E.s.r. study of the motion of spin trapped radicals in polyethylene in relation to the morphological changes induced by ball-milling

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INTRODUCTION

Mechanoradicals produced by the mechanical destruction of polymeric materials exhibit some unique and interesting properties[1-4]. However, these mechanoradicals are thermally unstable, and thus they are not suitable for high temperature studies. Nitroxide radicals are known to be stable at high temperature and they give simple, well-resolved, electron spin resonance spectra. Bullock *et al.*[5] successfully applied the spin label method to the study of polymers by the chemical binding of stable nitroxide radicals to the polymer chains.

The technique of spin trapping[6,7] in which the trapping of reactive free radicals by nitroxide compounds is carried out by an addition reaction to produce more stable radicals detectable by e.s.r. has previously been reported.

The technique had been applied to stabilize short-lived alkyl radicals produced from milling polyethylene powder into a stable nitroxide radical[8]: CH_3–$CH(\dot{N}O\phi)$–CH_2– ~. This suggests that the spin-trapping technique is a useful tool for the study of molecular motion at high temperatures. Furthermore, the special property of the mechanoradical which makes this study more attractive is that the mechanoradicals are only trapped on the fractured surface[1,3,9]. Therefore, the behaviour of the molecules on the surface can be exclusively examined.

However, X-ray diffraction spectra[10-13] and i.r. spectroscopic spectra[14] have shown that the plastic deformation of polyethylene produces a phase transformation in the crystal structure of polyethylene from the normal orthorhombic to the monoclinic phase. In a related study, Yemni and McCullough[15], working on energies of phase transformation in polyethylene, found the monoclinic phase to be energetically more stable than the orthorhombic phase. Tadokoro[16], using a different analytical approach, also reached the same conclusion.

Recently, Kurokawa and Sohma[17] reported the orthorhombic to monoclinic phase transformation induced by ball-milling. However, the method used in their data analysis from X-ray diffraction spectra was not clearly described.

There we report e.s.r. measurements of the effects of the ball-milling of polyethylene powder on its morphology, especially crystallinity and the orthorhombic to monoclinic phase transition, and their consequences with regard to the molecular motion of a spin-trapped radicals located on the fractured surface of the sample.

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EXPERIMENTAL

Characterization data for the polyethylene samples used are shown in *Table 1*. Nitrosobenzene was used as spin-trapping reagent, after purification by sublimation at room temperature under vacuum and trapping by liquid nitrogen.

The mixture of polyethylene and nitrosobenzene was milled as described elsewhere[8]. The excess nitrosobenzene after milling was eliminated by evacuation of the sample with a diffusion pump for more than 10 h.

E.s.r. spectra were obtained using a Jeol ME 3 e.s.r. spectrometer using an X-band.

X-ray measurement was carried out on an X-ray diffractometer model D-3F (Rigaku Denki Co.) using Ni-filtered CuKα radiation.

The crystallinity calculation from the X-ray diffraction spectra was based on the method of Mathew[18]. Shape analysis of the X-ray diffraction spectra was performed on a FACOM M-200 computer at Nagoya University Computer Center using a non-linear least-mean-squares program described elsewhere[19].

Density measurement was carried out with a specially designed pycnometer which permitted the addition of methanol as reference to a polyethylene powder sample under vacuum after thorough evacuation of the polyethylene sample.

RESULTS AND DISCUSSION

Effects of milling on the morphology of polyethylene

When PE Hz powder was subjected to milling at liquid nitrogen temperature, a change in the crystal structure of the lamellae occurred, as seen in the X-ray diffraction spectra taken after various milling times (*Figure 1*). The spectrum of the original sample consisted of two prominent peaks with a shoulder at the lower reflection angle; after milling, the intensity of the two original peaks decreases and two new peaks appear. After 23 h of milling,

Table 1 Characterization data for polyethylene samples

	$M_n \times 10^4$	$M_{vv} \times 10^4$	Crystallinity† (%)
Hizex Million PE Hz)		260*	76
Sholex 6050 (PE SI)	1.25	8.11(3.7*)	85
Sumikasen (PE Sk)	3.08	91.1	66

* Measured by viscometry, other samples by g.p.c.
† From X-ray diffraction spectra

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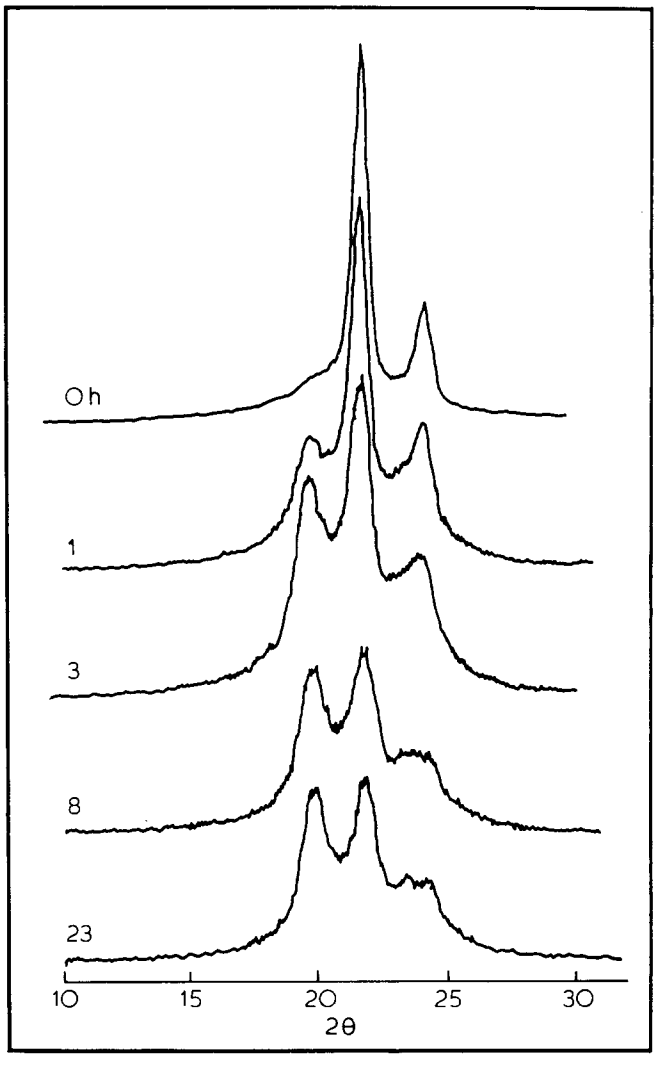

Figure 1 X-ray diffraction spectra of PE Hz observed after various milling times

the X-ray spectrum consists of four instead of two peaks. This indicates a change in the crystal structure of the polyethylene sample.

Analysis of the X-ray spectra by decomposition into components shows that the spectrum of the original sample consists of three components with peak positions centred at 2θ equal to 19.92°, 21.66° and 24.08° which correspond to the reflection from the amorphous region, (110) and (200) planes of the orthorhombic unit cell, respectively (*Figure 2a*)[18]. As seen in *Figure 1*, the spectrum of the milled sample consists of four components centred at 2θ equal to 19.75°, 21.66°, 23.19° and 24.08°. The new peaks at 19.75° and 23.19° are the reflections from the (001) and (200) planes of the monoclinic unit cell, respectively[12,13]. The reported values of the peak positions in literature[13] for the monoclinic (001) and (200) planes are 19.50° and 23.12°, respectively. The latter value is in excellent agreement with our result, but the former is slightly different. Because of the proximity of their positions, the monoclinic (001) peak convolutes the amorphous peak as can be seen in *Figure 1*. Besides causing the phase transformation, milling also damaged the lamellae and caused a decrease in the crystallinity of sample. Because of the convolution of the amorphous and the monoclinic peaks, we cannot calculate the crystallinity from the X-ray spectrum of the milled sample using Mathew's method.

Therefore, in order to estimate the crystallinity and the ratio of the monoclinic to orthorhombic phase in the sample, the density of polyethylene sample was measured. The densities of orthorhombic, monoclinic, and amorphous polyethylene are 1.000, 0.997[13] and 0.855, respectively. However, to calculate the crystallinity the densities of the monoclinic and orthorhombic polyethylene were assumed to be equal to 1.000. The crystallinity of the original sample obtained from density data was in good agreement with that obtained from the X-ray diffraction spectrum using Mathew's method.

If the amorphous content obtained from the density measurement is subtracted from the peak area of the observed X-ray spectrum for the milled sample, then the resultant spectrum can be decomposed into four components with peak positions centred at 2θ equal to 19.50°, 21.66°, 23.19°, and 24.08°: as shown in *Figure 2b*; hence, the amount of the orthorhombic and monoclinic phase can be calculated from the respective peak areas. *Figure 2b* also shows that the calculated spectrum fits well with that observed.

Figure 3 is the plot of crystallinity vs. milling time. It shows that while crystallinity decreases quickly from the original value of about 73% and then gradually levels off to a constant value of about 43%, the amount of the monoclinic phase, in a similar manner, increases from zero to about 12%.

For the PE S1 sample, ball-milling also produced the same phase transformation as for PE Hz as shown in *Figure 4*. The monoclinic phase produced by ball-milling disappeared completely after annealing the milled sample near the melting point as shown in *Figure 4*.

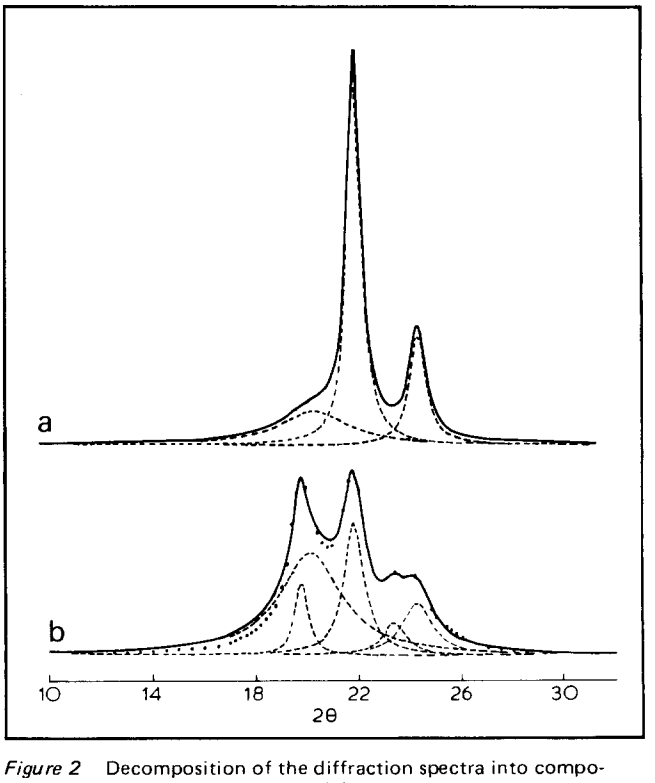

Figure 2 Decomposition of the diffraction spectra into components. (a) Original PE Hz sample; (b) sample after milling for 23 h

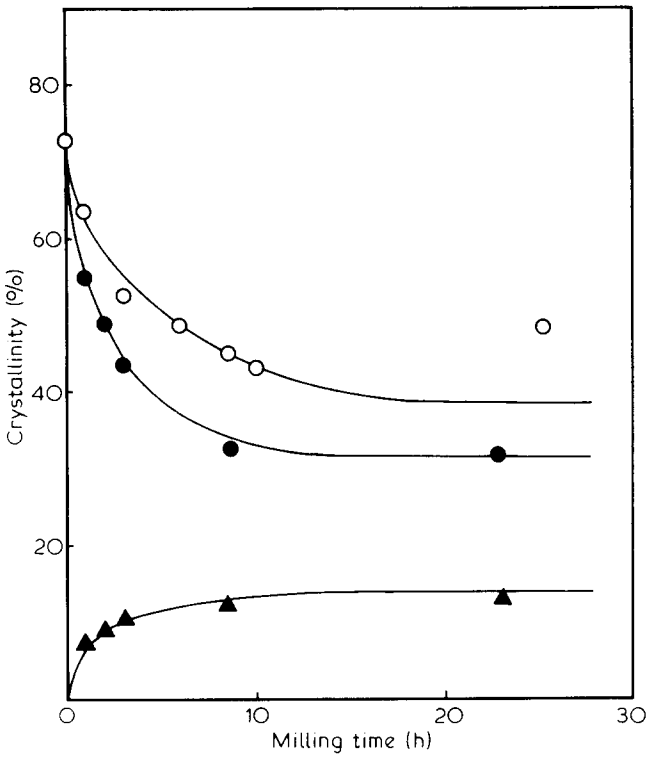

Figure 3 Variation of crystallinity as a function of milling-time. ○, Crystallinity; ●, orthorhombic phase; ▲, monoclinic phase

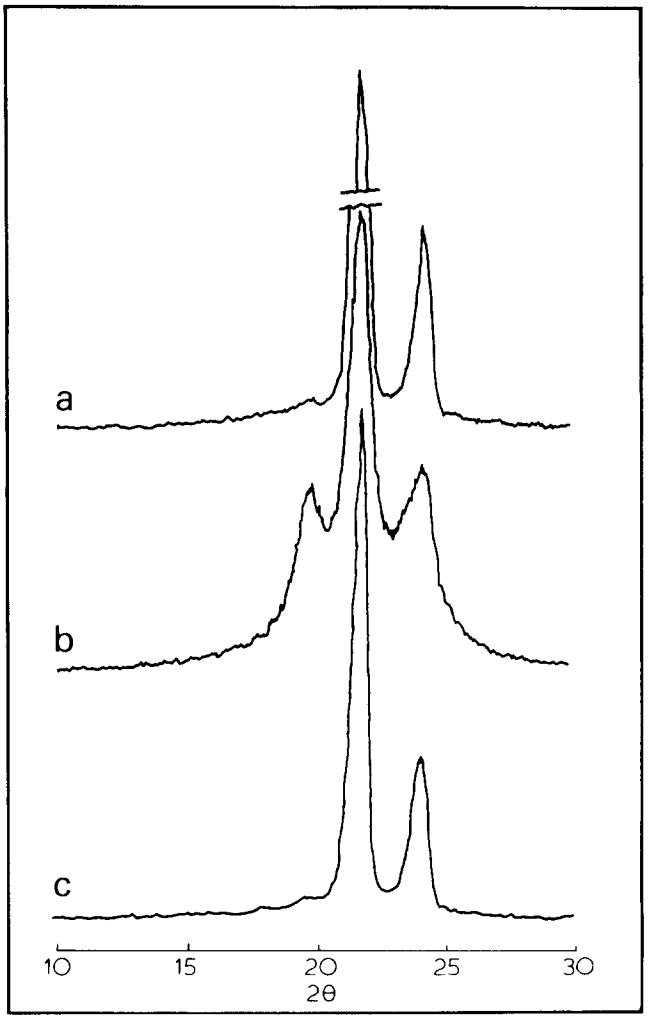

Figure 4 Effect of annealing on the crystal structure of milled PE SI sample observed from X-ray diffraction. (a) Original sample; (b) after 21 h milling; (c) annealing at 120°C for 50 h

Although the fracturing was carried out at a low temperature (77 K), and the fracture is thought to brittle, the above results indicate that even at this low temperature, the milling of polyethylene involves a large amount of distortion and destruction of the lamellae similar to a high temperature plastic deformation.

There are two schools of thought concerning the site of the ruptured chain caused by the mechanical treatment. Some authors[1-3] have suggested that chain scission occurs mostly at the tie molecules in the intercrystalline region. Others[4] have suggested that it also involves the scission of the chains within the lamellae (crystalline region). Our X-ray diffraction and e.s.r. measurements seem to indicate that the chain rupture for a severely milled polyethylene sample at 77 K occurs at both the amorphous (intercrystalline) and the crystalline regions, in a similar manner to plastic deformation (see below). The mechanoradicals thus produced are trapped on the fracture surface near the amorphous and crystalline regions.

Molecular motion of spin-trapped radicals from morphological changes of polyethylene

Figure 5 shows e.s.r. spectra obtained from the spin-trapped radical $CH_3\dot{C}H(\dot{N}O\varphi)$–$CH_2$–~, (identified in a previous paper[8]) observed at various temperatures. *Figure 6* shows the relationship between the extrema separation (W) and observation temperature for PE Hz samples with different milling times. The narrowing curve shifts to higher temperatures with increasing milling time, but above 10 h is almost independent of milling time.

From the extrema separation W, rotational correlation time (τ_c) in the slow motion region was calculated using Freed's equation for jump diffusion[20,21]:

$$\tau_c = a(1-S)^b \qquad (1)$$

where $S = WW/W'$ and W' is the rigid limiting value of the extrema separation. a and b are numerical constants. The values used are $a = 1.10 \times 10^{-9}$, and $b = -1.01$. *Figure 7* shows the plot of τ_c for the spin-trapped radical against the $1/T$; a break point is clearly identified. This implies different motions for the low and high temperature regions. A later paper will discuss this effect.

Table 2 shows that τ_c at 30 C (chosen arbitrarily) increases with the content of monoclinic phase as well as with the amorphous content of the sample.

In order to identify the effects of increasing the amorphous and monoclinic phases on the molecular motion of the spin-trapped radicals, two different polyethylene samples, PE S1 and PESk with crystallinities of 85% and 66% were milled with a lower tumbling frequency so that the phase transformation and the decrease in crystallinity occurred only slightly. Although the crystallinities of each sample decrease from 85% and 66% to 79% and 63%, respectively, we did not observe any significant changes in the X-ray diffraction spectra of the milled samples. Thus,

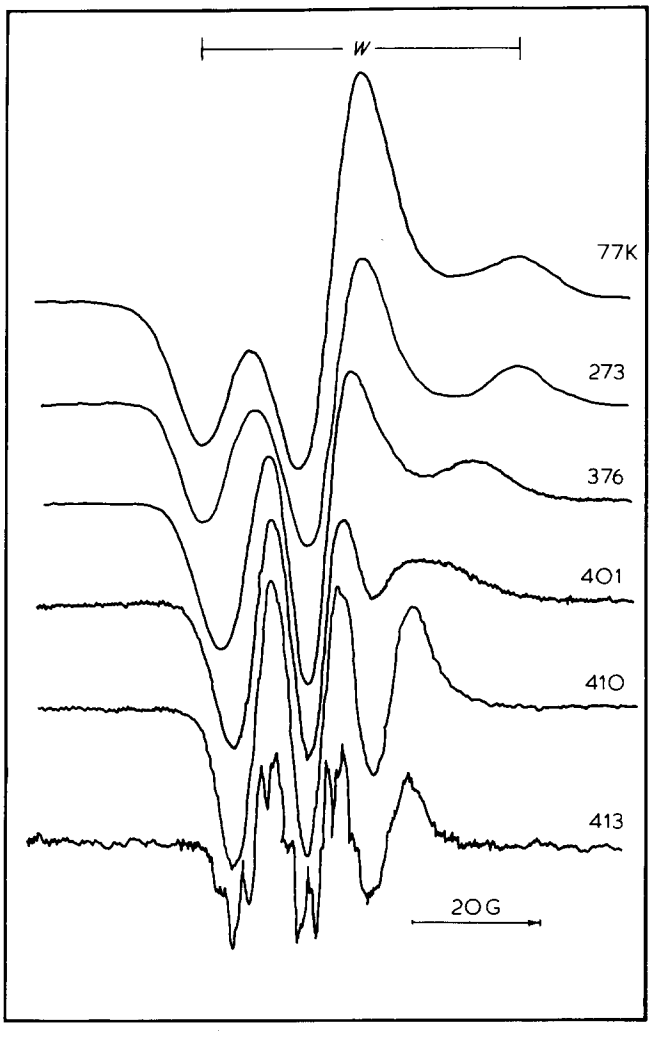

Figure 5 E.s.r. spectra of PE Hz sample observed at various temperatures

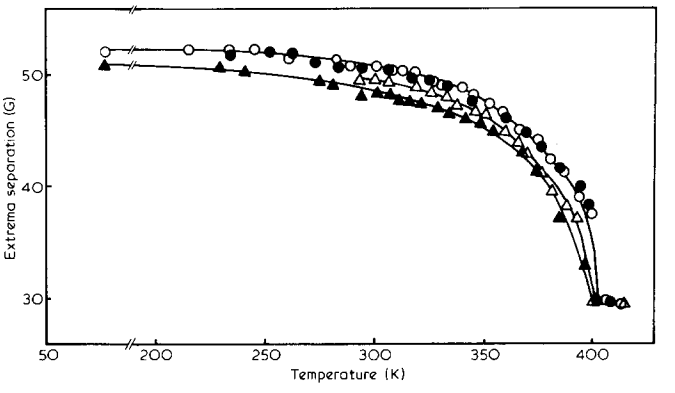

Figure 6 Variation of extrema separation with observed temperature for PE Hz samples with different milling times. ▲, 1 h; △, 4 h; ●, 10 h; ○, 25 h

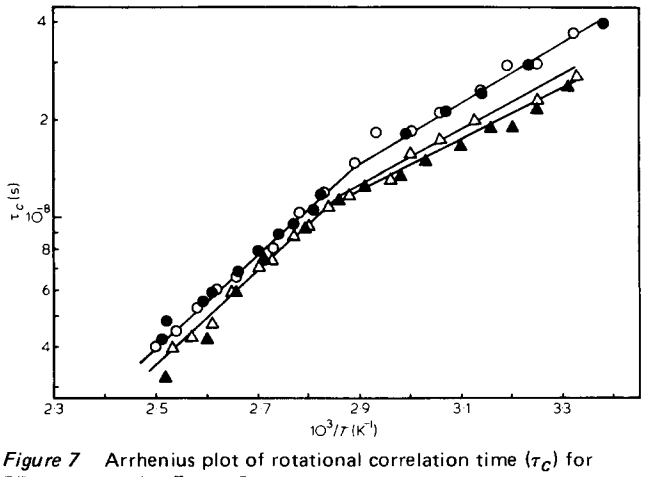

Figure 7 Arrhenius plot of rotational correlation time (τ_C) for PE Hz; key as for *Figure 6*

Table 2 Milling time and crystallinity dependence of rotational correlation time of spin trapped radical

Hixez Million				
Milling Time (h)	Orthorhombic (%)	Monoclinic (%)	Amorphous (%)	τ_C at 30°C ($\times 10^{-8}$ s)
0	73.4	–	26.4	
1	54.8	7.65	37.6	2.4
4	40.0	10.0	50.0	2.8
10	32.0	12.4	56.0	3.4
23	31.1	12.4	56.5	3.4
Sholex 6050 (high density)	79.0	–	21.0	2.5
Sumikasen (low density)	63.0	–	37.0	1.05

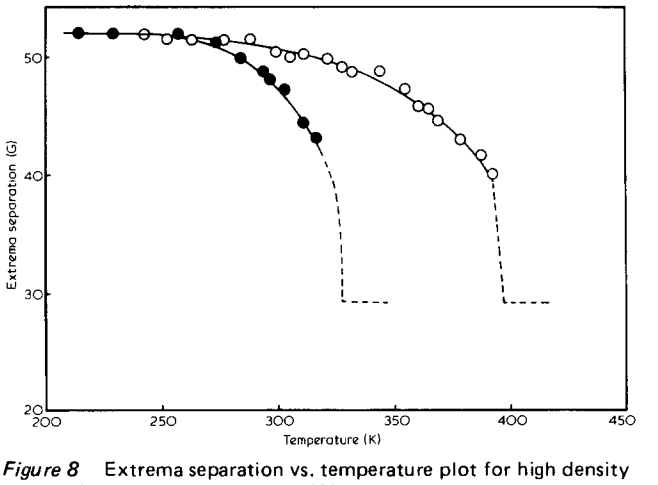

Figure 8 Extrema separation vs. temperature plot for high density PE SI (○) and low density PE Sk (●) showing the influence of amorphous content

the occurrence of the monoclinic phase is minimized. It appears that the curve narrowing of PE S1 tends to lower temperatures and that its τ_c at any temperature is smaller than that of PE Sk as shown in *Figures 8* and *9*, respectively.

Thus it seems that the increase in the amorphous phase content causes the curve narrowing to shift to lower temperatures, and the shortening of τ_c for spin-trapped radicals in the milled polyethylene sample. Therefore the increase in τ_c appears to be associated with an increase in the amount of monoclinic phase.

This can be explained if we assume that ball-milling produces the scission of molecular chains in the intercrystalline as well as the crystalline region, and because the tie chain at the intercrystalline region is the weakest

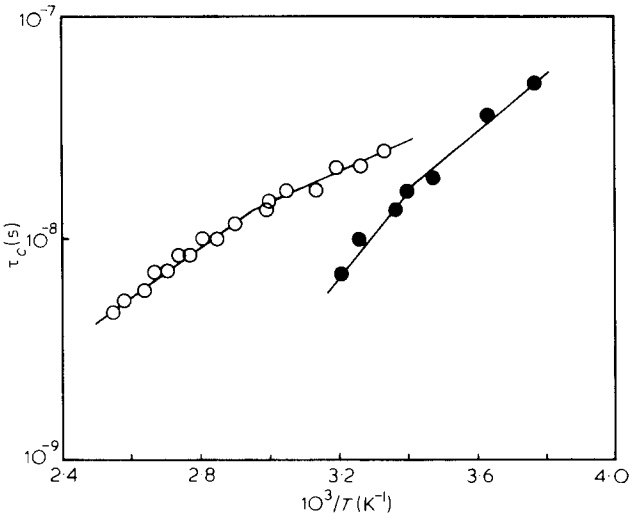

Figure 9 Arrhenius plot of rotational correlation time (τ_c) for PE SI and PE Sk; key as for *Figure 8*

link, it will break first to produce the mechanoradical on the amorphous surface. For the chain in the lamella to rupture, the crystalline structure must first be distorted from orthorhombic to monoclinic; rupture of the chain follows upon further milling to produce another kind of mechanoradical near the crystalline surface with a monoclinic structure. It is known that the motion of the chain in the crystalline region is slower than in the amorphous region due to its more ordered arrangement. This should affect the motion of the spin-trapped radical on different surfaces in a similar manner. Therefore, longer milling times produce a larger proportion of mechanoradicals on the monoclinic crystal surface (which is less mobile than the mechanoradical on the amorphous surface) and hence, a larger τ_c.

We have established that the spin trapping technique can be applied to the study of molecular motion of a spin trapped radical on a polymer surface. It was found that milling of polyethylene powder at 77K caused a large amount of orthorhombic to monoclinic phase transformation and a reduction in crystallinity, both of which affected the molecular motion of the spin trapped radical at the chain end.

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