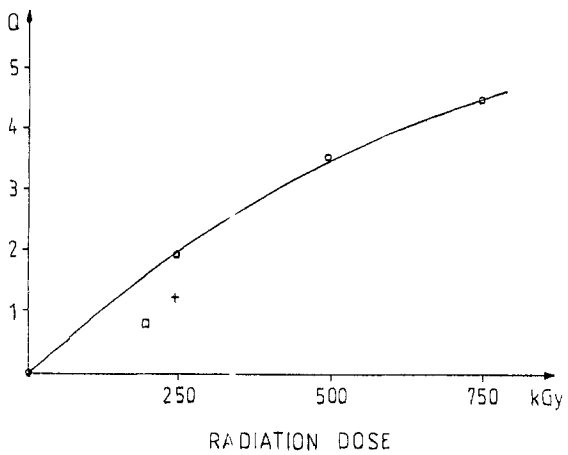



Fig. 2
Dependence of Q on the radiation dose (irradiated in: air O, gaseous nitrogen +, at about 1 Pa )

Therefore the intensity change of radical B or A might be due to radiation crosslinking or oxidation.
If we also consider those samples irradiated in gaseous nitrogen or under vacuum no correlation with the radiation dose is possible (Fig. 2).
The same behavior is valid for the dependence of Q on the gel content (Fig. 3).

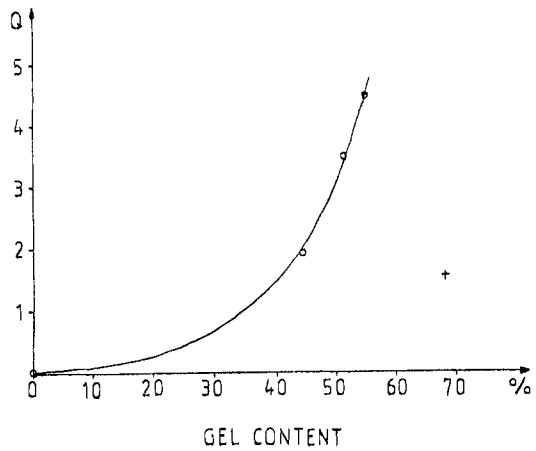



Fig. 3
Dependence of Q on the gel content
(irradiated in: air 0, in gaseous nitrogen +)

For explaining the divergent behavior of the samples irradiated in gaseous nitrogen or under vacuum we have to take into consideration that the very low concentration of oxygen will cause an increase of crosslinking but a decrease of the concentration of oxidized polyethylene.
In our case irradiation will always produce carboxylic, aldehyde and keto groups if oxygen is present. Looking for a dependence of the ESR signal on a chemical change we found that the correlation of Q with the $\nu$(C=O) absorption at 1730 $cm^{-1}$ is possible (Fig. 4), but in a nonlinear manner.

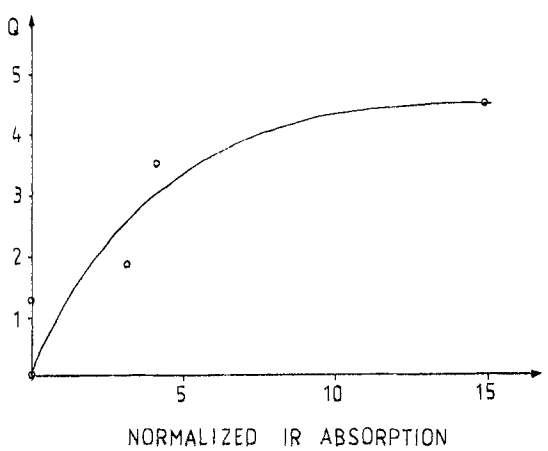



Fig. 4
Dependence of Q on the $\nu$(C=O) absorption

On the basis of these dependencies and the reactions of the nitroso compound with model compounds (e.g. n-hexan, cumylhydroperoxide, cumene) we have made an assignment for radical structures in irradiated PE which is shown in Fig. 5

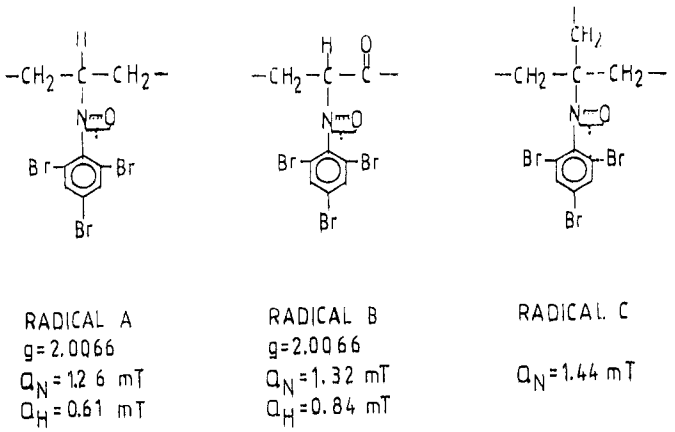



Fig. 5
Proposed structures of the observed radicals

We assume that radical A is caused by reaction of the unmodified polymer chain with the tribromonitrosobenzene.
Then radical B is attributed to the reaction of the spin labeling agent with a methylene group bound to an oxidized carbon atom while radical C is caused by reaction with a tertiary carbon atom.
Assuming that 2,4,6-tribromonitrosobenzene preferentially reacts with a methylene group in $\alpha$-position to a keto group the nonlinear correlation with the $\nu$(C=O) absorption can be explained.
The nonlinear behavior is due to the plot of Q against the $\nu$(C=O) absorption including carboxylate etc. It is needed to use ketone absorption intensity alone for this purpose.
With increasing radiation dose the ketone content of LDPE doesn't increase in the same way as the energy absorption because a part of the ketone is transformed into aldehydes and carboxylic acids which have been proved in LDPE in the literature (6,7).

## Conclusions

Nitroso labeling is a very suitable method to distinguish trapped radicals of the unchanged polyethylene from the partially oxidized polymer chain formed by irradiation.
The quotient Q is a selective measure to get the ketone content of the polyethylene irradiated in air.

Especially at low ketone concentrations Q is more sensitive than the $\nu$(C=O) absorption intensity in IR spectroscopy. Therefore the high sensitivity of ESR-spectroscopy is combined with a radical reaction to get well differented results of the ketone content in irradiated LDPE.

Acknowledgments

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