Melting and annealing effects on molecular motion of spin-labelled molecules at the polymer chain-end located on the polypropylene surface

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The samples of spin-labelled molecules at the polymer chain-ends located on the polypropylene surface were annealed and melted. The e.s.r. spectra of spin-labelled molecules were observed at various temperatures. A long layer distance was obtained by small angle X-ray scattering spectroscopy. The plot of extrema separation (W) with temperature of the sample shows two steps of narrowing. In the first step (I, low temperature region), melting of the sample increases both the value of activation energy (ΔE) and the characteristic temperature (T-I); so the mobility of the spin labelled molecules trapped in the interior of bulk is less than on the surface. These increases are ascribed to more crowded surroundings. The effect of annealing on the motion is dependent on annealing temperature. In the second step (II, high temperature region), annealing at high enough temperatures increases the value of the characteristic temperature (T-II). These increases are ascribed to an inclusion of the spin-labelled molecules in the crystal. The first step (I) shows the influence of trapping site on mobility of spin-labelled molecules, and the second step (II) shows the influence of a crystal.

Keywords Electron spin resonance; spin-label; molecular motion; polypropylene; surface

INTRODUCTION

Recently, many reports[1-6] on the study of molecular motion in a solid phase have described the utilization of spin-labelled polymers as mobility probes. Spin-labelled polymers are usually synthesized by chemical reaction of the polymers with spin-labelled reagents. In general, applications of this method are limited to polymers having reactive functional groups. Therefore, it is difficult to apply this method to a polymer such as polypropylene. In addition to this restriction, it is difficult to label specific sites in a polymer matrix, such as the surface.

The combination of mechanical degradation and spin trapping is a useful method for studying molecular motion on the surface; and as reported in our earlier papers[7,8], selective spin labelling on the surface is successful[8]. The preliminary study of the molecular motion on atactic polypropylene surface has been reported[9], and the study on polyethylene has also been reported[10,11]. In this study we also report a melting and an annealing effect on the molecular motion of spin-labelled molecule at the chain-end located on the isotactic polypropylene surface.

EXPERIMENTAL

Isotactic polypropylene was supplied by Mitsui Petrochemical Co. The polymer samples were dissolved in hot toluene, filtered, washed with acetone, and dried under reduced pressure. These treatments were repeated three times. The samples were then dried under vacuum for two days. Molecular weights were obtained by gel permeation chromatography: $M_w = 2.39 \times 10^5$, $M_n = 3.95 \times 10^4$.

Nitrosobenzene, a spin labelling reagent, was supplied by Nakarai Chemical Co. and was purified by sublimation under vacuum at room temperature.

Polymer flake (1.5 g) was milled with powdered nitrosobenzene (0.1 g) at 77K *in vacuum* for 21 h in a specially designed ball-mill system[12]. After the milling, unreacted nitrosobenzene was removed from the reaction system by sublimation under vacuum at room temperature. Several samples of isotactic polypropylene were prepared in this study: sample it-F was the sample as milled; sample it-F-H was produced by annealing of as milled sample at 433K for 68 h; sample it-M was obtained by melting at 480K and subsequently cooling the sample; sample it-M-H was obtained by annealing of the sample it-M at 423K for 51 h. All samples are very stable to the annealings. The concentration of free radicals were less than 0.01% by weight of polymer matrix.

E.s.r. spectra were recorded on a JEOL ME-3X X-band spectrometer with 100 kHz field modulation. Spectra were recorded without power saturation effects.
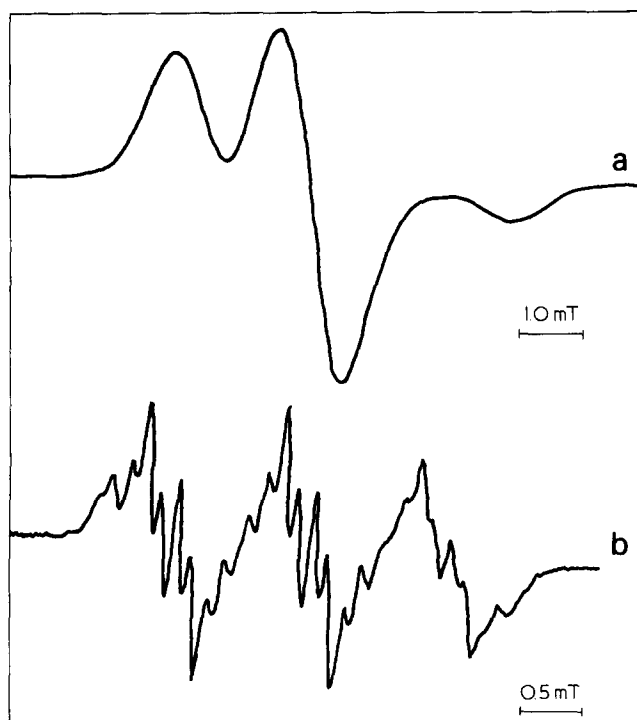
Figure 1 E.s.r. spectra of sample it-F observed at: (a) 77 K; (b) 480 K

RESULTS AND DISCUSSION

Spin labelled molecules

The e.s.r. spectrum observed at 77K from the isotactic polypropylene fractured with nitrosobenzene is a characteristic of a nitroxide radical in the rigid state[1-4], as shown in *Figure 1a*. However, one of us (M.S.) has reported that the mechano radicals produced by mechanical action on isotactic polypropylene consist of two types of chain-end radical[12-14]:

H   CH₃   CH₃ H
 | | | |
~C—C•   and   ~C—C•
 | | | |
H   H   H   H

(I)   (II)
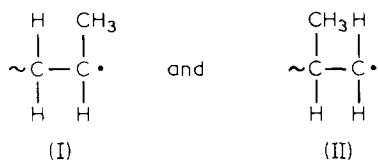
In addition, we have reported that the mechano radical is trapped on the fresh surface produced by the mechanical fracture[15], and reacts with nitrosobenzene, even at 77K, and then, converts to a nitroxide radical[7].

The radical, which has the e.s.r. spectrum shown in *Figure 1b*, is very stable, even at 480K; higher than the melting point (437K, obtained by d.s.c.) of the sample, and the major triplet splitting is characteristic of a nitroxide radical. The minor splittings have their origins in various protons in the radical[5,16,17]. The isotropic g value of this radical is 2.0058. It is reported [16,17] that the spin adduct[18] (the addition product of the short-lived radical to the spin trapping reagent) of nitrosobenzene is of

the type. Therefore, we conclude that
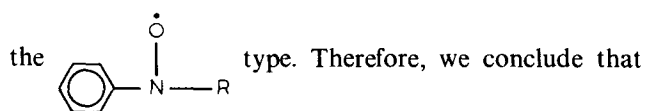
both the spin adducts of nitrosobenzene to polypropylene mechano radical are nitroxide type connected at the chain-end of the polymer as follows:
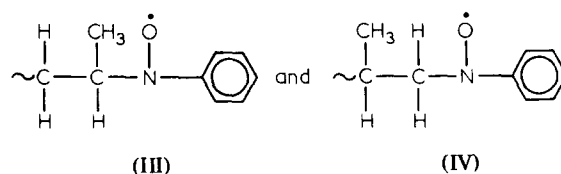
In this paper, we call both radicals (III) and (IV) 'spin-labelled molecules' without distinction.

Effect of melting on the motion of spin-labelled molecules located on the surface

E.s.r. spectra of sample it-F under various temperatures are shown in *Figure 2*. The e.s.r. spectrum observed at 77K (*Figure 2a*) shows that the spin-labelled molecules are at the rigid limit[1-6]. An extrema separation ($W=2A_\parallel$, see *Figure 2*) which is a useful parameter for estimating the rotational frequency of spin-labelled molecules, was measured and plotted against the observation temperature (T). *Figure 3* shows two steps of narrowing of W (denoted as I and II) with increasing T. The narrowing of W indicates an increase in mobility of the spin-labelled molecules. The temperature of the midpoint of each narrowing step is denoted as T-I (lower) and T-II (higher temperature), respectively. In region I, the motional narrow range of sample it-F is markedly different of sample it-M. This result indicates that a mobility of the spin-labelled molecules located in the interior of the bulk (sample it-M) is less than on the surface (sample it-F).
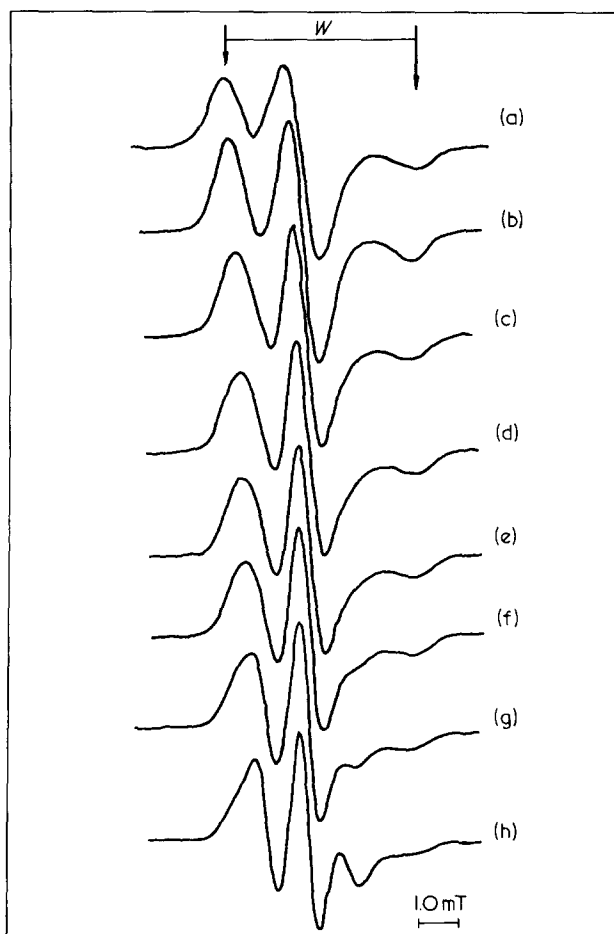

Figure 2 E.s.r. spectra of sample it-F observed at: (a) 77 K; (b) 327 K; (c) 355 K; (d) 361 K; (e) 368 K; (f) 375 K; (g) 385 K; (h) 405 K

For a more quantitative study, one can estimate the rotational correlation time (τ_c) of nitroxide by the following equation given by Freed et al.[19]:

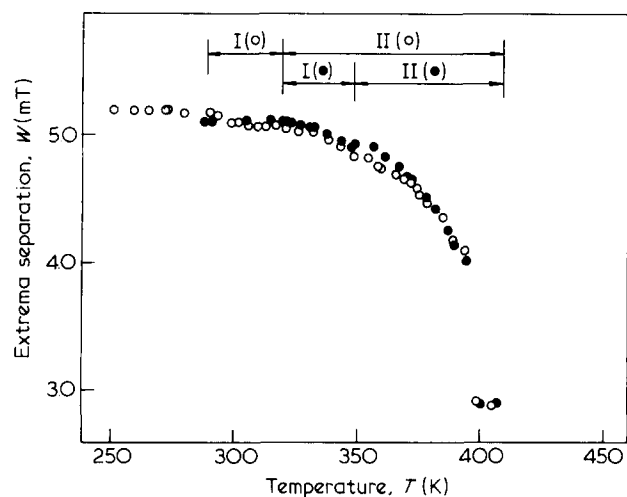$$\tau_c = a\left(1 - \frac{A_\parallel}{A_{\parallel 0}}\right)^b$$

Figure 3 Extrema separation (W) vs. temperature (T) plot for the samples with two steps of narrowing on W: Sample it-F; I (○), II (○) and sample it-M; I (●), II (●) showing the influence of trapping sites
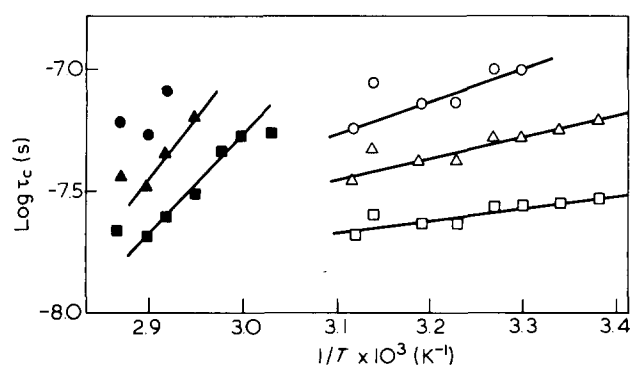

Figure 4 Arrhenius plots of rotational correlation time (τ_c) for sample it-F (○, △, □) and sample it-M (●, ▲, ■) with three models proposed by Freed et al.: (○, ●) Brownian diffusion model; (△, ▲) moderate jump diffusion model; (□, ■) strong jump diffusion model

where $A_{\parallel 0}$ is one-half the extrema separation for the rigid limit. From a and b values proposed by Freed et al., we have selected the following three hypotheses for the rotational reorientation with line width of 0.3 mT:

'Brownian diffusion model'	$a = 5.4 \times 10^{-10}$ s $b = -1.36$
'Moderate jump diffusion model'	$a = 1.1 \times 10^{-9}$ $b = -1.01$
'Strong jump diffusion model'	$a = 2.55 \times 10^{-9}$ s $b = -0.615$

since it seems unjustifiable to select one model rather than the other. According to the report of Freed et al.[19], it should be noted that the equation is applicable within the range: 7×10^{-9} s $< \tau_c < 1 \times 10^{-7}$ s. The equation is applicable to region I, however, it is not applicable to region II, since τ_c is out of the range.

Rotational correlation times τ_c are estimated for each extrema separation, and Arrhenius plot of τ_c is shown in Figure 4. The activation energies, ΔE, of the motion are summarized in Table 1. Both Figure 4 and Table 1 show that melting of the sample increases with activation energy.

In earlier papers, we reported that the spin-labelled molecules in 'as milled sample' (denoted it-F in this paper) are present on the surface produced by the fracture[10]. Melting transforms the polymer powder into a liquid state at self-diffusion freely. Therefore, spin-labelled molecules diffuse away from the surface into the interior. When the polymer melt is cooled down again, the spin labelled molecules are trapped in the interior of the bulk and result in more crowded surroundings. Figures 3 and 4, and Table 1 show that the melting of samples result in the increases of both T-I and ΔE, which suggest that the rotational motion of spin labelled molecules in the bulk is slower than that on the surface. We conclude that the decrease in the mobility of spin-labelled molecules in the interior of bulk is attributed to the much more crowded surroundings than on the surface; in other words, region I, first step, shows the influence of trapping site on mobility of the spin-labelled molecules.

We have reported[9] that the narrowing of extrema separation of atactic polypropylene spin-labelled has a

Table 1 Narrowing temperature $(T\text{-}I, T\text{-}II)$ and activation energy from τ_c vs. $1/T$ plot

Sample	it-F	it-F-H	it-M	it-M-H
Trapping site	Surface	Surface	Bulk	Bulk
Temperature range of I (K)	$290 < T < 320$	$290 < T < 320$	$320 < T < 350$	$320 < T < 350$
Narrowing temperature of I, T-I (K)	~300	~305	337	342
Activation energy, ΔE (kJ)	a b c 5 4 2	a b c − 4 3	a b c − 18 15	a b c 13 11 7
Temperature range of II (K)	$320 < T < 410$	$320 < T < 430$	$350 < T < 410$	$350 < T < 430$
Narrowing temperature of II, T-II (K)	396	420	396	412
Long layer distance, L (Å)	−	−	156	265

a: Brownian diffusion model
b: Moderate jump diffusion model
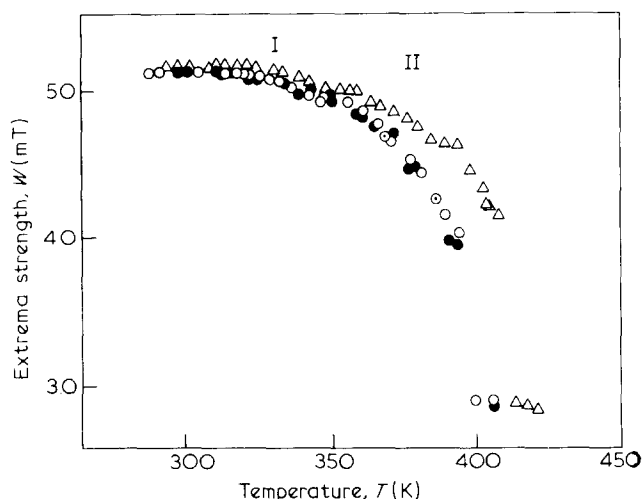c: Strong jump diffusion model by J. H. Freed et al.

Figure 5 Extrema separation vs. temperature plots for: ○ sample it-M; ● the sample (annealed at 409 K for 71 h); △ sample it-M-H (annealed at 423 K for 51 h), showing the annealing effect for the spin-labelled molecules trapped in the interior of bulk
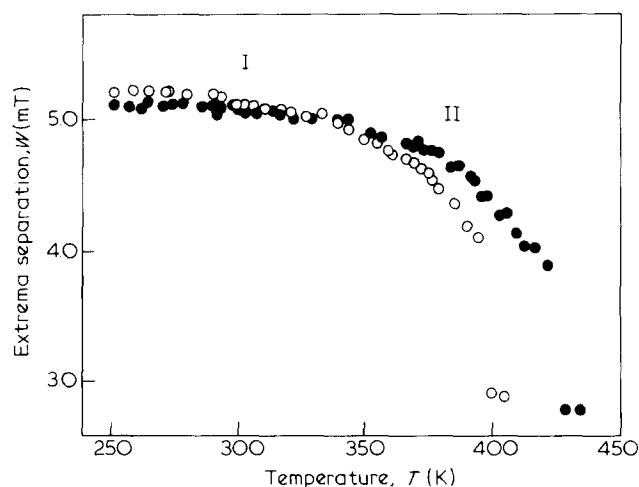

Figure 6 Extrema separation vs. temperature plots for sample it-F (○) and it-F-H (●) showing the annealing effect for the spin-labelled molecules trapped on the surface

single curve–one step narrowing. In contrast, the isotactic polypropylene samples exhibit two steps of narrowing. The T-II values of the sample show a near but lower melting point which reflects thermal deformation of the crystal. Therefore, it is reasonable that the two steps of narrowing are due to a crystalline polymer, isotactic polypropylene. The narrowing region I shows an influence of the trapping site described above, and the narrowing region II, second step, suggests influence of a crystal.

Effect of annealing on the molecular motion of spin-labelled molecules

Annealing of a crystalline polymer at a sufficiently high temperature increases the thickness of the lamellae, and annealing at even low temperatures, but high enough for translational motion of polymer chains, allows the crystal structure to change. The growth of lamellae involves translational motion of the polymer chains, and the position of the chain ends are changed. Therefore, this should affect the rotational motion of the chain ends. In

other words, annealing would affect the values of T-I and T-II.

When the sample it-M is annealed at a comparatively low temperature (409K), no significant change occurs in both values of T-I and T-II (see *Figure 5*). In contrast, annealing at higher temperature (423K) causes an increase in both values (see *Figure 5* and *Table 1*). Furthermore with sample it-F-H, annealing increases both values (see *Figure 6* and *Table 1*). *Table 1* shows that the long layer distance obtained with the peak position of small angle X-ray scattering spectrum increases by annealing: growth of lamellae, and both the T-I and the T-II shift to higher temperatures.

In an earlier paper with polyethylene, the annealing at high enough growing of lamellae results in a shift of T_n (related with T-II in this paper) to low temperature[3]. This phenomenon is explained by both an exclusion of chain end from crystal and a transition of crystal structure due to annealing.

Kurokawa and Sohma[20] have reported that the crystal structure of ball-milled polypropylene converts from pseudohexagonal (so-called Smetic) to monoclinic structure by the annealing at 385K for 24 h.

If we suppose that the change of crystal structure by annealing involves the shift of T-I and T-II, it should affect the value of T-I and T-II, when annealing takes place at higher temperature (409K) than 385K in polypropylene. However, they do not change. They change significantly with annealing at much higher temperature (423K), and in contrast with polyethylene they shift remarkably in the opposite direction; to higher temperature. Therefore, the crystal structure hypothesis (involving both the exclusion of chain end from crystal and the transition of crystal structure) seems to be inadequate for the explanation of the results of polypropylene.

Takayanagi *et al.*[21], and Hoffman *et al.*[22] have reported that chain ends on the surface of lamellae move into the crystalline region to form defects within the lamellae by a temperature high enough to involve an increase in lamellae thickness. Particularly, Takayanagi *et al.* have reported[23] that including the chain end in the lamellae of isotactic polypropylene is more enhanced at the annealing temperature over 420K. However, the molecular form in
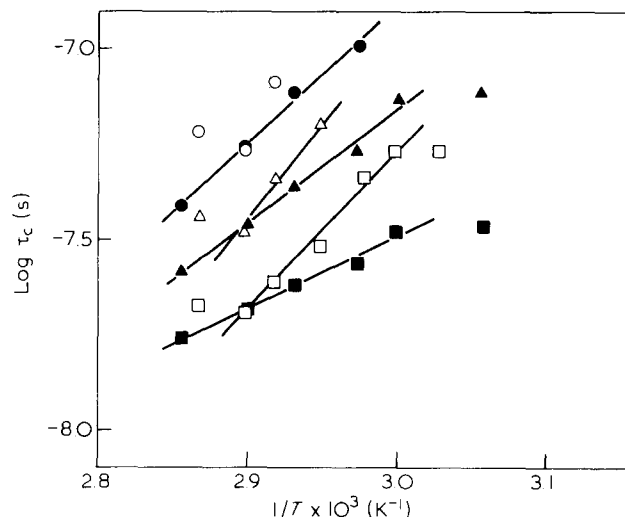

Figure 7 Arrhenius plots of τ_c for sample it-M (○, △, □) and it-M-H (●, ▲, ■); key as for *Figure 4*
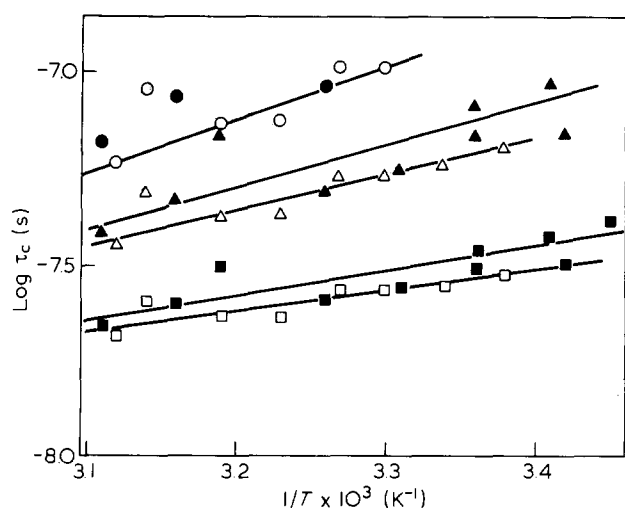
Figure 8 Arrhenius plots of τ_c for sample it-F (O, △, □) and it-F-H (●, ▲, ■); key as for *Figure 4*

crystal of isotactic polypropylene is 3_1 helix, and that of polyethylene is *trans* zig-zag. The density of each crystal is: isotactic polypropylene; 0.936 g cm^{-3}[24], polyethylene; 1.00 g cm^{-3}[25]. The molecular form in crystal of isotactic polypropylene is more bulky than polyethylene. Therefore, it is reasonable that the chain end (spin-labelled molecule) of isotactic polypropylene is included in the crystal.

From experimental results, it appears that when polypropylene samples are annealed at high temperatures, the polymer chains rearrange themselves so that the lamellae thicknesses increase. As a result, the spin-labelled molecules at the chain-end of the host polymer are included in the lamellae, forming defects and the value of T-I and T-II increases. Therefore, we conclude that the increase of T-I and T-II by annealing is due to an inclusion of spin-labelled molecules into lamellae.

The variation of T-II by the annealing was large compared with T-I which reflects the trapping site. This shows that the effect of annealing is greater in region II than region I. The values of T-II are slightly lower than the melting point which reflects a thermal deformation of crystal, whereas the value of T-I is much lower than the melting point. The mobility of spin-labelled molecule is mainly affected by a crystal, in region II.

The T-II value of each sample (it-F and it-M) is the same. When the spin-labelled molecules are not included in a crystal, the difference in trapping site could not be seen in region II.

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