Comparison of local molecular motions at chain end and inside of the polymer chain by use of spin trapping method

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The spin trapping method was applied to the study of local molecular motion in polyethylene. Spin trapping reagent, 2,4,6-tri-t-butyl nitrosobenzene, was mixed with polyethylene and the free radicals produced by γ-irradiation and thermal degradation were stably trapped by spin trapping reagent. Temperature dependences of e.s.r. spectra of the stable nitroxide radicals trapped were observed and widths of extrema separation and correlation times at various temperatures were compared for the local motions at inside of chain and at chain end. Less mobile character of the molecular motion at inside of the molecular chain was confirmed. Diluent effects to the molecular motions were also studied.

INTRODUCTION

Local mobility of the molecular chain of macromolecules is an interesting subject to study. However, the appropriate and simple method, which observes the different kind of mode of molecular motions separately, has not yet been devised. Recently, the spin trapping technique in e.s.r. application[1] to the study of free radicals has been established and it has been possible that the unstable free radical is converted to the stable radical by the reaction of spin trapping reagent with unstable free radicals. By the conversion of unstable radical into stable radical, temperature dependence of the spectrum of the radical can be observed in wide temperature range and hence much information of the radical sites at various temperatures can be obtained. This means that the circumstance of the molecular motions of the sites labelled by stable radicals can be observed. Also, it can be said that different kind of molecular motions at different kind of sites of molecular chain can be observed separately if the stable radical is labelled at each of the different kinds of the molecular chain. In order to observe the above mentioned circumstance actually, the spin trapping method is quite convenient. In the case of polyethylene, the difference between the local molecular motion at chain end and that at inner part of the molecular chain would be a very interesting subject of study. In the present paper, the comparison of the molecular motions at the chain end and inside the molecular chain of polyethylene will be made by use of the spin trapping technique.

EXPERIMENTAL

High density polyethylene, Sholex 6050 (Product of Showa Electric Co. Ltd), was used as sample. The pellets of polyethylene were purified by dissolving in boiling toluene, then precipitated by cooling at room temperature, washed in considerable amount of acetone, filtered, and dried in a vacuum oven. Spin trapping reagent 2,4,6-tri-t-butyl nitrosobenzene was dissolved into benzene and a powder of purified polyethylene was immersed into this solution. This immersed polyethylene was dried in order to remove the solvent. A portion of this polyethylene was thermally degraded at 141°C and 135°C under reduced pressure, and the other portion was γ-irradiated by use of ^{60}Co source. The total doses were 0.5, 1.0, 2.6, 2.8 and 4.0 Mrad. E.s.r. spectra were recorded on a JEOL ESR X-band spectrometer with 100 kHz field modulation. Spectra were observed at various temperatures and separations of the outermost peaks of the spectra of nitroxide radicals were measured as the parameter for getting information about the circumstance of the molecular motion at each of the temperatures. Similar experiments in the presence of diluent were also made, details of which will be described in the latter part of the next section.

RESULTS AND DISCUSSION

Identification of the stable radicals observed

Thermal degradation and γ-irradiation should produce free radicals in polyethylene and these radicals should stably be trapped by the presence of spin trapping reagent immediately. This means that the e.s.r. spectra observed were the spectra of the nitroxide radicals for both cases. The e.s.r. spectrum observed at low temperature was a broad triplet spectrum but much more fine hyperfine structure appeared at elevated temperature. Variation of the spectra with observation temperature is shown in *Figures* 1 and 2. At higher temperature, the spectrum of the free radicals trapped in the case of thermal degradation was triple–triplet and that of γ-irradiation was triplet–quartet. Though two possibilities of the trappings can be considered as shown in *Figure* 3, the stably trapped radicals in the present case are mainly case A because of the following reasons: from the observed spectrum shown in *Figure* 4(*a*), hyperfine coupling constants due to the

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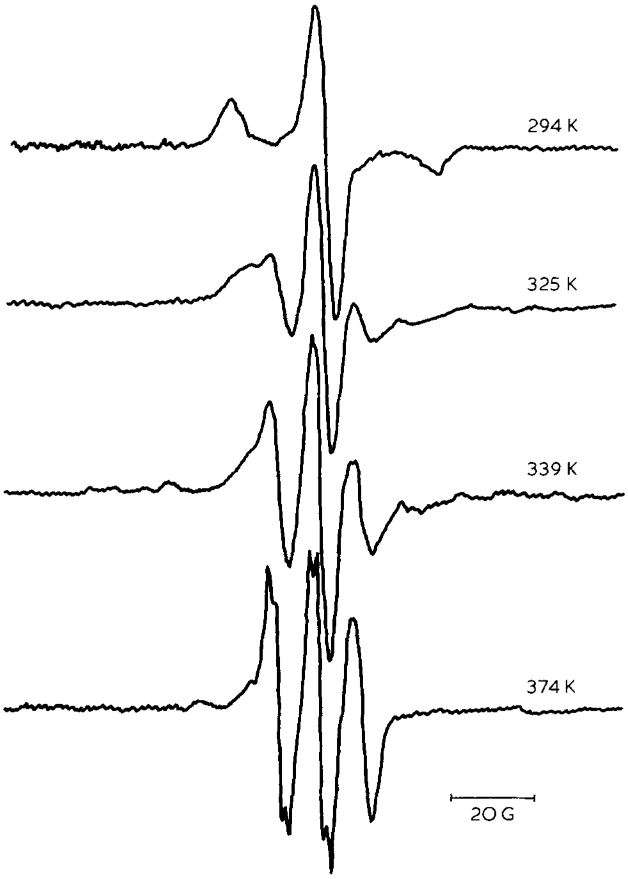
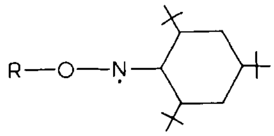
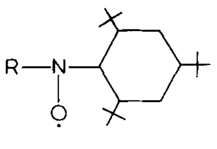


Figure 1 E.s.r. spectra of spin trapped polyethylene subjected to thermal degradation. Temperatures of observations are indicated at right hand sides of respective spectra

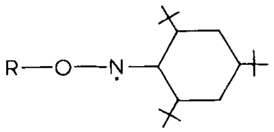
interaction with nitrogen nucleus, a_N, and that with methylene protons, a_H, were found to be 10.2 and 2.0 G, respectively, in the case of thermally degraded materials. In the other studies of the spin trapping method, it was reported that a_N was 11.5 G and a_H was less than 2.0 G in the case[2] of



and a_N was 13.5 G and a_H was 17.9 G in the case[3] of



Values of a_N and a_H observed in our study are quite close to the case of



Therefore, the identification mentioned above is quite reasonable. The weak wing peaks are seen in the spectra shown in *Figures* 1 and 2 also. These may be corresponding to the minor radicals of case B. In the case of irradiated materials, major radicals appeared as triplet spectrum at 449K (*Figure 4b*) caused by the interaction with nitrogen nucleus and each triplet component splits into quartet which indicates the interaction with one proton at the

Figure 2 E.s.r. spectra of spin trapped polyethylene subjected to γ-irradiation. Temperatures of observations are indicated at right hand sides of respective spectra

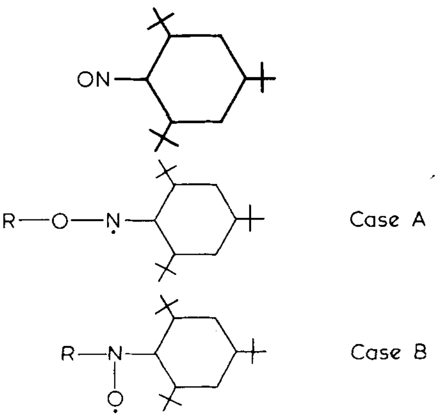


Figure 3 Two possibilities in spin trapping

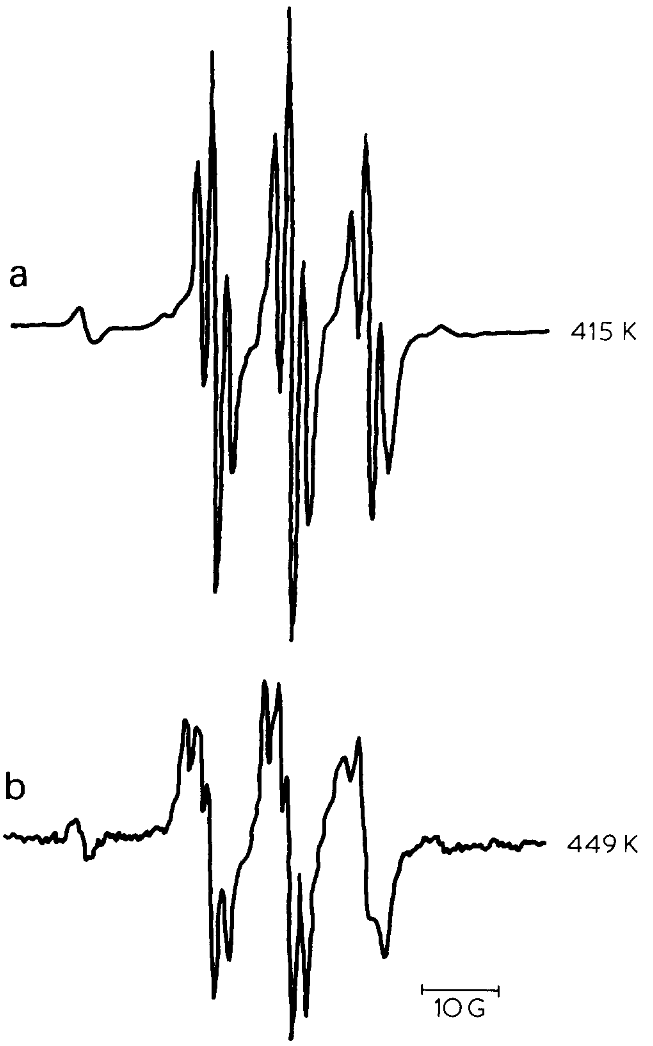
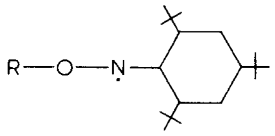


Figure 4 E.s.r. spectra of nitroxide radicals trapped to (a) thermally degraded and (b) irradiated polyethylene. Temperatures of observations are shown at right hand sides of respective spectra

trapping site and two meta protons of spin trapping reagent. In the case of



a_H due to proton in hydrocarbon molecule and that due to meta proton was reported to be the same[2]. This is also a support for our identification. Therefore, location of the radicals trapped in thermally degraded materials should be the molecular chain end and that of γ-irradiated materials should be inside of the molecular chain.

Temperature dependence of outermost peak widths

In order to discuss the local mobility of the molecular chain, the width between outermost peaks of the spectrum was used as a parameter[4]. The outermost splitting widths of the main triplet spectra due to hyperfine coupling caused by nitrogen nucleus were measured at various temperatures. Comparison of them in thermally degraded and γ-irradiated samples is shown in *Figure* 5. In the case of thermal degradation, the width of outermost peaks steeply changed. On the other hand, in the case of γ-irradiation, it narrowed more gradually than in the case of thermal degradation. This narrowing curve shifted to lower temperature when the observation was made with decreasing temperature and when the width was measured with increasing temperature again. But the curves obtained in decreasing temperature and in the second heating are seen to be the same. The inflection point of the narrowing curve will be called transition temperature and it appeared at about 50°C in the case of thermal degradation. In the case of γ-irradiation, the transition temperatures appeared at about 110°C for the first heating and at about 80°C for the second. At any rate, it can be said that the transition temperatures of thermally degraded material is lower than that of irradiated material. This is a reflection of the fact that the site of trapped radicals in γ-irradiated materials is less mobile than that in thermally degraded ones. This is quite reasonable because stable nitroxide radicals are trapped at the inside of the molecular chain in γ-irradiated materials and the radicals are trapped at the chain end in thermally degraded ones as mentioned above.

Irradiation effects

We found that the motion of radicals in the γ-irradiated materials was less mobile than that of thermally degraded ones. However, it might be the case that the molecular motion in γ-irradiated materials was affected by the interchain crosslinking induced by radiation. In order to elucidate this problem, several doses of radiation were irradiated to the materials and the same experiments of temperature dependences of outermost separation were made. In *Figure* 6, transition temperatures of the several materials irradiated up to various doses are shown. Open circles indicate the transition temperatures when the materials heated up first and black circles indicate the case of second heating. When the plotted points in *Figure* 6 are extrapolated to 0 Mrad, transition temperatures for both cases of first and second heatings tend to higher temperature than the case of thermally degraded materials. Transition temperatures of irradiated materials are nearly the same at various doses. Therefore, it can be said that the irradiation effect was little observed in our experiments and that the trapped radicals in the irradiated materials

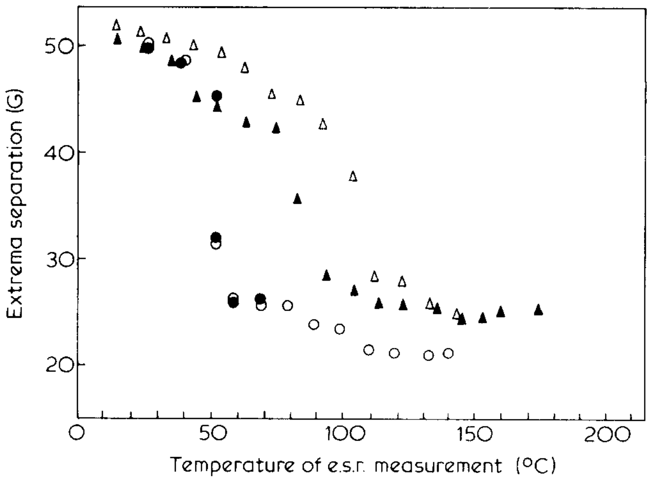


Figure 5 Variation of extrema separation of the spectra with temperature: thermally degraded materials (○) (first heating) and (●) (second heating); γ-irradiated materials (△) (first heating) and (▲) (second heating)

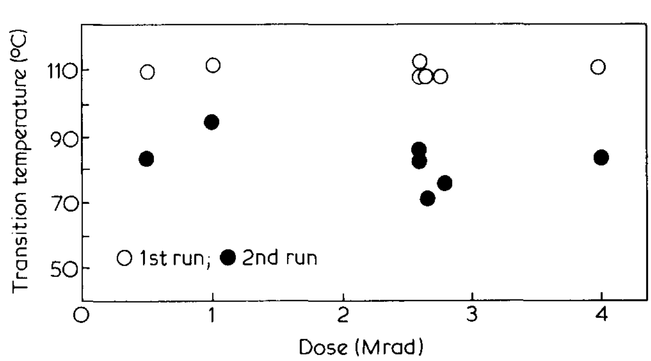


Figure 6 Variation of transition temperature with irradiation dose

are less mobile than that in thermally degraded ones. This means the fact that the stable nitroxide radicals in γ-irradiated materials exist mainly at the inside of the molecular chain and that in thermally degraded ones are located at the chain end.

Shift of transition temperature

As previously mentioned, transition temperature in irradiated materials was shifted to lower temperature at the second heating. This can be interpreted in terms of rearrangement of molecular chains after the melting due to the first heating. This rearrangement of molecular chain makes a change of mobility at the inside of the molecular chain. 'Bulky' arrangement of the molecular chain occluding large spin trapping reagent possibly occurs and the more mobile character can be attributed to such a bulky arrangement. On the other hand, in the case of thermally degraded materials, the mobility at the chain end was not affected by the probable rearrangement of molecules and the radicals trapped at the chain end did not show any shift of transition temperature after the first heating, since the material was heated up to higher temperature than melting temperature in order to make thermal degradation.

Correlation time

For the further comparison of molecular motions at the chain end and at the inside of the molecular chain, correlation times and apparent activation energies in narrowing temperature range will give us important information. Correlation times associated with molecular motions at various temperatures were conveniently estimated from the spectra. Rotational correlation times of the trapped radicals at respective sites were calculated by use of Freed's[5] and Kivelson's[6] equations. Usually, application of Kivelson's equation can be made only when the molecular motion is very rapid, i.e., correlation times are shorter than 10^{-9} s. On the other hand, when the correlation time is rather long, the estimation was made according to Freed's equation assuming the moderate jump model. Here, the correlation times at higher temperature range ($>120°C$) will mainly be compared. Correlation times estimated from thermally degraded materials were found to be of the order of 10^{-10} s and that for irradiated ones were 10^{-8} s. Apparent activation energies were estimated for thermally degraded and irradiated materials. Activation energy for thermal degradation was found to be 5 kcal/mol and that for irradiation was ~ 10 kcal/mol. These two results, correlation times and activation energies, support that local molecular motions at the chain end and at the inside of molecular chains are different and that the mobility in thermally degraded material is larger than that for irradiated material. Concerning the estimation of correlation time, more detailed discussions will be given in a subsequent paper in which activation energy of the γ-irradiated materials will be discussed including consideration of the distribution of the correlation times in solid polymer.

Diluent effect

As mentioned above, difference in the mobilities of respective sites appeared in the temperature dependence of the outermost separation from the spectra of nitroxide radicals. However, the nature of the molecular motion observed is not yet determined. In order to study this, the diluent effect on the temperature dependence of outermost separation was investigated. Such a diluent effect on the molecular motions in polyethylene was already studied by Kakizaki and Hideshima. They reported that β-relaxation shifted to lower temperature and γ-relaxation shifted to higher temperature by the presence

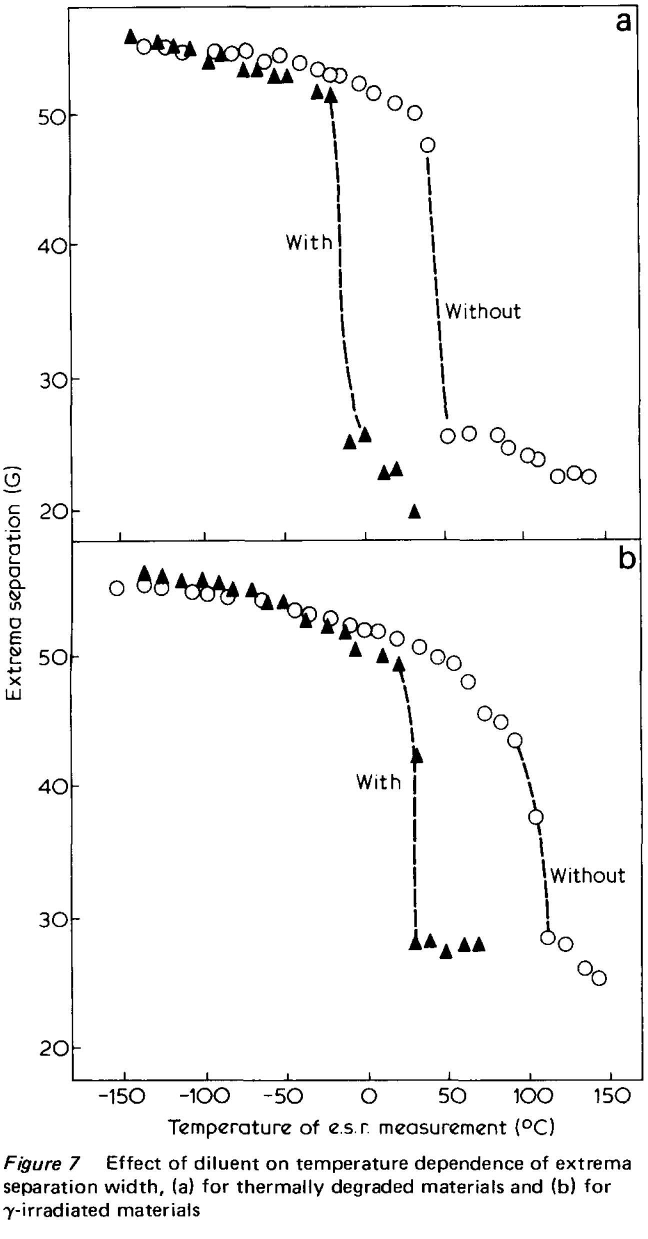


Figure 7 Effect of diluent on temperature dependence of extrema separation width, (a) for thermally degraded materials and (b) for γ-irradiated materials

of diluent. The former usually occurs at higher temperature than the latter. A diluent, tetrachloroethylene, was used in our study. The thermally degraded and γ-irradiated materials were immersed in the diluent under reduced pressure before e.s.r. measurements. The result of the diluent effect is shown in *Figure* 7. The narrowing curve shifted to lower temperature by the presence of diluent. This is coincident with the results for the β-relaxation process reported by Kakizaki *et al.*[7]; i.e., motion of γ-irradiated material is reflecting the β-relaxation associated with the micro-Brownian motion in molecular chain. On the other hand, motion of thermally degraded material looks likely to be affected by the β-relaxation process. In both cases of thermally degraded and γ-irradiated materials, the local mobilities in the respective sites increase by the presence of the diluent because of the increase in the relative amount of the amorphous region. The present paper presents an example of the usefulness of the spin trapping technique applied to the study of molecular motion by use of e.s.r. method when the original free radicals trapped are unstable. Concerning the β-relaxation process which was to be associated with the narrowing of width of the outermost peaks, much more detailed discussions will appear in a subsequent paper.

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