The Effect of Spin-Trapping Agent on Electron Spin Resonance Spectra of Spin Labelled Polyethylene

Somsak VIVATPANACHART, Hiroyasu NOMURA,* and Yutaka MIYAHARA

*Department of Chemical Engineering, Faculty of Engineering, Nagoya University,
Furo-cho, Chikusa-ku, Nagoya 464, Japan.*

(Received October 7, 1980)

ABSTRACT: The spectra of chain-end spin labels on the surface of polyethylene powder were measured for two different spin trapping agents, nitrosobenzene (NB) and *N-tert*-butyl- α -phenylnitrone (PBN). The influence of the spin-trapping agent on the line shape of the electron spin resonance (ESR) spectra, the extreme separation, and the rotational correlation time was investigated. As the temperature was raised, the ESR spectra of spin-trapped radicals become narrow, and finally at a temperature near the melting point of the polymer, the triplets approached isotropic spectra. In the case of PBN trapped radicals, there was a sub-splitting which started to appear at about 204 K. In contrast to this, no sub-splitting could be observed clearly with NB trapped radicals. Assuming a two-phase model (a more mobile phase and a less mobile phase) for the host polymer, we simulated the ESR spectra and compared them with the experimental results.

KEY WORDS ESR Line Shape / Spin-Trapping Agent / Polyethylene / Mechano Radical / Rotational Correlation Time / Size Effect /

In our previous papers,^{1,2} we reported on a new method for labelling a polymer chain by milling polymer powder with the spin-trapping agent nitrosobenzene at 77 K. The milling produced polyethylene mechano radicals which were subsequently trapped by nitrosobenzene to form stable nitroxide radicals. These spin-trapped radicals were identified as $\text{CH}_3\text{—CH}(\text{NO—}\phi)\text{—CH}_2\cdots$. The spin-trapped radicals are considered to exist exclusively on the fractured surface of the polymer, and the region where the polymer powder was fractured by milling action may be either in amorphous or crystalline phase. The mechano radicals thus produced were trapped on fractured surfaces situated possibly near either the amorphous or the crystalline region.

High temperature annealing decreases the rotational correlation time (τ_c) of high-density polyethylene. Melting decreases the values of τ_c for both high- and low-density polyethylene samples. These decreases are attributed to the change in the sites of the spin-trapped radicals.³ The motion of the radicals appeared to be influenced by the β -relaxation-

like segmental motion near the chain-end region.³

In this study, the mechano radicals of polyethylene were spin-trapped by 2 different spin-trapping agents. The influence of these agents on the molecular motion of the spin-trapped radicals as measured by ESR spectroscopy are discussed. Also based on the two-phase model ESR spectra have been simulated.

EXPERIMENTAL

Materials

The polymers used in this study were high-density polyethylene PE Hizex Million (PE HZ) with M_w of 2.6×10^6 and low-density polyethylene PE Sumikasen G201 (PE SK) with M_n of 3.08×10^4 and M_w of 9.11×10^5 .

The spin-trapping agents used were nitrosobenzene (NB) and *N-tert*-butyl- α -phenylnitrone (PBN) supplied by Aldrich Chem. Co., Inc.

Spin-Trapping Procedure by Ball-Milling Two grams of polymer powder and 100 mg of spin-trapping agent were mixed together in a specially designed ampoule having a volume of about 60 ml

* To whom correspondence should be addressed.

and containing 25 glass balls each with a diameter of 0.9 cm. The samples were degassed with a diffusion pump at a pressure less than 10^{-4} mmHg for about 10 h, and then sealed under vacuum. The samples inside the ampoule were milled at 77 K for 4 h by a vibrating ball-mill with a frequency of 130 cycle min^{-1} and a stroke of 4 cm long.

Swelling of Polyethylene Sample

NB spin-trapped PE SK samples were swollen with xylene or carbon tetrachloride. The samples and swelling solvent were placed in ESR tubes at room temperature, degassed by pumping and thawing and sealed under vacuum for one week before ESR measurement.

ESR Measurement

ESR spectra were measured with a JEOL JES-ME ESR Spectrometer manufactured by Japan Electric Co., Ltd., using an X-band and 100 kHz field modulation. In regard to the swollen samples, in order to prevent the evaporation of the solvent during high-temperature observation, the ESR tubes were filled with swelling solvent.

RESULTS AND DISCUSSION

In order to clarify quantitatively their effect on

molecular motion observed by ESR, it was necessary to use numerous spin-trapping agents of varying size. Accordingly, several nitroso and nitron compounds, nitrosobenzene, 2,4,6-tri-*tert*-butyl nitrosobenzene, 2-methyl-2-nitrosopropane, *N*-*tert*-butyl- α -phenylnitron, 5,5-dimethyl-1-pyrroline-1-oxide, and 1-nitroso-2-naphtol were tested as spin-trapping agents in the manner described in the experimental section. Unfortunately, only nitrosobenzene (NB) and *N*-*tert*-butyl- α -phenylnitron (PBN) effectively reacted and stabilized the polyethylene mechano radicals. Room temperature millings were also tested by this procedure but to no avail. Thus our discussion is based solely on the results obtained with nitrosobenzene (NB) and *N*-*tert*-butyl- α -phenylnitron (PBN) trapped radicals.

Effect of Spin-Trapping Agents on the ESR Line-Shape

Figures 1a and 1b show the ESR spectra of PE HZ mechano radicals trapped by PBN and NB respectively, both are typical triplets of nitroxide radicals. At low temperatures where the radicals are immobile, the spectra are broad and asymmetric (anisotropic spectrum). With the rising in temperature, the spectra become narrower, and finally at a temperature near the melting point of the polymer

Figure 1. Derivative ESR Spectra for various temperatures (written on the right hand side in K): a, PE HZ mechano radicals trapped by PBN; b, PE HZ mechano radicals trapped by NB; c, PE SK mechano radicals trapped by NB and swollen with xylene.

where the radicals become freely mobile, the triplets approach isotropic spectra (isotropic triplet spectrum). One noted difference between the two spectra is that, for the PBN trapped radicals, there is a sub-splitting which starts to appear at about 204 K, but for the NB trapped radicals, no such phenomenon is observed.

In our previous paper³ in which the effect of swelling agents on the transition temperature of the narrowing region of extrema separation was examined, it was unexpectedly found that the addition of xylene and carbon tetrachloride to PE SK samples not only lowered the transition temperature, but also resulted in the appearance of a sub-splitting between the central and high field peaks as shown in Figure 1c.

It can be seen from Figure 1a that the intensity of the sub-splitting increases with the rising in temperature. This was observed in spin probe^{4,5,6} and spin label^{7,8,9} studies of polymers. Kusumoto⁶ attributed this sub-splitting to the motion of the probes located in a more mobile environment of the host polymer. Bullock⁷ suggested that this sub-splitting indicates the onset of the local motion of the radicals in a direction perpendicular to the main chain. Robb and Swith⁸⁾ understood this as the absorption of polymer chains onto the silica-

solution interface in the "train conformation." In brief, this sub-splitting is interpreted as resulting either from the segmental motion of the chain in the more mobile environment or from the anisotropic local motion of the chain proposed by Bullock.⁷

It is generally known that molecules of the swelling agents can only diffuse through the amorphous phase of the polymer. Therefore, it seems that the addition of a swelling agent increases the mobility of spin-trapped radicals situated near the amorphous phase and gives rise to a narrowing of the ESR spectra of the radicals in that phase. Sub-splitting appears as a result of the superimposition of the ESR spectra of the radicals located near the mobile amorphous phase on those located near the immobile crystalline phase. We reported³ that the motion of the radicals observed in this temperature range is greatly influenced by a β -relaxation-like motion of the chain-end region. Thus, this sub-splitting is not likely to arise from the local motion of the radicals in a direction perpendicular to the main chain as proposed by Bullock.⁷

As an explanation for the fact that sub-splitting is clearly observed on dry PBN spin-trapped radicals but not on dry NB spin-trapped radicals, we can only speculate that larger PBN spin-trapped radicals are more sensitive to the motion of the polymer

Figure 2. Comparison of simulated and experimental Spectra of (a—b) PE HZ mechano radical trapped by PBN at 157 K and 320 K. (c—d) PE SK mechano radicals trapped by NB and swollen with xylene at 271 K and 298 K: - - - - -, more mobile component; - - - - -, less mobile component; , overall simulated ESR spectra; —, experimental spectra.

chain than NB spin-trapped radicals. Thus, the difference in the mobilities of the polymer chain ends located near the amorphous phase and those located near the crystalline phase should appear in the ESR spectra of PBN trapped radicals but not in those of NB trapped radicals.

To verify the above prediction regarding the ESR line shape, ESR spectra were simulated for both NB and PBN trapped radicals at various temperatures from the frozen to the mobile state, assuming that each spectrum was composed of two components, one, an isotropic triplet corresponding to the more mobile phase (high-temperature spectrum) and the other, an anisotropic triplet corresponding to the less mobile phase (low-temperature spectrum). The proportion of the two components was allowed to vary with temperature in such a way that the intensity of the more mobile component increases with temperature. The ESR spectra thus simulated show all the features of the experimental spectra, and the simulated and observed spectra fit very well with each other at all temperatures. The sub-splitting appears in the simulated spectra of both the NB and PBN trapped radicals. Some of these simulated spectra are shown in Figure 2.

The results from the spectrum simulation confirm the explanation that the sub-splitting arises from the different rotation rates of the polymer chain-ends due to environmental differences, that is, one is near the amorphous region and the other is near the crystalline region.

Effect of Spin-Trapping Agents on the Observed Molecular Motion

In this section, we compare the molecular motion observed for NB and PBN spin-trapped radicals. It would be very informative if we could follow, separately, the motions of the spin-trapped radicals in the more mobile and less mobile phases. Unfortunately, sub-splitting has not been clearly observed in the case of dry NB spin-trapped radicals, and it is difficult to measure the extrema separations (W) of the more mobile phase of PBN spin-trapped radicals accurately. Our discussion is thus based solely on the extrema separation of the less mobile phase. We discuss the temperature dependence of W of PBN on curve "a" not on curve "b" which shows the transition behavior of the more mobile phase in Figure 3.

The appearance of sub-splitting gives rise to some doubt in regard to the true value of extrema separations. In most of the past work on spin probe and spin label, sub-splitting was neglected in determining the value of W . However, it may be that the superimposition of the two components broadens the outer triplet, thus resulting in an erroneous value of W . In order to avoid this error, the ESR spectra of Figures 1a and 1c were decomposed into the components shown in Figure 2, and the W of the mobile and immobile components were measured separately. By so doing, it was found that for PBN trapped radicals, the observed values and those of the simulated less mobile component were identical

Figure 3. Variation in extrema separation with temperature: ○, PE HZ mechano radicals trapped by PBN (a, outer triplet and b, inner triplet); ●, PE HZ mechano radicals trapped by NB.

(Figures 2a and 2b). Therefore, the value of W can be measured directly from the observed ESR spectra of PBN without the need for correction. In the case of PE SK swollen with xylene, the observed value of W was smaller than the simulated one due to the interference of the mobile component (Figure 2d).

Figure 3 shows the variation in extrema separation with temperature for both NB and PBN spin-trapped radicals. The values of W for the former are smaller than those of the latter throughout the whole temperature range observed. However, the temperature ranges in which the extrema separations gradually decreased, followed by a sharp decrease, are the same for both radicals. This indicates that the values of W are dependent on the spin-trapping agent employed, and that the manner in which W varies with temperature is determined by the mobility of the polymer chains bonded to the spin-trapping agents.

In order to make a more quantitative study of the molecular motion of the radicals, rotational correlation time values (τ_c) were determined from W , using Freed's equation^{11,12} with the moderate jump diffusion model, assuming a residue line width (δ) of 3 G,

$$\tau_c = 1.1 \times 10^{-9} (1.0 - W/W^*)^{-1.01} \quad (1)$$

where W^* is the value of W in the frozen state.

Figure 4 shows the changes in τ_c with reciprocal absolute temperature for the narrowing region of W . The two curves for the NB and PBN trapped radicals consist of two straight lines each with a distinct break point. The value of τ_c for the PBN trapped radicals is larger than that of NB, indicating a slower motion for the former radical. This may be attributed to the greater molecular weight and molar volume of the spin-trapping agent, PBN. The molecular weight of PBN is 177, compared with 107 for NB. Similar results were reported in the study using spin probes,^{4,7,12} which also showed that the larger probe rotates at a slower rate than the smaller one. The temperatures corresponding to the break points are approximately the same, being 350 and 346 K for PBN and NB trapped radicals, respectively. The activation energies calculated from the slopes of the curves in Figure 4 are 2.7 and 6.4 kcal mol⁻¹ for PBN, and 3.1 and 6.4 kcal mol⁻¹ for NB in the high and low temperature range, respectively. The activation energies related to the

Figure 4. Changes in rotational correlation time with reciprocal absolute temperature. The symbols used here are the same as in Figure 3.

motion of the spin-trapped radicals are discussed in our previous paper.³ Since the values of τ_c and the activation energies obtained by the method used here are only tentative, no further discussion is necessary.

The fact that for both spin-trapped radicals, the values of τ_c show the break points at the same temperature indicates that these break points as well as the variation in τ_c with temperature arise from the mobility of the polymer chains bonded to the spin-trapping agents. This behavior is independent of the particular spin-trapping agent used. However, the values of τ_c are depend strongly on the spin-trapping agent.

The results of this study show that although our method of spin-labelling can be used for observing changes in the molecular motion of the polymer chain, care must be taken in comparing the absolute values of τ_c and the activation energies for different spin-trapped radicals.

Acknowledgement. We would like to express our gratitude to Prof. H. Kashiwabara of Nagoya Institute of Technology for permitting us to use the ESR spectrometer and also to Mr. H. Itoh of Nagoya University for his helpful advice in regard to computer simulation of the observed ESR spectra.

REFERENCES

1. S. Vivatpanachart, H. Nomura, Y. Miyahara, H.

- Kashiwabara, and M. Sakaguchi, *Polymer*, **22**, 132 (1981).
2. S. Vivatpanachart, H. Nomura, Y. Miyahara, H. Kashiwabara, and M. Sakaguchi, *Polymer*, **22**, 263 (1981).
3. S. Vivatpanachart, H. Nomura, Y. Miyahara, H. Kashiwabara, and M. Sakaguchi, accepted for publication in *Polymer*.
4. G. P. Rabold, *J. Polym. Sci., A-1*, **7**, 1203 (1969).
5. S. C. Gross, *J. Polym. Sci., A-1*, **9**, 3327 (1971).
6. N. Kusumoto, M. Yonezawa, and Y. Motozato, *Polymer*, **15**, 793 (1974).
7. A. T. Bullock, G. G. Cameron and P. M. Smith, *Eur. Polym. J.*, **11**, 617 (1975).
8. I. D. Robb and R. Smith, *Eur. Polym. J.*, **10**, 1005 (1974).
9. M. C. Long and C. Noel, *J. Polym. Sci., Polym. Phys. Ed.*, **15**, 1329 (1977).
10. J. F. Freed, G. V. Bruno and C. F. Polanazek, *J. Phys. Chem.*, **75**, 3385 (1971).
11. S. A. Goldman, G. V. Bruno and J. F. Freed, *J. Phys. Chem.*, **76**, 1858 (1972).
12. N. Kusumoto, "Molecular Motion in Polymer by ESR," MMI Press Symposium Series, Vol. 1, R. F. Boyer and S. E. Keinath, Ed., Harwood Academic Publishers, New York, N.Y., p 223 1980.