

# Ionic products from the mechanical fracture of solid polypropylene

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When polypropylene was fractured with tetracyanoethylene (TCNE) in the dark *in vacuo* at 77 K, the TCNE anion radical, TCNE<sup>-</sup> was detected (using e.s.r. methods). The TCNE<sup>-</sup> is produced by the attraction of an electron by TCNE from an anion arising from the mechanical fracture of solid polypropylene. This is presumably by 'heterogeneous scission' of main-chain carbon-carbon bonds in the polymer. Free radicals of the chain-end type arising from the mechanical fracture of solid polypropylene are also produced by 'homogeneous scission'. At least 37% of scission occurs by the heterogeneous process.

**(Keywords: anion; fracture; heterogeneous scission; polypropylene; electron spin resonance; tetracyanoethylene)**

## INTRODUCTION

As destruction of polymeric materials is important for practical purposes, many investigations on fracture phenomena in polymers have been carried out from experimental as well as from theoretical points of view. It is well known that e.s.r. spectroscopy is a sensitive detector of free radicals or unpaired electrons. E.s.r. spectroscopy thus provides a powerful experimental technique enabling the study of free radicals in fractured polymers, and a great amount of information on free radicals can be obtained by the analysis of e.s.r. spectra; such as the identification of radical species<sup>1-8</sup>; radical conversions<sup>9</sup>; the decay of radicals<sup>10</sup>; the copolymerization of radicals<sup>11,12</sup>; and the mobility of radicals<sup>13-15</sup>. The species of free radical produced by mechanical fracture of polypropylene<sup>8</sup>, poly(methyl methacrylate)<sup>7</sup>, and polytetrafluorethylene<sup>8</sup> were identified with 'chain-end' type radicals, which were produced by the rupture of the main-chain.

Chain-end type radicals are produced by the homogeneous scission of main-chain carbon-carbon bonds. The ionic species produced by heterogeneous scission cannot normally be detected by e.s.r. spectroscopy. In this paper we report a technique for converting anionic species to anion radicals which are detectable by e.s.r., and it is shown that anions are produced in the mechanical fracture of polypropylene.

## EXPERIMENTAL

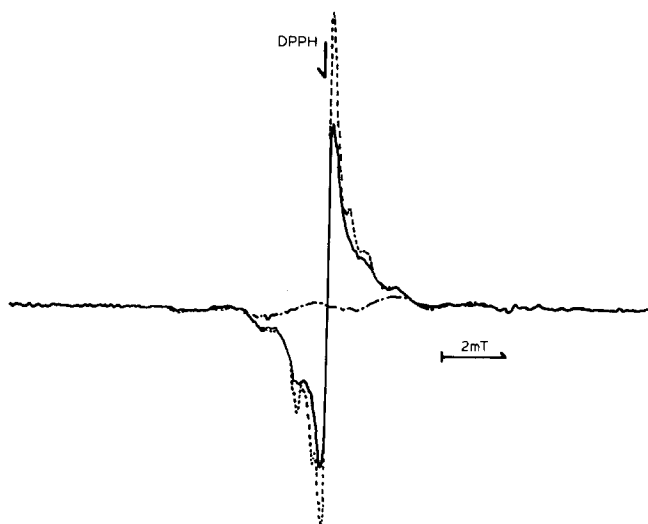
Isotactic polypropylene, (PP), was supplied by Mitsubishi Petrochemical Co. Ltd. The polymer samples were dissolved in hot toluene, filtered, washed with acetone, and dried under reduced pressure. This procedure was

repeated three times. The samples were then dried *in vacuo* for two days. The viscosity average  $M_w$  was  $4.0 \times 10^5$ . *n*-Dotoriacontane, C<sub>32</sub>, (Tokyo Kasei Co.) was used without purification. Tetracyanoethylene, TCNE, (Katayama Chemical Co.) was purified by sublimation at 353 K *in vacuo*. Polymer samples were fractured in the dark at 77 K for 21 h by the glass ball-mill method<sup>5</sup>. All samples were observed in the dark, at 77 K by e.s.r. spectrometry (with 100 kHz modulation). E.s.r. spectra were observed at 2  $\mu$ W to avoid power saturation. Subsequent photo-irradiation of samples was carried out at 77 K with a filtered infrared lamp (Toshiba 125 WRH lamp, Toshiba IRP 70 filter; 400 nm <  $\lambda$  < 800 nm). DPPH was used to calibrate the e.s.r. signal positions.

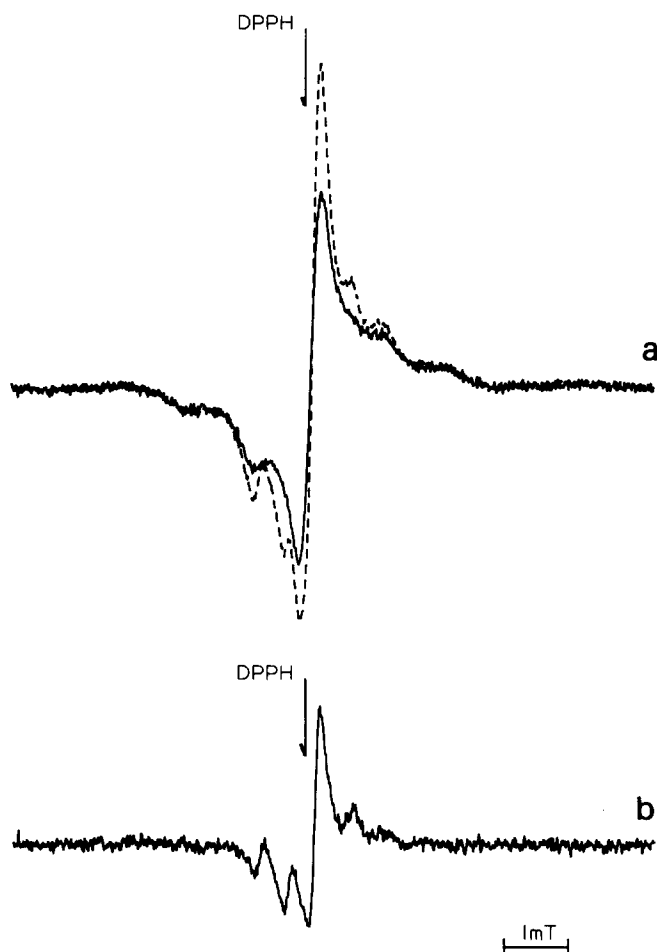
## RESULTS AND DISCUSSION

The PP flake (1.5 g) was fractured in the dark *in vacuo* at 77 K for 21 h by the glass ball-mill method<sup>8</sup>. *Figure 1(a)* shows three e.s.r. spectra. Polypropylene (PP) fractured in the dark, *in vacuo* at 77 K shows the characteristic pattern of free radicals (chain-end type) produced by the homogeneous scission of the main-chain PP. When PP flake (1.5 g) was fractured with TCNE a sharp and a strong signal was produced which was superimposed on the broad signal due to the free radicals produced by homogeneous scission. (This sharp signal was saturated over 2  $\mu$ W). Photo-irradiation of the PP fractured with TCNE, significantly enhanced the sharp signal.

The e.s.r. spectrum in *Figure 1(b)* was produced by computer subtraction of the solid line (—) e.s.r. spectrum from the broken line (---) e.s.r. spectrum in *Figure 1(a)*. The hyperfine coupling constant (0.51 mT) and *g* value (2.0031) of the subtracted spectrum, are



**Figure 1(a)** E.s.r. spectra for polypropylene (all e.s.r. spectra are observed at 77 K and at 2  $\mu$ W. (---) E.s.r. spectrum from the fractured polypropylene; (—) e.s.r. spectrum from the polypropylene fractured with tetracyanoethylene; (-·-·-) e.s.r. spectrum following photoirradiation for 20 min of the polypropylene fractured with tetracyanoethylene



**Figure 1(b)** E.s.r. spectrum obtained by subtracting (—) from (---) shown in (a)

similar to those for  $\text{TCNE}^-$  reported by Watts *et al.*<sup>16</sup>, Kasai<sup>17</sup> and Symons *et al.*<sup>18</sup>). In this way the subtracted e.s.r. spectrum and the sharp signal on the e.s.r. spectrum of the PP fractured with TCNE are due to  $\text{TCNE}^-$ .

Blank experiments with unfractured PP showed that photo irradiation alone, did not produce radicals (by

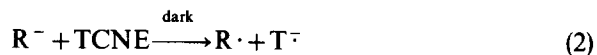
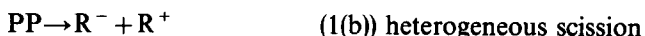
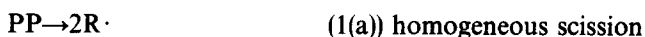
homogeneous scission) or ions by heterogeneous scission. Samples of dotriacontane ( $\text{C}_{32}$ ) fractured, both with and without TCNE powder failed to give any e.s.r. signals. It can be concluded that the presence of TCNE and carbon-carbon bond scission in a reaction system are required to produce the  $\text{TCNE}^-$ .

Since TCNE has a large electron affinity (2.88 eV)<sup>19</sup>, it is probable that TCNE attracts an electron from an anion and produces  $\text{TCNE}^-$ . Therefore, we conclude that the TCNE, in the system of PP fractured with TCNE, attracted an electron from the anion which was produced by the heterogeneous scission of main-chain bonds in PP during the mechanical fracture process.

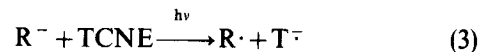
It must be emphasized that the  $\text{TCNE}^-$  is produced by the reaction even in the dark. But the yield is significantly enhanced by photoirradiation by an unknown mechanism. One can speculate that the different types of anion may react spontaneously with TCNE in the dark, whilst buried anions may be brought to the surface by a photo-chemical process.

An estimate of the minimum fraction of scission occurring by heterogeneous scission can be obtained from the e.s.r. spectra as follows. Assuming that all the anions react only with TCNE, the following mechanism describes the overall process:

During milling in the dark



In photo-irradiation state



where  $\text{T}^-$  is  $\text{TCNE}^-$ . Both types of scission ultimately give 2 radicals, so taking  $R_1$ ,  $R_2$  and  $R_3$  as the free radical yields from homogeneous; heterogeneous followed by (2); and heterogeneous followed by (3) scission reactions respectively,  $T_2$  and  $T_3$  as the anion yields from heterogeneous followed by (2) and (3) scission reactions respectively, then the ratio of the total radical concentrations after and before photo-irradiation is given by the area ratio of the total e.s.r. signal after and before irradiation,  $A$ ,

$$A = (R_1 + R_2 + R_3)/(R_1 + R_2) \quad (i)$$

Taking the ratio of the concentration of  $\text{T}^-$  before and after photoirradiation as the ratio of the heights of the sharp peak due to  $\text{T}^-$  in the e.s.r. spectrum,  $B$ ,

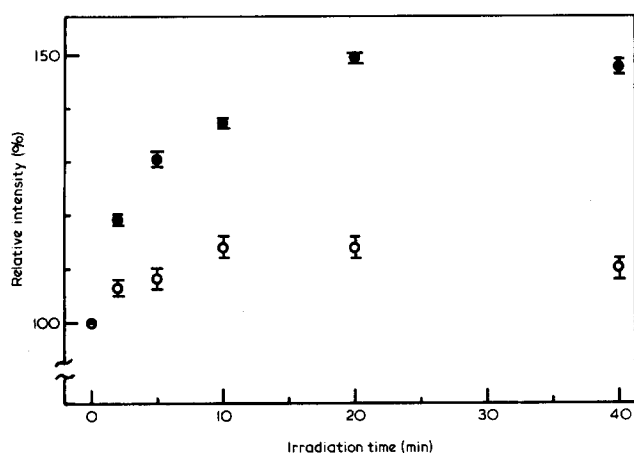
$$B = (T_2 + T_3)/T_2 = (R_2 + R_3)/R_2 \quad (ii)$$

the fraction of heterogeneous scission occurring,  $P$ , according to the mechanism given can easily be calculated from  $A$  to  $B$ :

$$P = \frac{R_2 + R_3}{R_1 + R_2 + R_3} = \frac{B(A - 1)}{A(B - 1)} \quad (iii)$$

Values of  $A$  and  $B$  reach an equilibrium state after 20 min photoirradiation, (see Figure 2), i.e.,  $A = 1.14$ ,  $B = 1.49$ . From (iii)  $P = 0.37$ .

Obviously anions produced by heterogeneous scission may not all react with TCNE or indeed they may react in



**Figure 2** Effect of irradiation time relative intensity. (○) Relative intensity from double integration of the e.s.r. spectrum arising from the polypropylene fractured with tetracyanoethylene versus time of the photoirradiation. (●) Relative intensity from the peak height of the centre peak due to the tetracyanoethylene anion radical on the same e.s.r. spectrum as that used for the acquisition of the value for the corresponding open circle

some other way. The value of  $P$  therefore, can only be regarded as a minimum value;  $P > 0.37$ .

## CONCLUSION

It has been found that both free radicals (chain-end type) and anions are produced by the mechanical fracture of solid polypropylene (by homogeneous and heterogeneous scission respectively, of main-chain carbon-carbon bonds

of polypropylene). It has not been possible to detect the cations produced in the heterogeneous scission.

The fraction of scission which occurs by the heterogeneous reaction is at least 0.37. This heterogeneous scission may be an origin of triboelectricity in polypropylene.

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