polymer communications

Spin trapping in γ-irradiated low density polyethylene

N. Kusumoto and T. Sakai
Department of Industrial Chemistry, Faculty of Engineering, Kumamoto University, Kumamoto 860, Japan

(Received 19 June 1979)

Introduction

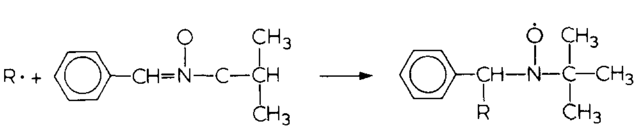
The free radical reaction in γ-irradiated polymers has been studied in relation to molecular motions and the higher order structure of polymeric systems. The spin trapping technique which has recently been developed, enables us to observe unstable free radicals by trapping and transforming them into stable ones. We have done some preliminary work on the spin trapping reaction in solid polymers irradiated by γ-rays [1-3],and now describe a study on low density polyethylene. This study may also offer a new method for spin labelling synthetic polymers which have no functional groups suitable for studying molecular motions of polymers.

Experimental

The material used was low density polyethylene (LDPE, Nihon Unicar Co. DXM 189). Spin trap phenyl N-tert-butylnitrone(PBN) was mixed with the xylene solution of purified low density polyethylene, and cast to form sheets at room temperature. The conditions for sample preparation are listed in *Table 1*. In *Table 1* F_t is the trap factor defined as a ratio of the number of PBN added to the reaction system to the expected number of polymer radicals estimated from *G*-value. The sheets were irradiated by ^{60}Co γ-rays to the total dose of 5 Mrad at -196°C in vacuum. The irradiated samples were annealed stepwise for 3 min from -196°C at various temperatures and e.s.r. was observed in each step at -196°C. e.s.r. spectra were recorded by Nihon Denshi model JES-3BSX spectrometer using X-band and 100 kHz field modulation.

Results and discussion

Figure 1 shows e.s.r. spectra of the annealed samples at -196°C. Sample I shows well known sextet spectra caused by the alkyl type radical $-CH_2-\dot{C}H-CH_2-$[4] and the intensity of spectra decreases with increasing annealing temperature. However the sample containing the spin trap shows the same spectra as that of the polyethylene sample before annealing, but begins to show an asymmetric line shape at about -70°C. This triplet spectrum can be caused by the nitroxide radical formed by the spin trapping reaction between the spin trap and the alkyl radical. The spin trapping reaction may take place as follows:



In order to determine the temperature at which the spin trapping reaction initiates, the change of spectral line shape was inspected by a line shape parameter. *Figure 2* defines the line shape parameter which is sensitive to the change from the sextet to the triplet, respectively. The broken line represents the spectrum containing both the sextet and the triplet, whose peak *P* shifts from P_1 to P_2 when the component of the triplet increases. *Figure 3* shows the change of the line shape parameter with temperature. It is noted that the parameter is kept almost unchanged for sample I in the whole temperature range, while it begins to decrease at about -70°C and becomes constant above

Table 1 Sample preparation

No	Sample	F_t	Polymer (gr)	PBN(g)
I	LDPE	0	0.0471	–
II	LDPE	5	0.0525	0.00016

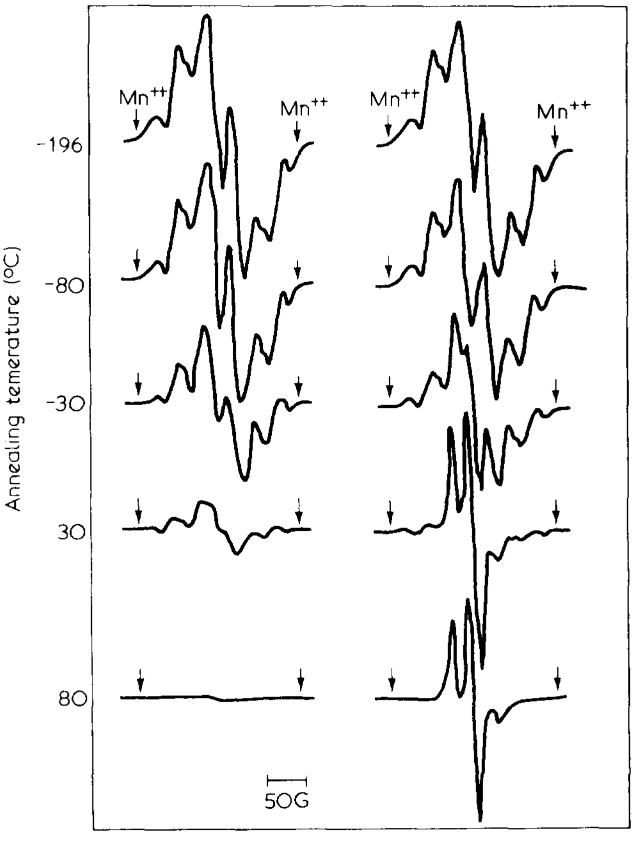


Figure 1 E.s.r. spectra of LDPE at various annealing temperatures. (a), Sample I; (b) Sample II

0032-3861/79/101175-03$02.00

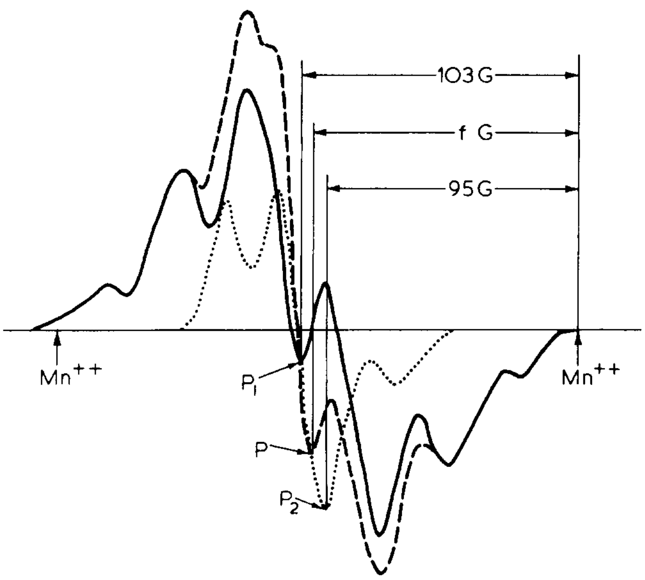


Figure 2 Definition of line shape parameter *f*

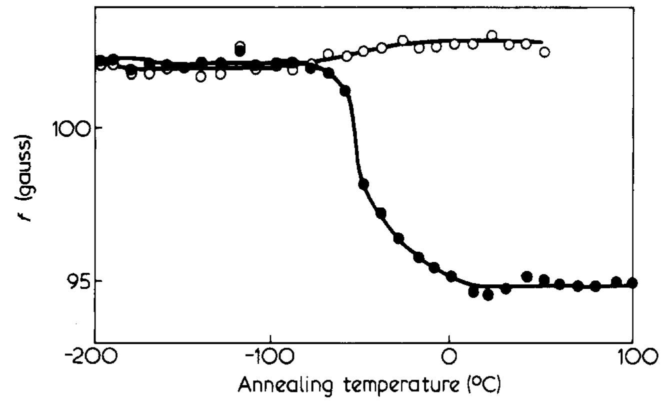


Figure 3 Change of line shape parameter with temperature. ○, Sample I; ●, Sample II

30°C for sample II containing PBN. This change clearly indicates that the spin trapping reactions takes place at – 70°C and are complete at 30°C.

Figure 4 shows the change of radical concentration with annealing temperature for the sextet and the triplet spectrum for sample II. Three steps of radical decay are observed as shown in the figure by the arrows. The final step of radical decay (step III) takes place at about – 80°C and this decay has been attributed to β-relaxation in polyethylene[5]

This spin-trapping reaction can also be treated as a competition reaction of the alkyl radical with the spin trap and another radical as follows.

$$-\mathrm{d}c_a/\mathrm{d}t = k_1 C_a^2 + k_2 C_a C_t \qquad (1)$$

$$-\mathrm{d}c_t/\mathrm{d}t = k_2 C_a C_t \qquad (2)$$

where k_1 is the rate constant of recombination reaction of the alkyl radical, k_2 is the rate constant of the spin trapping reaction, C_a is the concentration of the alkyl radical, and C_t is the concentration of the spin trap. k_1 can easily be estimated from the equation of the second order reaction.[6] k_2 was calculated by computer by the Runge-Kutta-Gill method. *Figure 5* shows the Arrhenius plot of k_2. This plot can be regarded as a linear line which has a breaking point at 35°C. The activation energy of the spin trapping reaction calculated from the slope of the plot was found to be 1.5 and 5.4 kcal/mol below and above the breaking point, respectively. This change in the activation energy suggests a change in the mechanism of the spin trapping reaction. Below 35°C it can be considered that alkyl radicals were trapped by the traps which are located very near to the alkyl radical. Above 35°C the trapping reaction may possibly proceed by the reaction between the alkyl radical and the trap which tumbles and diffuses through a polymer matrix. This deduction is supported by the fact that the spin probe (2,2,6,6-tetramethyl-4-piperidinol-1-oxyl) having similar size to that of PBN diffuses through in LDPE above 20°C).[7]

Figure 6 shows e.s.r. spectra of spin labelled LDPE, formed by the spin trapping reaction. At low temperatures

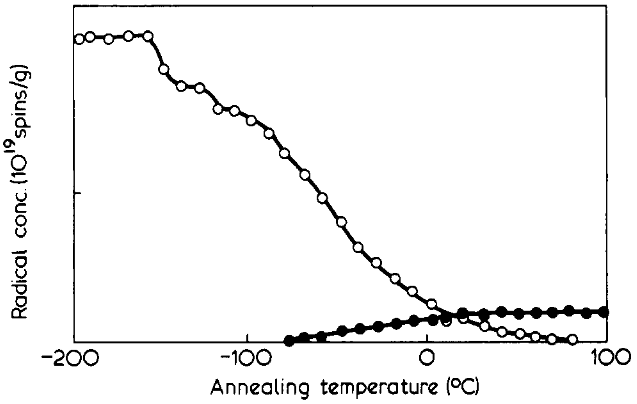


Figure 4 Change of radical concentration with annealing temperature. ○, sextet; ●, triplet

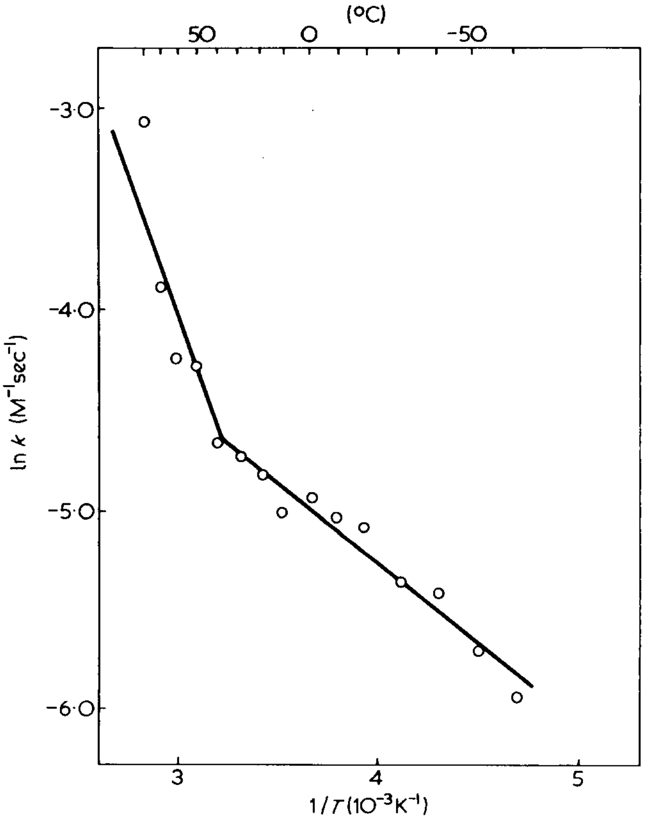


Figure 5 Arrhenius plot of k_t

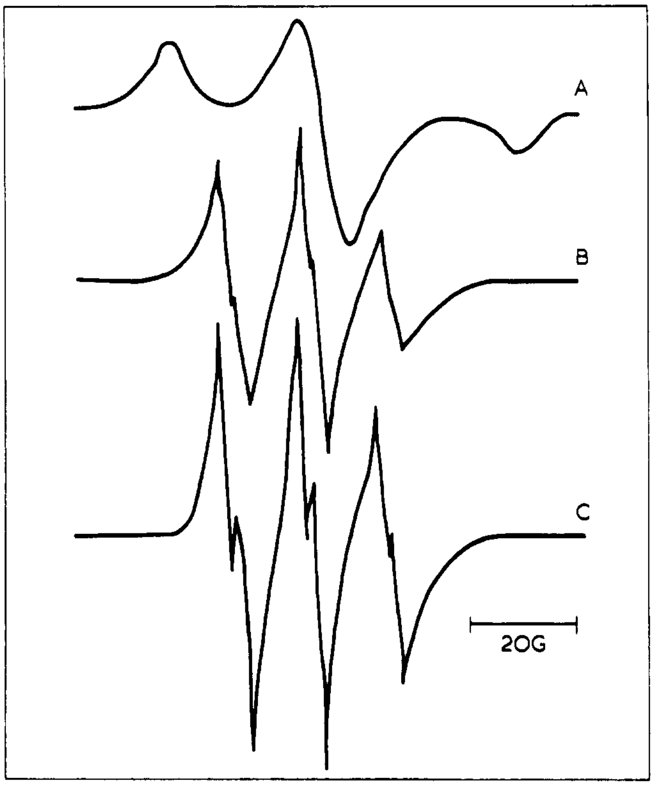


Figure 6 E.s.r. spectra of PBN-labelled LDPE at various temperatures. (a), – 110°C; (b), 90°C; (c), –110°C

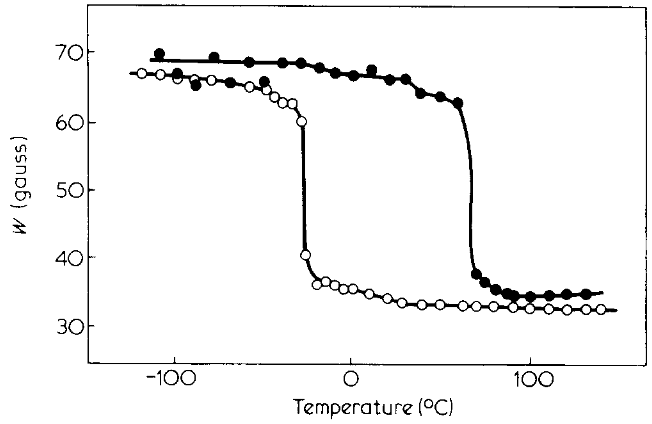


Figure 7 Change of line separation with temperature. ○, spin probe; ●, PBN-labelled

the spectrum has a broad asymmetric line shape, indicating that the label is in an immobilized state (*Figure 6a*). The line becomes sharper and the line separation narrows as temperature increases (*Figure 6b*). At 110°C the triplet changes into a triplet of doublets (*Figure 6c*).

This doublet may be caused by the β-proton in the label, whose interaction is masked by the line width of the triplet below 110°C.

Figure 7 shows the temperature variation of the separation of the triplet. The result of the spin probe method is shown in the same figure. It is found that a small narrowing takes place at about – 20°C and rapid one at 67°C. Comparing the result of the spin label with that of the spin probe, it is noted that the narrowing temperature is considerably shifted to higher temperatures by formation of a chemical bond between the radical and the host polymer. In the previous paper we proposed a theory on the relation among the narrowing temperature $T_n(\simeq T_{50G}$, T_g and the molar volume ratio of the segment of the host polymer to the probe[8] and this theory was experimentally proved.[9,10] According to this theory, this increase in T_n value is attributed to the mechanism that larger activation volume for jumping of the radical site into an adjacent hole becomes necessary for formation of spin labelled segement of host polymer.

References

1 Kusumoto, N. Reports on Progress of Studies in Facility of Japan Atomic Energy Research Institute 1975, p 138
2 Kusumoto, N. ibid. 1976, p 138
3 Kusumoto, N. ibid. 1977, p 132
4 Lawton, E.J., Balmit, J.S. and Powell, R.S. *J Chem Phys* 1960, **33**, 359
5 Kusumoto, N. and Haga, Y. *Polymer* 1975, **16**, 231
6 Nagamura, T., Kusumoto, N. and Takayanagi, M. *J Polym Sci* 1973, **11**, 2357
7 Kusumoto, N., Inoue, T. and Hamada, K. *Rep. Progr. Polym Phys Jpn* 1979, **22**, in press
8 Kusumoto, N., Sano, S., Zaitsu, N. and Motozato, Y. *Polymer* 1976, **17**, 448
9 Kusumoto, N., Sano, S. and Kiljima, T. *Rep Progr Polym Phys Jpn* 1977, **20**, 519
10 Kusumoto, N. Midland Macromolecular Monographs, Volume 8, published for MMI Press by Harwood Academic Publishers GmbH, Chur, Switzerland, 1979

Excimer and charge transfer complex trapping of excitons in carbazole containing polymers

S. Beck, A. Hallam and A.M. North
Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow G1 1XL, UK
(Received 15 June 1979)

The carbazolyl chromophore can confer photo-activity on a polymer, and a number of such polymers have been studied.[1] Of these poly(N-vinyl carbazole) is the most important technically, and shows very efficient excimer formation and exciton migration characteristics. When the carbazolyl chromophore is attached to the backbone by a spacing group (as in a series of carbazolyl substituted methacrylate polymers) both excimer formation and exciton migration are reduced. Poly(2-(9-ethyl) carbazolyl methyl methacrylate), **I**, exhibits excimer formation without long range exciton migration [1],and as such forms a useful reference material for the study of excimer trap characteristics. Poly(9-carbazolyl methyl methacrylate), **II**, forms charge transfer complexes with tetracyano ethylene (TCNE), but exhibits no appreciable excimer emission or exciton migration.

In this preliminary communication we report the progress of continuing study of these phenomena.

Excimer characteristics

The absorption and emission spectra of the polymer are illustrated in *Figure 1*. The fluorescence from 'monomeric'

0032-3861/79/101177-03$02.00