E.s.r. studies on free radicals generated in poly[*p*-(2-hydroxyethoxy) benzoic acid] fibres at low temperatures

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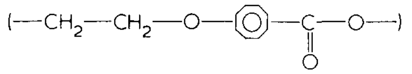
Free radicals generated in stretched and ground poly[*p*-(2-hydroxyethoxy) benzoic acid] (PEOB) were studied by e.s.r. spectroscopy in an effort to isolate those formed by main chain scission. PEOB fibres stretched at −86°C in a dry nitrogen atmosphere gave an asymmetric spectrum, which had patterns characteristic of both phenoxy and peroxy radicals in addition to some unknown peaks. The shape of the spectrum changed with increasing temperatures, finally becoming identical to that of phenoxy radicals at room temperature. The phenoxy radical was observed in all PEOB films ground or γ-irradiated in liquid nitrogen. In some cases a small peak of peroxy radical was observed. Theoretical spectra calculated for possible radical species or combinations of them were compared with those observed. No direct evidence was observed of the formation of alkyl type and radicals which were assumed to be formed with phenoxy radicals upon main chain rupture of PEOB. However, the relatively unstable peroxy radical observed in these experiments is thought to arise from them.

INTRODUCTION

Attempts have recently been made to use modern analytical techniques to correlate the molecular occurrences in a material with the observed macroscopic mechanical properties. These investigations are not only important in resolving the causal molecular events in deformation and fracture, but also provide insights into systematic means by which the mechanical properties might be improved.

E.s.r. spectroscopy is one of the most promising methods in such investigations and has provided valuable information and insight[1-4]. Tensile deformation is a convenient mode of deformation for studying the relationships between molecular events and macroscopic properties, because it is easy to simultaneously monitor free radical formation (chain rupture) and macroscopic mechanical properties. In order to prevent the decay and chemical reactions of radicals formed by chain rupture, it is desirable to stretch polymer samples at low temperatures. Brittle fracture, however, generally occurs when samples are tested well below the glass transition temperature, generating few radicals. Therefore, most e.s.r. studies on radical formation during tensile deformation have been made at or near room temperature, where some polymers generate enough free radicals that are sufficiently stable to produce concentrations detectable by e.s.r. spectroscopy. Molecular chain rupture detected by e.s.r. during tensile deformation has been directly correlated with macroscopic deformation and tensile strength in some of these polymers. One problem associated with such studies has been that the radical species detected were generally secondary radicals, and not the primary radicals produced by rupture of the main chain. This problem was resolved for one polymer by Nagamura *et al.*[5,6] who detected primary phenoxy radicals during tensile deformation of poly[*p*-(2-hydroxyethoxy)benzoic acid] fibres at room temperature. They reported many similarities in the free radical kinetics for this primary radical under various stretching conditions with those of the secondary radicals observed in nylon-6 and other materials as previously reported[8-10]. Furthermore, in some unpublished studies at the University of Utah, in which primary radicals were produced by γ-irradiation or by carefully grinding or slicing various polymers at liquid nitrogen temperature, it was observed that upon warming there was essentially a one-to-one conversion of primary to secondary radicals. These in turn, upon further warming, decayed away with what appeared to be a combination of first and second order kinetics depending on free radical concentration, polymer type and temperature.

Although a phenoxy radical was detected and successfully identified in PEOB, its counterpart (the alkyl-type end radical) which should be formed when homolytic chain scission occurs (judging from the chemical structure PEOB)



$(\!-\!CH_2\!-\!CH_2\!-\!O\!-\!C_6H_4\!-\!C(=O)\!-\!O\!-\!)$

has not been detected in previous experiments undertaken at room temperature[5-7]. Alkyl-type end radicals are highly reactive and have only been observed below about −138 C[11]. These results might be interpreted as suggesting that alkyl-type end radicals, formed at room temperature, decay immediately by reactions with impurities (e.g. oxygen), other polymer chains or recombination[5].

In the present study, the straining of the PEOB fibres and simultaneous detection of generated radicals were performed at low temperatures in an attempt to freeze in or capture for detection the alkyl-type end radical. The

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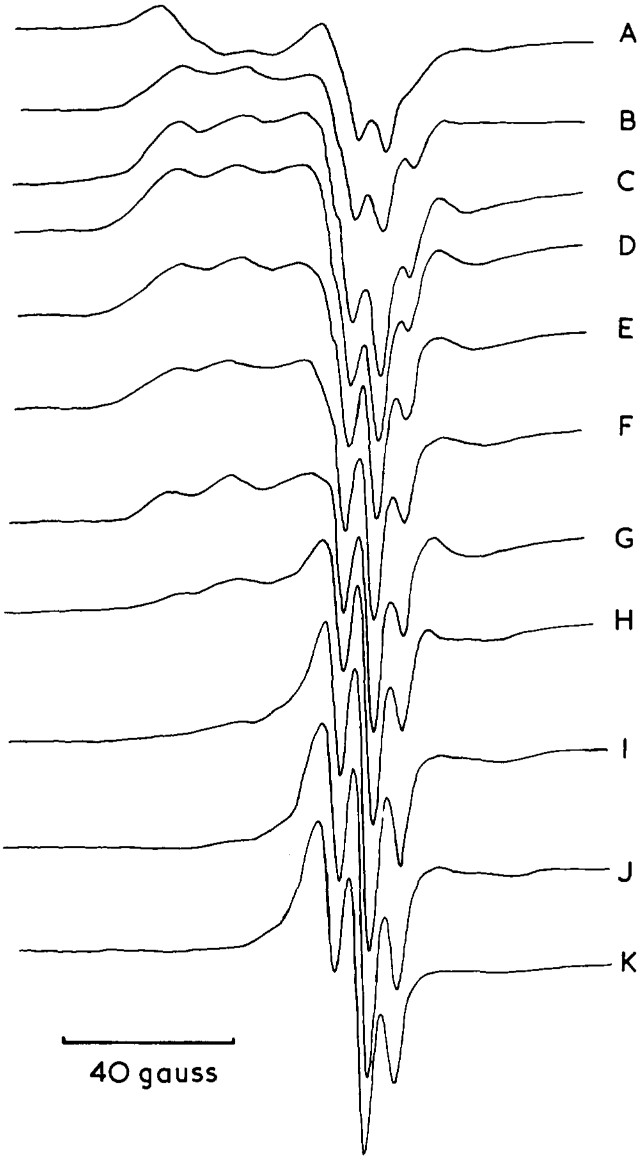


Figure 1 E.s.r. spectrum observed during stretching PEOB fibres at −86°C in nitrogen gas and the subsequent spectral changes with increasing temperatures and times. A, Taken immediately after stretching to 16.1% strain; B, taken 10 min later; C, taken immediately after further stretching to 18.1% total strain; D, 5 min later. E to K were taken after maintaining the sample for 5 min at the following temperatures: (ϵ = 18.1% for all tests) E, −68;; F, −59; G, −50; H, −32; I, −14; J, +4; and K, +20.5°C. The sensitivity of the spectrometer was the same for all cases

radicals were produced by both mechanical degradation (by tensile fracture and grinding) and γ-irradiation at cryogenic temperatures.

EXPERIMENTAL

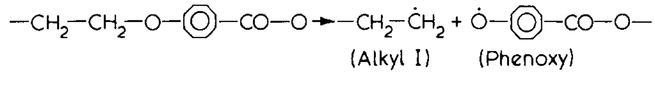
The PEOB used in this experiment was the same as that previously reported[5–7] and was supplied by Professor M. Takayanagi of Kyushu University, Japan, in a form of multifilaments (yarns) of 90.2 d/24 fil. A bundle of 200 multifilaments was prepared with great care according to the procedure previously reported[5–7], to avoid macroscopic length distributions. Each bundle was stretched in the microwave cavity of a Varian E-3 e.s.r. spectrometer (X-band, 100 kHz magnetic field modulation) in a nitrogen atmosphere at several temperatures. All measurements were made at low microwave power (1.25 mW) to avoid power saturation effects. A suitably modified Varian E-4557/E-9540 variable temperature accessory and controller was employed to control the temperature to within ±1°C. The deformation was controlled by a servo-controlled hydraulic loading system and frame constructed about the cavity–magnet assembly (detailed description, ref 12). The PEOB pellets were compression-moulded in a laboratory press at 260°C and quenched in water to form a film. For the grinding experiments this film was ground under liquid nitrogen using a dental burr. The powder produced was then transferred into a quartz e.s.r. sample tube. The liquid nitrogen was removed by evacuation while the part of the tube containing the powder remained immersed in liquid nitrogen and the sample tube was sealed. For the irradiation experiments, the compression-moulded films or fibres were sealed in a glass tube evacuated to high vacuum and irradiated at −196°C with γ-rays from a ^{60}Co source. The e.s.r. measurements were made at ∼ −150°C for both series of experiments.

RESULTS AND DISCUSSION

The e.s.r. spectrum obtained by stretching PEOB fibres at −86°C in nitrogen gas and the subsequent spectral changes after annealing at various temperatures and times are shown in *Figure 1*. Although tensile deformation at −100°C was tried, it resulted in a brittle fracture and the production of few radicals. It was possible to stretch PEOB fibres up to 18% strain at −86°C without observable macroscopic fracture. Spectrum A, taken immediately after stretching to 16.1% strain, is highly asymmetric and has the characteristic spectrum of a peroxy radical (peak at the lowest magnetic field), superimposed with peaks corresponding to a phenoxy radical. The shift of the lowest magnetic field peak to the higher side and the increase of the second lowest peak with time shown in spectrum B can be attributed to the partial averaging of the g tensor of the peroxy radical caused by the local motion of polymer chains. A similar shift of the lowest field peak to a higher side has been reported in spectra of polytetrafluoroethylene peroxy radicals during heating from −196°C to room temperature[13]. Further stretching at −86°C increased the intensity of the whole spectrum as shown in spectrum C, indicative of additional polymer chain rupture. With increasing temperature, the intensity of the peroxy radical signal decreased and that of the phenoxy signal increased as shown in spectra E to K. The peroxy signal seemed to have completely decayed by −14°C. The spectrum observed at room temperature may be attributed almost solely to the phenoxy radical.

The possible radical species and their reactions are assumed to be as follows:

(a) initial chain rupture



(b) reactions of alkyl I radical with PEOB chains

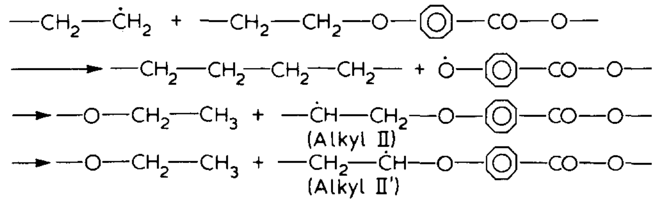


Table 1 g-Values and hyperfine coupling constants of various types of radicals

	g Value			Hyperfine coupling constant (gauss)			
Radical species	g_1	g_2	g_3	α^{α}	α^{β}	α^{β}	Refs.
Phenoxy	2.0023		2.0094	6.8	2.2	–	5.15
Alkyl I	2.0023	–	–	23.0	23.0	46.0	16
Alkyl II, II′	2.0023	–	–	14–26	28		17
Alkyl III	2.0023	–	–	21	23–25		18
Peroxy	2.00385	2.0079	2.0023	–	–	–	13

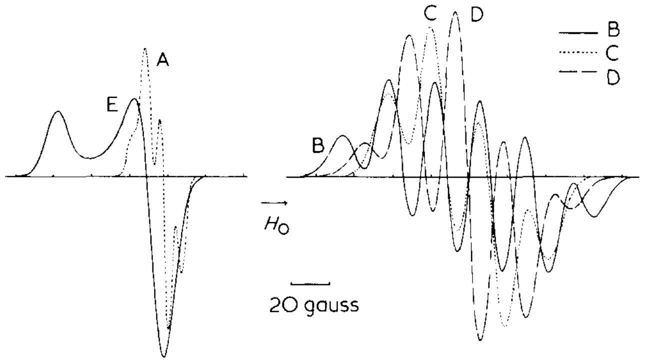


Figure 2 Calculated e.s.r. spectra for: A, phenoxy; B, alkyl I; C, alkyl II; D, alkyl III; and E, peroxy radicals. The line widths of Gaussian component lines are 3.5, 17.0, 17.0, 17.0, and 12.0 gauss, respectively. See text for details

(c) reactions of alkyl I radical with oxygen

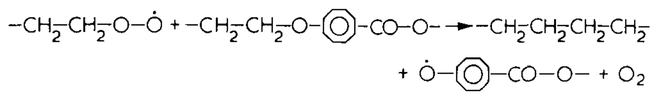
$$—CH_2—\dot{C}H_2 + O_2 \longrightarrow \underset{\text{(Peroxy)}}{—CH_2—CH_2—O—O}$$

(d) radical migration

$$—CH_2—\dot{C}H_2 \longrightarrow \underset{\text{(Alkyl III)}}{—\dot{C}H—CH_3}$$

(e) reactions of alkyl II, II′, III and peroxy radicals

Alkyl II, II′, III + O_2 ⟶ corresponding chain-type peroxy radicals



(f) recombination of phenoxy radicals or reaction of phenoxy radicals with oxygen to form peroxides[5].

The theoretical spectra for these radicals were calculated using a computer with 'known values' of hyperfine splitting constants and g factors as listed in *Table 1*.

The spectrum of phenoxy radicals was calculated by Sands' equation[14] taking into account the axial symmetry of the g tensor as previously reported[5]. An example of a calculated spectrum is shown in *Figure 2A*[5,15]. The alkyl type I radical, $-CH_2-\dot{C}H_2$, has larger splitting constants and is expected to show a sextet pattern with a spectral width of about 80 gauss as shown in *Figure 2B*[16]. The g values for alkyl II, II′ and III radicals are assumed to be equal to 2.0023. The splitting constant of an α proton (a^{α}) of the alkyl type II radical changes in the range of 14–26 gauss according to the relative orientation of p orbital and α proton[17]. The calculated spectra of the alkyl II radical show a quartet pattern similar to that shown in *Figure 2C*. The different values of a^{α} mainly affect the resolution of the quartet spectrum. The alkyl type III radical is expected to have a quintet pattern as shown in *Figure 2D*[18]. Peroxy radicals have anisotropic g values as listed in *Table 1*[13]. The calculation of the spectrum for peroxy radicals was carried out with a Kneubühl's equation taking into account the anisotropy of the g tensor[19]. The calculated spectrum for the peroxy radical is shown in *Figure 2E*.

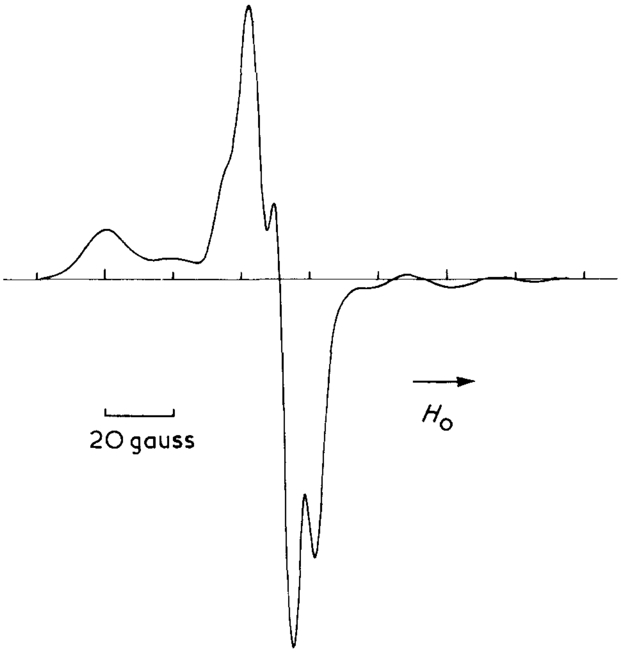


Figure 3 Example of the simulated spectrum obtained with a combination of phenoxy, peroxy, and alkyl I radicals. The fraction of each species is 0.5, 0.25, and 0.25, respectively. The component line widths are the same as those given in *Figure 2*

Spectral simulations of observed e.s.r. spectra shown in *Figure 1* were tried on the basis of a few hundred combinations of these possible radical species. We were not successful in completely reproducing the entirety of the spectra with these simulations. An example of these calculated spectra is shown in *Figure 3*. The lowest magnetic field peak is unambiguously attributed to peroxy radicals. Although no direct indication of the alkyl type I end radical which should be generated upon the initial chain rupture could be obtained, the coexistence of phenoxy radicals and relatively unstable peroxy radicals suggests that the reactive alkyl-type I end radical generated reacts with oxygen to form these peroxy radicals. It has been found that it is almost impossible to exclude small amounts of oxygen from the system since it is

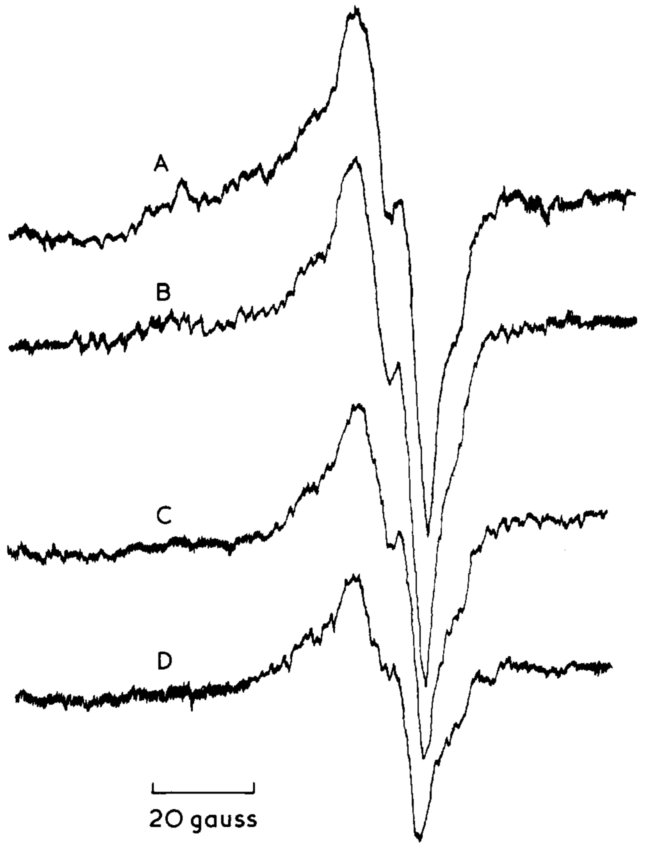


Figure 4 E.s.r. spectrum observed in a PEOB film ground in liquid nitrogen. All spectra were measured at −140°C under the same conditions. The sample was kept at the following temperatures for 5 min. A, −140; B, −100; C, −50; and D, 0°C

present to some extent in commercial pure nitrogen and/or dissolved in the polymer.

The radical formation behaviour during the mechanical degradation and during γ-irradiation of PEOB films and fibres at liquid nitrogen temperature was studied to obtain further information on radical species. The PEOB film ground in the liquid nitrogen gave e.s.r. spectra as shown in *Figure 4*. It appears that the spectrum recorded at −150°C consisted mostly of phenoxy radicals with an additional peak at the lower end of the magnetic field. Heat treatment of the sample at higher temperatures increased the symmetry as shown in *Figure 4*. (The e.s.r. spectra were recorded at −150°C in all cases after annealing at the temperatures and times indicated.) These results suggest that the peroxy radical contributing to the asymmetry rapidly decays with increasing temperature.

The e.s.r. spectra observed in a γ-irradiated PEOB film at liquid nitrogen temperature and the resulting spectral changes with annealing are shown in *Figure 5*. Again, all spectra were recorded at −150°C. Similar spectra were observed for a γ-irradiated PEOB fibre. The spectra observed at −150°C can be attributed primarily to phenoxy radicals but superimposed with a small amount of peroxy radicals. The resolution of the spectrum is relatively poor due to hindered molecular motions. Taking the spectra at higher temperatures may have resulted in some molecular motional narrowing of the spectra as discussed by Ovenall[21] and Iwasaki[21] for fluorine-containing polymers. The spectra here were taken at −150°C to provide a much more reliable comparison with the data on samples 'kept' at the lower temperatures. The peroxy radicals decayed completely between −50° and 0°C as indicated in *Figure 5* by the disappearance of the lowest magnetic field peak.

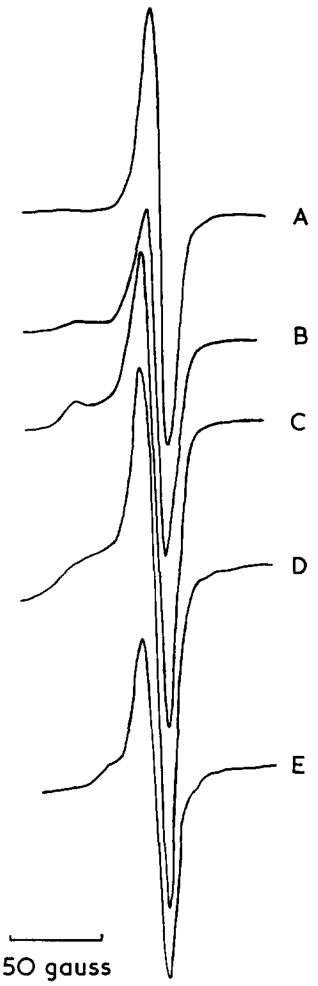


Figure 5 E.s.r. spectra observed in a PEOB film irradiated by γ-rays to 3×10^6 rad at −196°C in evacuated sealed tubes. All spectra were measured at −150°C. The sample was kept at the following temperatures for 5 min. A, −150; B, −100; C, −50; D, 0, and E, +30°C. The relative sensitivity of the spectrometer is 1 for A and B, 4 for C, and 20 for D and E

In conclusion, despite rather extensive efforts, we have been unable to detect alkyl-type radicals, even in samples that were mechanically degraded or γ-irradiated at liquid nitrogen temperature. We attributed this as being due to the rapid reaction of alkyl end radicals with PEOB chain or with small amounts of oxygen remaining in the e.s.r. sample tube or dissolved in the polymers, or the recombinations of these highly reactive radicals at temperatures as low as −150°C. Therefore, although the generation of alkyl-type I end radicals which should be formed by the chain rupture at the ether linkage of a PEOB molecule could not be conclusively demonstrated by this study, there is strong evidence from which its existence can be inferred. The peroxy radical that is detected in conjunction with the phenoxy radical was found to be highly reactive, even at cryogenic temperatures, and is most probably formed from this alkyl-type I radical.

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