A STUDY OF THE EFFECT OF HIGH ENERGY IRRADIATION UPON THE INTERNAL MOTION OF POLYETHYLENE BY PULSED NMR METHOD

BY

Takao KAWAI

ABSTRACT

The internal motions of both the unirradiated and the irradiated polyethylene were investigated by measuring the spin-lattice relaxation-time (T_1) inclusive of its minima (T_{1min}) of proton in the temperature range from liquid nitrogen up to about 300°C by pulsed NMR method at 25 Mc/sec.

For the unirradiated polyethylene, two minima of T_1 were observed: one at the higher temperature corresponding to the internal motion in the crystalline region, and the other at the lower temperature corresponding to the internal motion in the amorphous region of the sample.

For the irradiated polyethylene, the increase in the value of T_1 and the flat V-shaped curve were observed at the comparatively weaker irradiations. For stronger irradiations, however, the value of T_1 decreased and only a single T_{1min} was observed.

These results can be qualitatively explained by the effects of both the cross-linkings and the loss of crystallinity by irradiation.

1. Introduction

Many investigations have been published for both the unirradiated and the irradiated polyethylene (1, 2, 3).

Among others, the effect of high energy irradiation upon the dynamic-mechanical properties and nuclear magnetic resonance (NMR) behavior by steady-state method has been extensively studied, for both the branched or low-density polyethylene and the linear or high-density polyethylene (4, 5, 6, 7).

These researches are summarized in a recent review by Sauer and Woodward (8).

However, the NMR method which has been widely used is the steady-state method by which we can measure the line-width, the second moment, and the line-shape. Only a few works have been performed on the spin-lattice relaxation time (T_1) of proton for the unirradiated polyethylene (9), but nothing for the irradiated one. So we have performed more precise investigations about the internal motions of the unirradiated and the irradiated polyethylene by measuring T_1 of proton in a temperature range as wide as possible. The detailed

descriptions of the used samples, the experimental method and the results, and
also the discussions will be given below.

2. Samples

The original or unirradiated polyethylene used was of medium-pressure, and
high-density type (Marlex 50, manufactured by the Phyllips Petroleum Company).
The material was compressed into moulded tips to have the required dimensions
for NMR measurement. Those samples had the room-temperature density of
0.96 g/cm³, a degree of crystallinity of approximately 93%, an average molecular
weight of 35000, and a melting point from 134 to 135°C. Those samples were
irradiated in the air at a room temperature by means of Van de Graaff accelerator
at 1.5 MeV, 100 μA in intensity. They received the following irradiations; a)
1×10^6 r, b) 9×10^6 r, c) 2.7×10^7 r, d) 9×10^7 r, e) 2.7×10^8 r, and f) 5×10^8 r, respec-
tively.

3. Experimental method and results

To measure T_1 of proton for the unirradiated and the irradiated polyethylene,
the conventional 90°–90° pulse method was used (10, 11).

The experiments were performed at 25 Mc/sec. Details of the apparatus
have already been given in this Memoirs (12, 13). The obtained data on the
temperature dependence of T_1 for the unirradiated and the irradiated samples
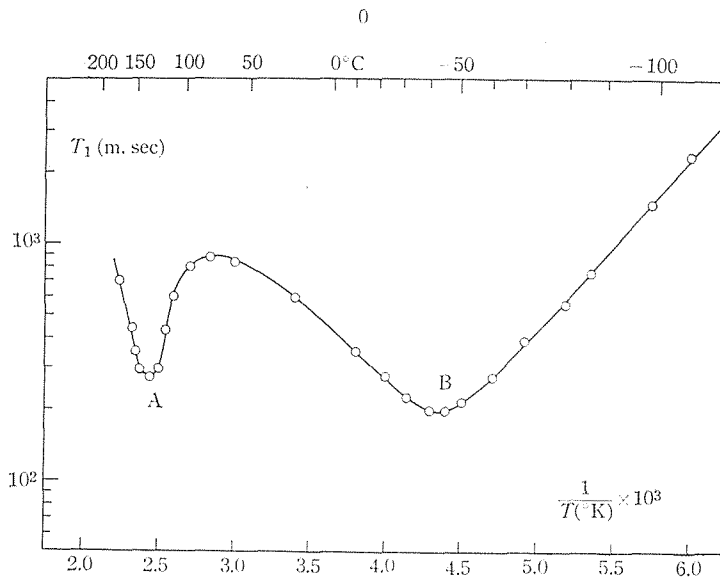are given in Figs. 1~7.

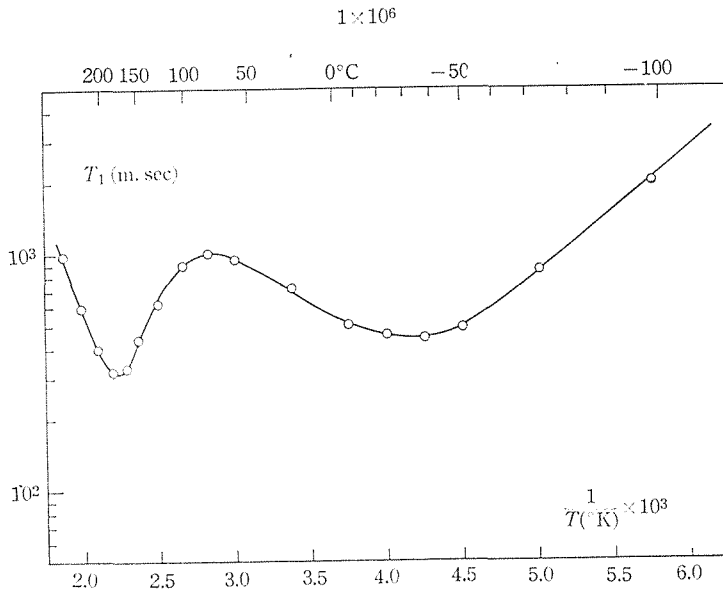Fig. 1.   Temperature dependence of T_1 of proton in PE.
(0 r)

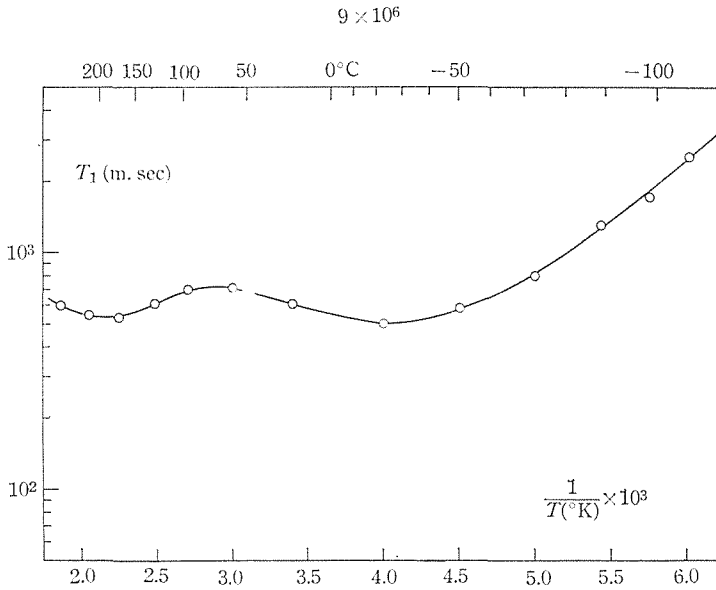Fig. 2.   Temperature dependence of T_1 of proton in PE.
$(1 \times 10^6 \text{ r})$

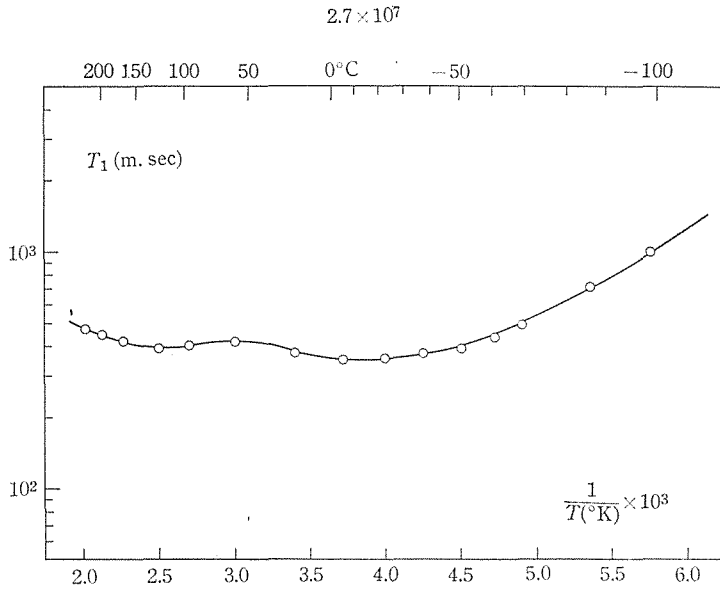Fig. 3.   Temperature dependence of T_1 of proton in PE.
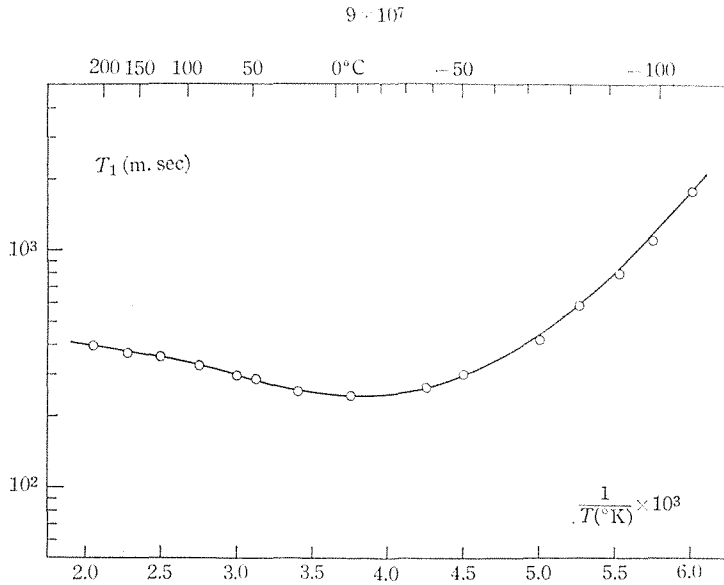$(9 \times 10^6 \text{ r})$

2.7×10^7

Fig. 4.   Temperature dependence of T_1 of proton in PE.
$(2.7 \times 10^7 \text{ r})$

9×10^7

Fig. 5.   Temperature dependence of T_1 of proton in PE.
$(9 \times 10^7 \text{ r})$
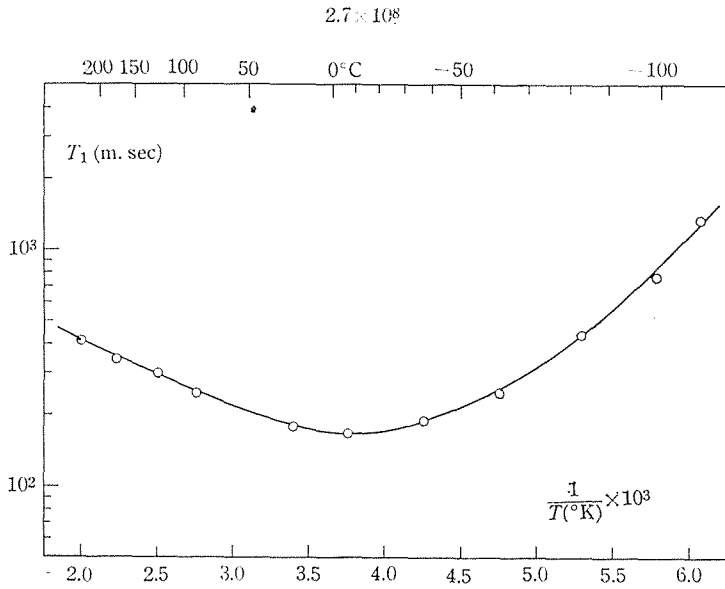
2.7×10^8

Fig. 6. Temperature dependence of T_1 of proton in PE.
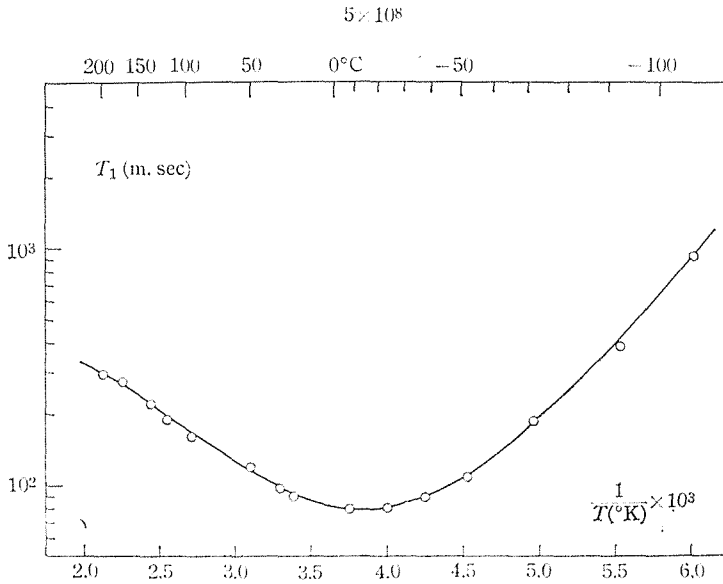$(2.7 \times 10^8 \text{ r})$

5×10^8

Fig. 7. Temperature dependence of T_1 of proton in PE.
$(5 \times 10^8 \text{ r})$

The estimated error of the measured T_1 was about 10% above room temperature, but for lower temperature range it became worse up to about 30% due to the weak signal and the short free induction decay-time (T_2), and partly due to the transition between the "amorphous" and the "crystalline" modes.

In the case of Marlex 50, the signal shape of the free induction decay following the 90° pulse changed with the temperatures from 0°C to −100°C.

This fact corresponds to the change in the derivative line-shape obtainable by the steady-state method.

It is interesting to note that a considerable difference exists in the signal shapes of the free induction decay, between such partially crystallined high polymers as Marlex 50 and the almost amorphous ones previously studied (15).

4. Discussions

To interpret the data on T_1, we follow the BPP theory which is based on the assumption of a single correlation-time (16, 17), and consider that one mode of the internal motion corresponds to one V–shaped part of the curve T_1 *versus* $1/T$.

Thus, first, the V–shaped part of curve at higher temperatures marked with A in Fig. 1 for the unirradiated polyethylene corresponds to the motions in the "crystalline" region of the polymer.

Next, the V–shaped part at lower temperatures, marked with B, in which a minimum of T_1 occurs at about −45°C is due to the motions in the "amorphous" region of the sample.

By other experimental techniques, such as infrared spectroscopy, an X–ray diffraction etc., it has been proposed that Marlex polyethylene consists mainly of unbranched polymethylene chains, of which each one terminates at one end in a vinyl group and at the other end in a methyl group. Such a structural regularity results in a highly crystalline and dense polymer.

Meanwhile, from NMR experiments by the steady-state method (4, 5, 6, 7, 8), it has been reported that the derivative line-shapes for the unirradiated polyethylene are complex below room temperature, and suggested that one can consider those derivative lines as a superposition of two components, one broad and weak, and the other narrow and intense, and further that the broad part of the line is associated with the crystalline phase of the polymer and the narrow component with the amorphous phase.

As already pointed out in the papers by Hahn (10, 11), our apparatus cannot detect the nuclear resonance signal due to protons in the rigid state. Furthermore, the samples used in our experiments consisted of the linear polyethylene

Marlex 50, with high density and high crystallinity, so it is reasonable that they cannot contribute much to the nuclear resonance signal due to protons at temperatures lower than about 0°C.

This conclusion coincides with the experimental facts by many workers that the more crystalline the material is, the more restricted are the motions of the amorphous regions and thus the higher becomes the temperature necessary to bring about the considerable chain motions in these lower temperature regions.

The T_1 minimum observed in the data in Fig. 1 at higher temperatures is associated with the large-scale chain motions of molecules. This circumstance can arise when the crystalline regions undergo a melting or some other first order transition.

Now, we consider the application of the BPP formula based on a "single correlation-time (τ_c)" to the mode of the internal motion which arises from the "amorphous" part of the polymer marked with B in Fig. 1. Although some difficulties are expected if we attempt to analyze the behavior in these temperature regions, we have tentatively used the BPP theory for the analysis (14), namely;

$$\frac{1}{T_1} = \frac{3}{10}\frac{\gamma^4\hbar^2}{b^6}\left\{\frac{\tau_c}{1+\omega^2\tau_c^2}+\frac{4\tau_c}{1+4\omega^2\tau_c^2}\right\}, \quad \tau_c = \tau_0 \exp\left(\frac{\Delta E}{RT}\right),$$

where b is the "effective" interproton distance, that is, an appropriate average of the distance between protons which are effective for the relaxation, τ_c is the correlation-time of the motion, and ΔE the activation energy. The analyzed results are as follows:

$$b = 2.5 \text{ Å} \quad \text{and} \quad \Delta E = 3.6 \text{ Kcal/mol.}$$

As to these results, we noticed that the value of 2.5 Å is somewhat larger than that estimated from the consideration of molecular structure of polyethylene, based on the view of "planar zigzag" configuration, and the activation energy ΔE is smaller than that derived from the second moment by the steady-state method.

It may be necessary to consider the existance of the distribution of correlation-times for the internal motions due to amorphous regions. In general, both the increase in the value of T_1 and the flatness of the V–shaped curve are to be expected when we take the distribution of correlation-times into account, as seen in our previous paper (19).

Now, we shall discuss the case of the irradiated polyethylene. Before attempting to analyze the experimental data in Figs. 2~7, it is desirable to consider the various influences of irradiation upon the molecular motion that may exist in the polyethylene. Here, some remarks must be made about the effect of free radicals

upon the value of T_1 for the irradiated polyethylene. Our test showed no difference in the value of T_1 within the experimental errors between the annealed and the non-annealed irradiated samples.

The two most important restricting influences upon the chain motion by a large amount of the high energy irradiation are: (i) the irradiation-induced cross-linking and (ii) the loss of crystallinity.

In order to explain the behavior of T_1 of the irradiated polyethylene from Figs. 2~7, it will be sufficient to discuss how the above two effects are produced in the "amorphous" and the "crystalline" phases of the polymers. These two effects are opposite in tendency; the first tending to tighten the chain structure and the second to loosen it. The increased value of T_1 observed in Figs. 2~4 is due to the predominant effect of the cross-linking over the crystallinity loss at the weaker irradiations: 1×10^6 r, 9×10^6 r, 2.7×10^7 r, and then the reverse effect was observed at the stronger irradiations: 9×10^7 r, 2.7×18^8 r, 5×10^8 r.

Further, we observed the shift to the higher temperature side of $T_{1\,\mathrm{min}}$, which has been originally observed at 135°C in Fig. 2, the increase in the value and the flattened curves of T_1 as shown in Figs. 2~4, which are due to the restraints imposed by the cross-linking on the motions in the amorphous regions. The disappearance of $T_{1\,\mathrm{min}}$ near 135°C occurs at about 2.7×10^7 r irradiation, and this fact is due to the loss of crystallinity. At a considerable amount of irradiation, for instance, as seen from the data in Fig. 7, the effect of the loss of crystallinity largely exceeds the effect of cross-linkings.

5. Conclusions

We could clearly separte the two modes of internal motions of the highly crystalline high polymer (Marlex 50, polyethylene), caused in the "amorphous" and the "crystalline" phases of the polymer, by measuring T_1 of proton resonance by the pulsed NMR method. We could not discuss our data quantitatively, because of the complex natures of partially crystalline high polymers, the lack of both the suitable formula (theoretical and experimental) to analyze the irradiated polyethylene and the precise experimental data (particularly in the lowest temperature range). For further discussions, experiments on the samples with various crystallinity would be necessary, and they must be irradiated in vacuum if possible. But our results are excellently consistent with other experimental data, such as obtained by dynamic-mechanical or steady-state NMR method, and we believe that our results are more direct for the understanding of internal motions for the samples, irradiated and unirradiated.

Finally, it may perhaps be unnecessary in our NMR method to consider the

effect by a considerable amount of fairly stable free radicals that would be produced in the process of high energy irradiation on high polymer, though it might be an important object that must be investigated in the field of irradiation effects by the electron spin resonance (E.S.R.) method (20, 21).

Acknowledgements

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