Spin trapping of radicals produced by glow discharge on low-density polyethylene

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An electron spin resonance study of radicals produced by glow discharge on low-density polyethylene powder shows three kinds of radicals, depending upon experimental conditions. The first formed, alkyl radicals, are unstable at room temperature and react rapidly with oxygen to form peroxide radicals. If a spin trapping compound, N-tert-butyl-α-phenyl nitrone, is added to the polyethylene, before discharge, nitroxide radicals are formed in place of peroxide. The interest in forming nitroxide radicals is their stability at room temperature. This simple method can be helpful for the observation and identification of radicals produced in polymers, for example by electrical treeing.

Keywords Electron spin resonance; radicals; spin traps; polyethylene; glow discharge; degradation

INTRODUCTION

The production and detection of free radicals in polymeric systems has been extensively studied, generally by electron spin resonance (e.s.r.). For polyethylene, about ten different radicals have been reported as produced by ionizing radiation, corona discharge, mechanical abrasion or other excitation mechanisms[1-11]. Many of these have very short lifetimes at room temperature. A number of radicals obtained in low-density polyethylene (LDPE) have been observed only at liquid-nitrogen temperature or below. At higher temperatures, these radicals rapidly disappear through spontaneous decay, reaction with the atmosphere, migration, or crosslinking[1,2,5-7], thus rendering their detection and study impossible.

For some time, our group has been using e.s.r. to study the degradation of LDPE by electrical treeing[12-15]. It is to be expected that radicals will be produced in this process. However, each time an e.s.r. signal has been positively identified, except for that due to char[13,14], these signals have always been due to metallic ions[14,15]. A likely explanation for the absence of signals due to radicals is that, since our experiments are carried out at room temperature, unlike those mentioned above, the lifetime of any radicals is shorter than the time necessary for e.s.r. measurements. It is therefore of considerable interest to stabilize the radicals, as may be done by spin trapping[16-23]. Recently, Kusomoto and Sakai[10] have stabilized radicals produced in LDPE by γ-irradiation, by prior doping of the material with a spin trap. We propose that the same technique should work for the case of activation by electrical means.

As electrical treeing is a complex process[13], the experiments we report here have employed a simpler activation technique, glow discharge, which Bamford and colleagues[3,24] have shown to produce free radicals in LDPE. We report here the stabilization of such radicals as the result of prior doping with a spin trap.

EXPERIMENTAL

The material used was LDPE powder (Petrothene type NA310-06) containing Santanox R antioxidant, and ground under cryogenic conditions. A series of mixtures of LDPE powder and solid spin trap, N-tert-butyl-α-phenyl nitrone (PBN), were prepared; the compositions studied were 0, 1.97, 11.03, 20.33, 100% by weight of PBN in LDPE.

A 'Suprasil' quartz tube (99.99% pure silica) containing the mixture was evacuated to an average pressure of 2×10^{-3} Pa (1.5×10^{-5} Torr). A glow discharge was generated in the lower part of the tube by means of a Tesla coil. The duration of this treatment was limited to 90 s, as it was found that the intensity of e.s.r. spectra did not increase significantly thereafter. The Tesla discharge was carried out either at room temperature or at liquid-nitrogen temperature. For the study of the effect of oxygen on radicals, an oxygen pressure of 1.33×10^2 Pa (1 Torr) was established in the tube just after discharge. In this case the sample tube was always kept in liquid nitrogen until e.s.r. measurements were carried out.

E.s.r. spectra were recorded on a JEOL spectrometer, model JES-ME-3X, using X-band (9.4 GHz), with 100 kHz modulation field. The cylindrical cavity has a TE 011 resonance mode. The g factors were determined by measuring the operating frequency with a high-precision frequency meter and determining the resonance magnetic field with a proton n.m.r. probe.

As already mentioned, the role of spin trapping is to stabilize and increase the life of a radical. The trap molecule, PBN in this case, reacts with the original radical to form a new, stable species, a nitroxide radical in the present case. For PBN, the reaction is[10,19]:
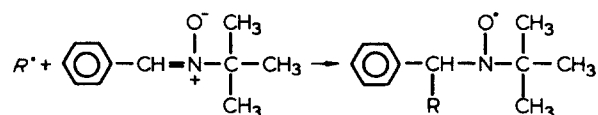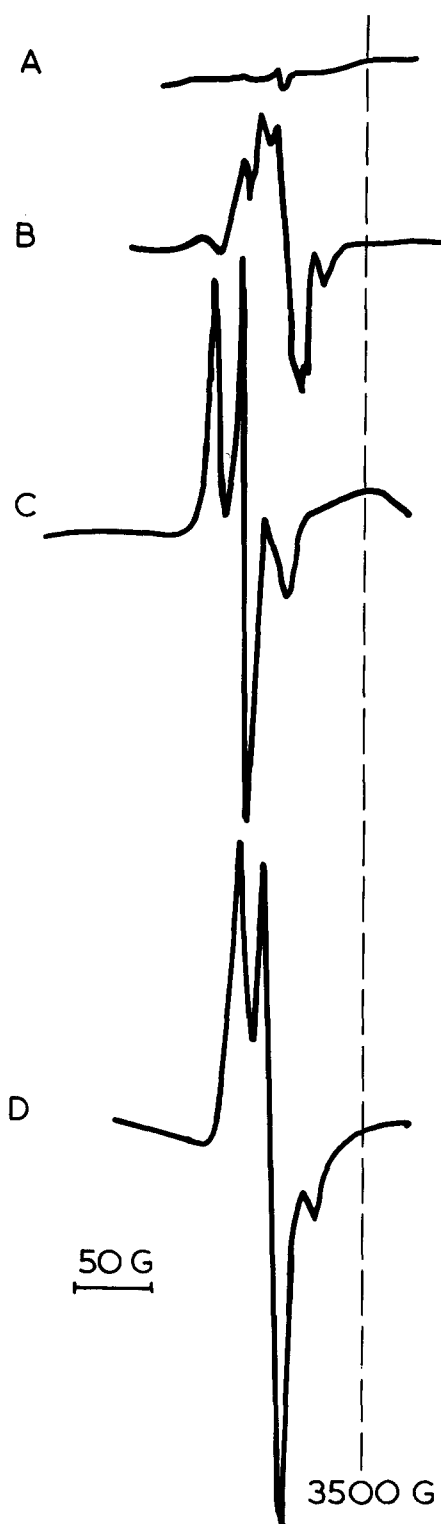
The new radical will continue to show an e.s.r. hyperfine structure related to that of the parent, from which the identity of the parent can be deduced.

RESULTS AND DISCUSSION

Figure 1 shows e.s.r. spectra after glow discharge for the different samples. For this series of experiments, the discharge took place at liquid-nitrogen temperature, and

the recording at room temperature. *Figure 1*, trace A (0% PBN) shows that LDPE alone displays no significant e.s.r. signal; but a signal appears, and increases rapidly with the addition of a small amount of PBN. Between 0 and 10 wt% PBN the form of the signal changes from a sextet to an asymmetric triplet; between 10 and 20 wt% it remains a triplet but increases in intensity. At 100 wt% PBN, no signal is observed. As best spectral resolution for the minimum of spin trap concentration occurs at about 10 wt%, this latter mixture was used in all subsequent experiments.

The observed asymmetric triplet (11.03% PBN) resembles that of e.s.r. signals due to nitroxide[10,18,20] or peroxide[1,3,4,7,8] radicals. To distinguish between these two radicals, the observation of their stability as a function of time and of temperature is very useful. The nitroxide radicals are quite stable in time at room temperature; when these samples are heated, the triplet signal changes from an asymmetric form to a symmetric one[10,18,20]. In contrast, peroxide radicals have short lives ($\leqslant 30$ min) at room temperature; when samples are heated, the lifetime is even shorter, but the triplet is not modified[3,4].

The e.s.r. spectra at room temperature of the 10% samples may be observed for periods exceeding two days, following glow discharge activation at liquid-nitrogen temperature; that is, they are quite stable. When the recording temperature was raised from $-10°$ to $190°C$ we observed a change from an asymmetric triplet to a symmetric one. The field interval between the outermost peaks, indicated by arrows in *Figure 2*, remained essentially constant $\sim 5.5 \times 10^{-3}$ T (~ 55 G) at low temperatures ($-196°$ to $\sim 25°C$), then diminished rapidly between a temperature just above room temperature and about $100°C$, and finally reached a new constant value of about 2.9×10^{-3} T (29 G) for still higher temperatures, as can be seen in *Figure 3*. This may tentatively be explained in terms of molecular motion, which is very limited at liquid-nitrogen temperature, but increases with increasing temperature in a manner which is characteristic for a given polymer. Comparing *Figures 2* and *3*, we can see that the first plateau of the curve of peak separation versus temperature corresponds to the asymmetric triplet, and that the second one is reached when the triplet becomes completely symmetric. The symmetric signal does not change significantly after this point except in intensity; the signal intensity decreases quite rapidly at the highest temperature, when melting of the mixture begins. These results, in accord with those obtained by other workers[10,18,20], indicate that we probably form the nitroxide radical.

Figure 4 shows the evolution of e.s.r. spectra corresponding to radicals formed in pure LDPE when exposed after glow discharge to an increasing quantity of oxygen, and increasing temperature. At the lowest temperature ($-196°C$), the presence of a small amount of oxygen gives the same e.s.r. spectrum, which is transformed slowly into an asymmetric triplet when the tube is opened to atmosphere at low temperature. This latter spectrum is characteristic of peroxide radicals, ROO˙ [1,3,4,7,8]. Peroxide radicals have short lives at room temperature; in fact, within 15 min at room temperature, the triplet signal disappeared completely. When the sample was heated, the lifetime was even shorter. If a 10% PBN sample was submitted to a discharge, the asym-
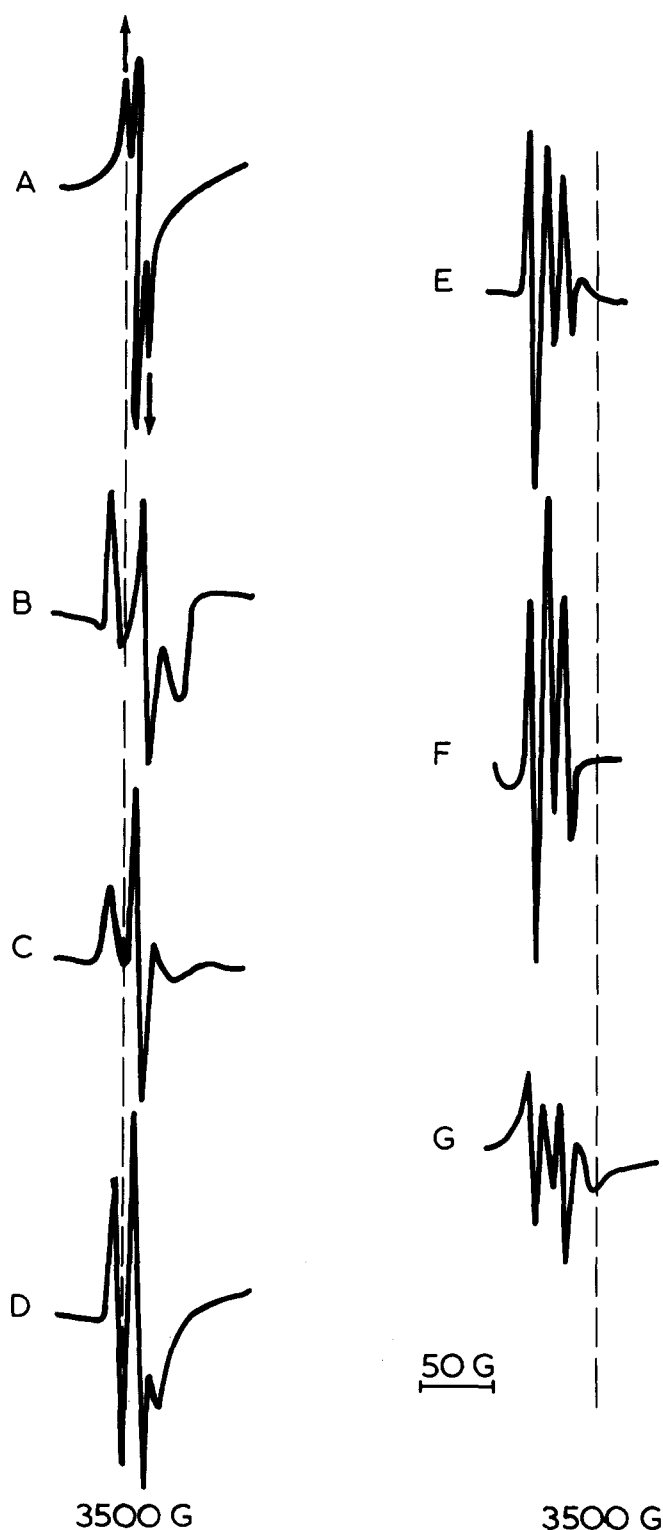
Figure 2 Evolution of e.s.r. spectra of 10% mixture of PBN in PE with increasing temperature. Trace A, −10°C; B, 23°C; C, 60°C; D, 90°C; E, 120°C; F, 150°C; G, 180°C. Arrows indicate the extreme separation of peaks (see text). The scale of 50 G applies to traces B to G; the same width represents 100 G for trace A

metric triplet was observed and remained stable even if it was exposed to oxygen. We therefore conclude that reactions taking place in LDPE/PBN mixture after glow discharge activation result in the formation of nitroxide rather than peroxide radicals.

The g value measured for the stable triplet (*Figure 1*, trace C), 2.0048, is nearer than obtained[4] when the parent radical is an alkyl, 2.0025, rather than a peroxide radical;

in the latter case one finds[4] $g = 2.014$. Further, the separation between two adjacent lines of the triplet spectrum is 2.0×10^{-3} T (20 G). For the sextet spectrum (*Figure 4*, trace A) obtained at low PBN concentration, this separation is 2.5×10^{-3} T (25 G). A sextet spectrum with a splitting of about 3.0×10^{-3} T (30 G) and with a lifetime of about a day at liquid-nitrogen temperature is characteristic of an alkyl radical $-CH_2-\dot{C}H-CH_2-$[2,5,6,10]

We conclude that the most likely source of the sextet spectrum is alkyl radicals which are somehow stabilized by the presence of small amounts of spin trap. When there is more than 2% PBN in the mixture, they transform into nitroxide radicals, giving rise to the observed triplet spectrum.

CONCLUSIONS

Low-pressure glow discharge (obtained with a Tesla coil) is a relatively simple method of producing radicals in polyethylene powder. Bamford and Ward[3] used this approach at liquid-nitrogen temperature under hydrogen atmosphere, and they recorded their e.s.r. spectra at the same temperature. We have activated our samples, containing variable quantities of PBN spin trap, in partial vacuum at liquid-nitrogen temperature, but have recorded most of our e.s.r. spectra at room temperature.

Bamford and Ward observed alkyl radicals, which yield a sextet e.s.r. signal, and after exposure to oxygen, peroxide radicals, with a triplet spectrum. Both of these were observed to exhibit short lifetimes, especially at higher temperatures. From the experiments reported here, it seems that the alkyl radicals were stabilized by small quantities of spin trap, which accounts for the observation that their e.s.r. signals persisted at room temperature for several days, even in the presence of oxygen. In addition, we observed a triplet signal, due to nitroxide radicals, presumably the daughters of alkyl radicals at higher PBN concentration. A glow discharge under oxygen yields peroxide radicals, but these are not stabilized by the PBN. An approach similar to the one described here might be used to study the formation of radicals in electrical trees in solid polymeric insulation.
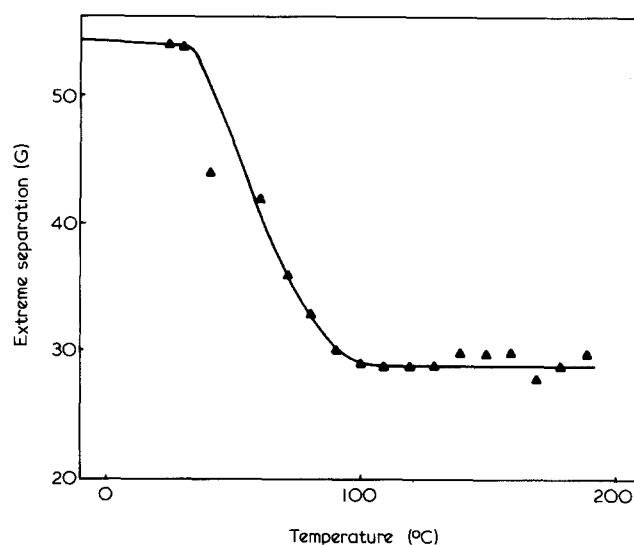
Figure 3 Extreme field separation between e.s.r. peaks for a PE/0.1 PBN sample, as a function of temperature
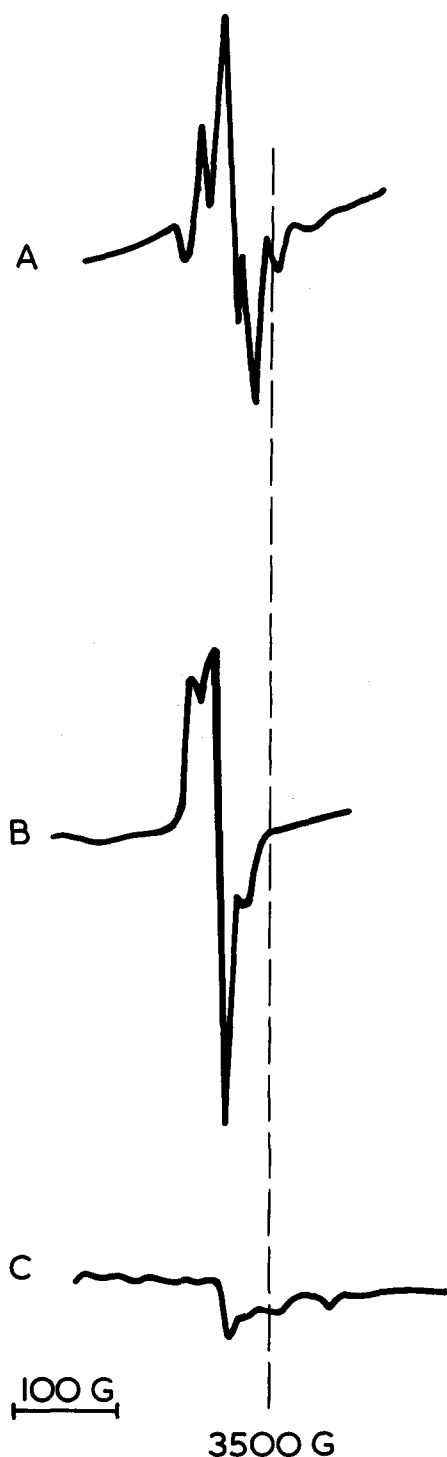
Figure 4 E.s.r. spectra of irradiated polyethylene in presence of oxygen at liquid-nitrogen and room temperature. Trace A, LDPE with a small quantity of oxygen at −196°C; B, air admitted at −196°C; C, temperature increased to 23°C

REFERENCES

1   Loy, B. R. *J. Polym. Sci.* 1960, **44**, 341–347
2   Lawton, E. J., Balwit, J. S. and Powell, R. S. *J. Chem. Phys.* 1960. **33**, 395–404
3   Bamford, C. H. and Ward, J. C. *Polymer* 1961, **2**, 277–293
4   Ohnishi, S., Sugimoto, S. and Nitta, I. *J. Polym. Sci. A* 1963, **1**, 605–623
5   Ohnishi, S., Sugimoto, S. and Nitta, I. *J. Chem. Phys.* 1963, **39**, 2647–2653
6   Salovey, R. and Yager, W. A. *J. Polym. Sci. A* 1964, **2**, 219–224
7   Tsuji, K. *J. Polym. Sci.* 1973, **2**, 1407–1419
8   Davis, L. A., Pampillo, C. A. and Chiang, T. C. *J. Polym. Sci.* 1973, **2**, 841–854
9   Shimada, S., Marda, M., Hori, Y. and Kashiwabara, H. *Polymer* 1977, **18**, 19–23
10 Kusumoto, N. and Sakai, T. *Polym. Commun.* 1979, **20**, 1175–1177
11 De Vries, K. L., Smith, R. H. and Fanconi, B. M. *Polymer* 1980, **21**, 949–956
12 Wu, C. Y., Wertheimer, M. R., Yelon, A., Boggs, S. A. and Densley, J. Annual Report, Conference on Electrical Insulation and Dielectric Phenomena, Washington, DC, 1978, p. 354
13 Bacquet, G., Dib, J., Wu, C. Y., Wertheimer, M. R., Yelon, A., Densley, J. R. and Boggs, S. A. *IEEE Trans. Elect. Insul.* 1978, **EI13**, 157
14 Dib, J., Dorlanne, O., Wertheimer, M. R., Yelon, A., Bacquet, G. and Densley, J. R. Conf. Record IEEE Int. Symp. on Elect. Insul., 1978, p. 134
15 Dorlanne, O., Wertheimer, M. R., Yelon, A. and Densley, J. R. Annual Report, Conference on Electrical Insulation and Dielectric Phenomena, Washington, DC, 1980, p. 136
16 Janzen, E. G. and Blackburn, B. J. *J. Am. Chem. Soc.* 1969, **91**, 4481–4490
17 Lagercrantz, C. *J. Phys. Chem.* 1971, **15**, 3466–3475
18 Shiotani, M. and Sohma, J. *Polym. J.* 1977, **9**, 283–291
19 Evans, C. A. *Aldrichimica* 1979, **12**, 23–29
20 Sakaguchi, M. and Kashiwabara, H. *J. Polym. Sci., Polym. Lett. Edn.* 1980, **18**, 563–567
21 Kinnell, P. O., Rånby, B. and Runnström-Reio, B. (Eds. 'E.S.R. Application to Polymer Research', Almqvist and Wiksell, Stockholm, 1972
22 Rånby, B. and Rabek, J. F. 'E.s.r. Spectroscopy in Polymer Research', Springer-Verlag, New York, 1977
23 Boyer, R. F. and Keinath, J. E. (Eds.), 'Molecular Motion in Polymers by E.S.R.', Harwood, New York, 1980
24 Bamford, C. H., Jenkins, A. D. and Ward, J. C. *Nature* 1960, **186**, 712–713