Proton Resonance in Oil Paraffin

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Introduction

Wilson and Pake[1] proposed a nuclear magnetic resonance method to determine the degree of crystallinity of linear polymers and made an extensive study of the resonance line shape and the spin lattice-relaxation time of polytetrafluoroethylene, 'Teflon.'[2] Though their method is quite straightforward and seems useful for the structural study of linear polymers, further investigations of this method seem necessary, and the present authors have planned to make proton resonance study of oil paraffin which is one of the most typical linear polymers with simple molecular structure and structurally well studied[3].

Experimental

Samples. — Samples investigated are commercial oil paraffins and microcrystalline paraffin waxes. The samples of the former are seven species, from No. 1 to No. 7, differing in their melting points by about 5°F from one another in the range from 115°F (47.7°C) to 145°F (62.8°C); samples from No. 1 to No. 4 are 1 : 1 mixtures of two kinds of crude oil paraffin produced in Ceria and Southern Sumatra, and those from No. 5 to No. 7 are the ones produced in Southern Sumatra.

Apparatus. — The apparatus used for the proton resonance measurement is one of the autodyne—detector type with a narrow band amplifier and phase sensitive detector. The schematic diagram and some descriptions of the apparatus were given elsewhere.[4] The magnetic field applied is of about 4,000 gauss produced by an electromagnet which is charged by storage batteries. The inhomogeneity of the magnetic field over the specimen is about 50 milligauss. Derivative curves are recoreded automatically by the field modulation, whose amplitude is about 0.3 gauss.

Measurement.—For the measurements at room temperature, the oil paraffin specimens are made into rods of 5 mm$\phi \times$15 mm and mounted in a *rf* coil whose axis is perpendicular to the magnetic field. The microcrystalline waxes are sealed in glass tubes with diameters of 5 mm. For the measurements of temperature dependence of the resonance, samples sealed in glass tubes of 3 mm. diameter are mounted in *rf* coil, inserted in a Dewar vessel, and warmed up by a heater. To get the temperature equilibrium in the vessel, about half an hour was taken before the onset of the measurement at each temperature. The temperature range investigated is from room temperature to just below the melting point of the sample. Temperature measurements were made by a copper—constantan thermocouple with one junction 5 mm. apart from the sample.

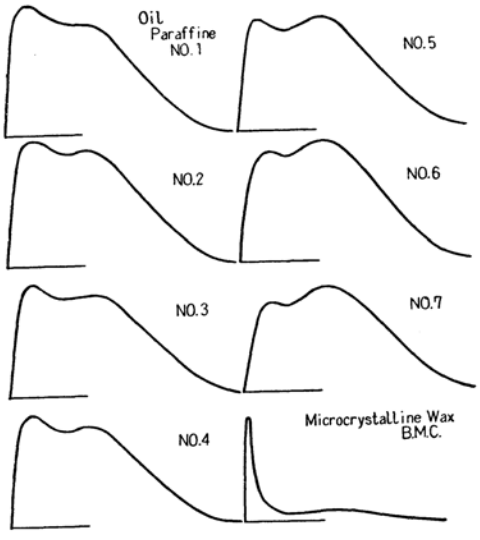

Fig. 1. Experimental derivative curves (at room temperature).

Results and Discussion

Fig. 1 shows the derivative curves of the proton resonance absorption lines at room temperature. According to Wilson and Pake, a resonance curve with the line shape as shown in Fig. 1 may be assumed as a superposition of two lines;[1] a very narrow and a broad one. With the results of their investigations of line shape and relaxation time, they concluded that such a structure of the resonance line was due to coexistence of two components in the sample;[2] one is motional and amorphous and the other rigid and crystalline. According to their proposal, our results may

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[1] C. W. Wilson III and G. E. Pake, *J. Polymer Sci.*, **10**, 503 (1953).

[2] C. W. Wilson III and G. E. Pake, *J. Chem. Phys.* **27**, 115 (1957).

[3] A. Müller, *Proc. Roy. Soc.*, **A 120**, 437 (1928); **A 127**, 417 (1930).

[4] S. Fujiwara, S. Hayashi and G. Hattori, *J. Chem. Soc. Japan, Ind. Chem. Sec.*, **59**, 803 (1956).

be treated as shown in Fig. 2, where the derivative curve is decomposed into two parts with the assumption that the line shape of the narrow part is of Gaussian type. In Fig. 2, two components with narrow line-width and with broad one are referred to I and II, respectively. The line-width, ΔH, defined as the separation between the maxima of the derivative curve, and the second moment, $\langle \Delta H^2 \rangle$, are measured for component II (see Figs. 3 and 4).

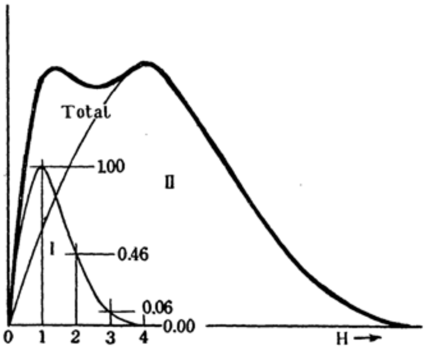

Fig. 2. Decomposition of experimental derivative curve. Experimental curve is decomposed with the assumption that the Part I of the absorption curve is of *Gaussian* type.
▬ Experimental curve
— Decomposing curve

The weight percent. of the component II, X_{II}, is also calculated from the area occupied by II in the integrated absorption line (Fig. 5), which is referred to the degree of crystallinity as defined by Wilson and Pake.[1] The correlation time, τ_c or $(1/\nu_c)$, characteristic time scale for the molecular motion which causes the motional narrowing of the line-width, is calculated from the line-width (Fig. 6). In practice, we made a calculation of the correlation time with the assumption that the ΔH value for normal paraffin in rigid state was 15 gauss, being equal to the value for rigid polyethylene.[5]

Since the correlation time, $(1/\nu_c)$, may be related with temperature as $(1/\nu_c)=(1/\nu_0)\exp(V/kT)$,[6] where $(1/\nu_0)$ is a time constant characteristic of the sample, the activation energy V for the molecular motion in the sample to cause the narrowing of the line-width may be calculated by the measurements of the temperature dependence of the line-width.

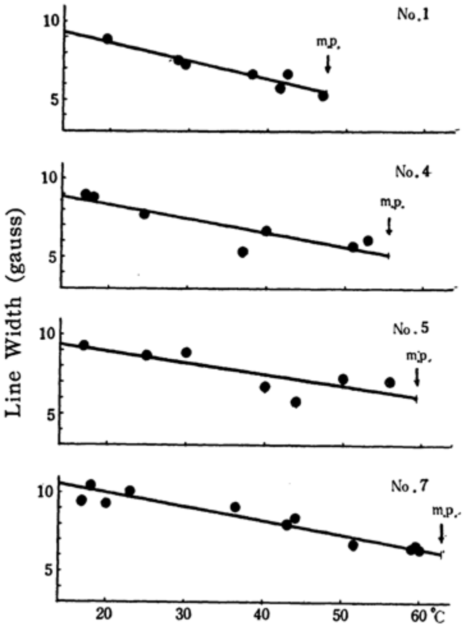

Fig. 3. Temperature dependence of the line widths. $(\Delta H)_{II}$

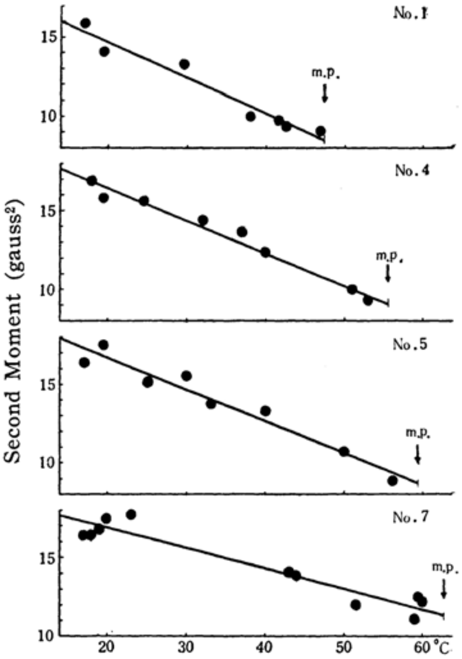

Fig. 4. Temperature dependence of the second moments. $\langle \Delta H^2 \rangle_{II}$

The experimental results of $(\Delta H)_{II}$, X_{II}, and $\langle \Delta H^2 \rangle_{II}$ at 19°C and V_{II} are listed in Table I, and the data of temperature dependence depicted in Figs. 3, 4, 5 and 6, where the straight lines are obtained from about ten adequate points for each sample

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[5] A. Nishioka, private communication.

[6] H. S. Gutowsky and L. H. Meyer, *J. Chem. Phys.*, **21**, 2122 (1953).

TABLE I

Samples	m. p. °C	$(\Delta H)_{\mathrm{II}}$* gauss	$\langle\Delta H^2\rangle_{\mathrm{II}}$* gauss^2	X_{II}* %	V_{II} kcal./mol.
No. 1	47.7	8.8	14.1	92.9	3.6
2	50.4	9.7	15.7	96.7	—
3	52.9	9.6	16.0	96.7	—
4	55.6	9.8	15.8	96.3	2.8
5	59.4	10.2	17.1	98.0	2.4
6	60.8	10.2	17.0	97.6	—
7	62.8	10.5	16.6	97.0	2.5

* at 19°C

by the method of least squares, and the suffix II refers to the data for the component II.

Findings in Table I and Figs. 3, 4, 5 and 6 may be summarized as follows: first, there seems to be intimate correlation between the nuclear magnetic resonance data, such as $(\Delta H)_{\mathrm{II}}$ and $\langle\Delta H^2\rangle_{\mathrm{II}}$, and the composition of the samples; second, $(\Delta H)_{\mathrm{II}}$ values are reduced gradually with temperature and become about 6 gauss just below the melting point; third, X_{II} values are not much reduced with temperature; lastly, the magnitudes of the activation energies V_{II} are almost equal to one another among the samples with the value of 2—3 kcal./mol.

According to the first finding, $(\Delta H)_{\mathrm{II}}$ and $\langle\Delta H^2\rangle_{\mathrm{II}}$ values for the samples with higher melting point are larger than those with lower melting point. This may suggest that the component II in the samples with higher melting point is less motional than that in those with lower melting point. In another words, line-width data of the component II may be useful for the qualitative analysis of the melting point.

The second finding on the temperature dependece of the line-width of component II seems valuable to answer the question, "What kind of molecular motion would occur prior to melting of linear polymers?" Information we have had so far for this problem by any method such as dielectric measurements is rather insufficient.[7] According to the present results, as seen in Fig. 3, the molecular motion in component II increases with temperature, but the magnitude of this motion, of vibrational or diffusional nature, appears to be small* and the molecular state to be relatively close to the rigid lattice state up to melting.

As shown by one of the present authors,[9] the difference in the line-width, and consequently in the correlation time, among the samples with the same magnitude of V is attributed to the difference in the degree of polymerization among the samples. Thus the difference in line-width or correlation time among the samples No. 1, 4, 5 and 7 seems to be attributed to the difference in their molecular dimensions.

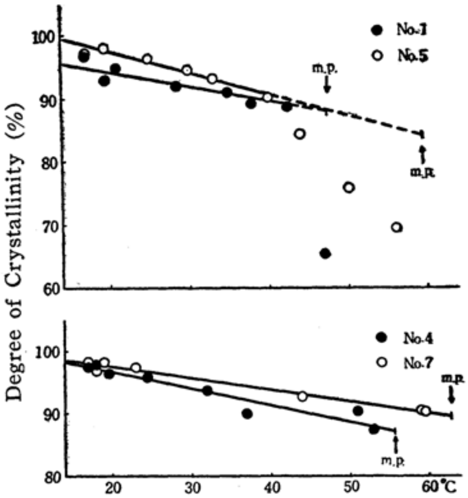

Fig. 5. Temperature dependence of the degree of crystallinity. $X_{\mathrm{II}}\%$.

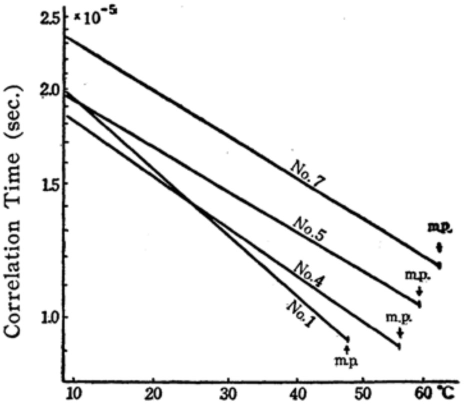

Fig. 6. Temperature dependence of the correlation time. $1/\nu_c$.

It is noted, especially, that the degree of crystallinity, X_{II}, is not much reduced prior to melting. This will suggest that the molecules maintain relatively rigid configurations between the nuclear nearest neighbors up to melting.

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[7] R. F. Boyer, *J. Appl. Phys.*, **25**, 825, (1954).

* Magnetic dipolar broadening of the line-width value is easily reduced to one half or one third of the rigid lattice value by any molecular rotation[8]. In the present results, the $(\Delta H)_{\mathrm{II}}$ values are ranged around 6 to 10 gauss, which are compared with the rigid value of 15 gauss.

[8] E. R. Andrew, *J. Chem. Phys.*, **18**, 607 (1950).

[9] S. Fujiwara, to be published in this Bulletin.

Throughout the cases of the experiments, it was also found that both line-width and second moment values kept sizable magnitudes up to just below the melting point. These findings are very prominent and in contrast to the result on cyclohexane, where rapid decrease of the second moment occurs 130°C prior to melting.[10] Namely, in the latter case, the molecular reorientation with fixed center of mass occurs 130°C prior to melting, whereas in the former, the molecules are relatively static up to just below the melting point.

The degree of crystallinity of microcrystalline paraffin waxes is much smaller than that of oil paraffins, and is about 90% at room temperature. This result perhaps shows the segments in microcrystalline waxes are much smaller and easier to diffuse in the sample than that in oil paraffins.

Many thanks are due to Mr. Kenzo Fusegawa of Dai Nippon Seiro Co., who gave us the samples used in the present experiments.

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10) E. R. Andrew and R. G. Eades, *Proc. Roy, Soc.*, **A 216**, 398 (1953).