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# NMR PULSE APPARATUS AND ITS APPLICATION TO THE INVESTIGATION OF INTERNAL MOTION OF HIGH POLYMER (POLY-PROPYLENE)

BY

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## ABSTRACT

After detailed report in this Memoirs of a NMR pulse apparatus, some improvements were made on the apparatus. The first part of this paper deals with the construction of the improved parts and the second part with the application of the improved apparatus to the investigation of the internal motion of high polymer (poly-propylene). As a result, we could definitely separate the internal motions of poly-propylene, into the segmental motion, and the internal motion of methyl groups. The experimental data about the spin lattice relaxation time ( $T_1$ ) for internal motion of methyl groups were analysed following BPP theory, and  $b$ ,  $\tau_0$  and  $\Delta E$  were determined to be 2.2 Å,  $4 \times 10^{-12}$  sec and 1.9 Kcal/mol respectively.

## 1. Introduction

The spin lattice relaxation time ( $T_1$ ) in nuclear magnetic resonance (NMR) is a very useful quantity for investigations of the dynamical character of substances. To measure  $T_1$  of proton, particularly in high polymers, we had constructed a NMR pulse apparatus, whose detailed description was already reported in this Memoirs (hereafter referred to as I) (1). Some results obtained by using that apparatus to investigate the sorbed water (2) and the segmental motion of some high polymers (3) were also reported. In performing experiments we realized the necessity to improve the apparatus such that the stability of apparatus is increased, the stronger rf pulse is obtained, and  $T_1$  at lower temperatures (at least, as low as liquid nitrogen temperature) and the spin echo decay time ( $T_2$ ) can be measured.

In the first part we shall report the construction of the improved apparatus, though there are several papers published about the NMR pulse apparatus, (4, 5, 6), since the data on  $T_1$  for various substances are now demanded by many researchers and the apparatus for measuring  $T_1$  is not fully commercialized.

In the second part we shall describe the application of this improved NMR apparatus to the investigation of the internal motion of poly-propylene, as a





the capacity of low capacitance coaxial cable about 40 cm long, a variable condenser, and the output capacity of power tube (Eimac 4-125A), to constitute a resonance circuit of 25 Mc/sec. This resonance circuit serve both as a plate load of the power tube and as an input circuit to the nuclear signal receiver. Eimac 4-125A seems to be the best choice for our purpose, owing to low output capacity and moderate power handling capacity. The pulse width for 90° pulse was about 5  $\mu$  sec.

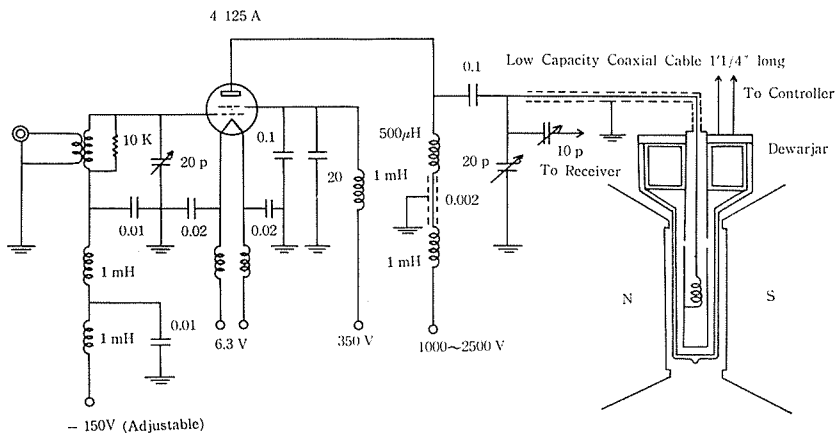


Fig. 4. Circuit diagram of final power amplifier and associated circuits.

#### (D) Delay III

This circuit was attached in order to measure the spin echo decay time ( $T_2$ ). If the time interval between the first pulse and the second is  $\tau$ , the spin echo signal appears after the time interval  $2\tau$  from the first pulse. The time delay of delay III should be equal to that of delay I. Delay III was a monostable multivibrator as was delay I, as described in I. R and C elements in both delays, which determine the time delay, have accuracy of 0.5% and are ganged. If the synchroscope trigger selector is set at 4 (Fig. 1), only the spin echo signal appears on synchroscope screen. This spin echo signal decays exponentially with the time constant  $T_2$ , when we vary the pulse interval  $\tau$ .

#### (E) Temperature controller

This is a commercial product. The voltage from the copper constantan thermocouple is compared with a pre-set standard voltage and the error voltage is used for automatic temperature control. The constancy of cryostat is about  $\pm 1^\circ\text{C}$  for a temperature range above room temperature and near the liquid nitrogen temperature, and falls to about  $\pm 3^\circ\text{C}$  between them, due to performance of the cryostat.

The procedure of measuring  $T_1$  was already reported in I. Accuracy in measuring  $T_1$  is about  $\pm 5\%$  under good S/N condition and about  $\pm 30\%$  or more under bad condition (such as at lower temperatures in the present case).

Now, we consider the nuclear signal amplitude just after the first pulse ( $y_1$ ). In principle,  $y_1$  is proportional to the number of resonant nuclei. However, our apparatus cannot detect the nuclear signal of protons in rigid state. This is because the pulse width for  $90^\circ$  pulse ( $t_w$ ) is not so narrow and the receiver recovery time ( $t_{\text{dead}}$ ) is not so small as to detect the resonance signal of protons in rigid state. Rough estimation can be made as follows. Assume that the resonance line can be described by Bloch equation with  $T_1$  of infinity and  $T_2$  of  $2/\gamma \cdot \Delta H_{1/2}$  (11) (which is a very rough approximation in solid (12)), and further assume an exact resonance excitation. Then, the ratio of apparent nuclear signal amplitude just after the first pulse for broad line (long  $T_2$ ) to that for narrow line (short  $T_2$ ) becomes  $\exp(-t_w/2T_2) \cdot \exp(-t_{\text{dead}}/T_2)$  (13). Inserting the values  $t_w = 5\mu$  sec,  $t_{\text{dead}} = 15\mu$  sec and  $\Delta H_{1/2} = 10$  gauss (typical values for proton in rigid state), we obtain the value of 0.1. So we can roughly consider that  $y_1$  is proportional to the number of moving protons. The accuracy in measuring  $y_1$  is not so good and about  $\pm 30\%$ , since  $y_1$  critically depends on various factors, such as resonance condition,  $90^\circ$  pulse setting, filling factor of the sample, etc. However, careful measurement of  $y_1$  is very helpful for interpreting the data on  $T_1$ , as in the study of the sorbed water (2) and in the present case (see below).

### 3. Study of internal motions of poly-propylene

As an example of the application, we shall report the investigation of the internal motion of poly-propylene (PP) ( $-\text{CH}_2-\text{CHCH}_3-$ ) $_n$ . This polymer has been already studied by steady state NMR method by several workers (14, 15, 16, 17). Their main interests consisted in effects of crystallinity, steric configuration and segmental motion near glass transition temperature on NMR line width. We have studied the internal motion of this polymer, particularly the internal motion of methyl groups. For this kind of study, the NMR pulse method is very powerful, as one of the authors (T. K.) reported concerning the study of internal motions of acryl and methacryl group high polymers (18).

The sample used was commercial product of Moplen M-2 manufactured by Montecatini Co. and kindly supplied through Dr. K. Hayashi of Japanese Association of Radiation Research on polymers. The degrees of tacticity and crystallinity of the sample were about 60~70%.

The experimental results of the temperature dependence of  $T_1$  and  $T_2$  of proton of PP are shown in Fig. 5, where plots of the values of  $T_1$  and  $T_2$  versus

$1/T$  are given on semi-logarithmic scale.  $T_2$  cannot be measured below  $70^\circ\text{C}$ , where no spin echo signal appears. The temperature dependence of  $y_1$  is also shown in Fig. 5 in linear arbitrary scale.

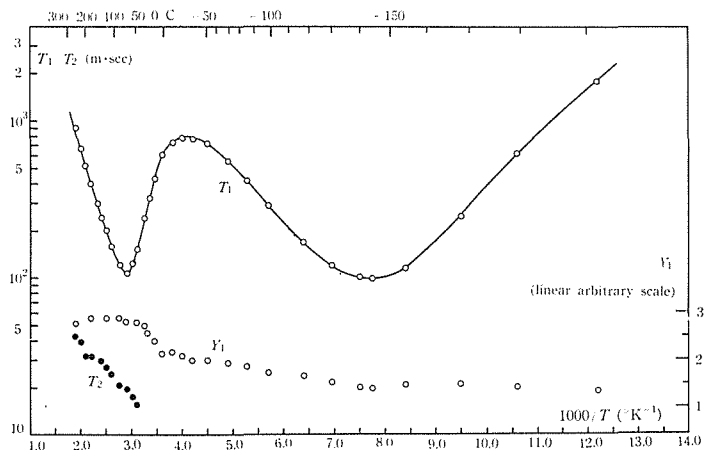


Fig. 5. Experimental data of temperature dependence of  $T_1$ ,  $T_2$  and  $y_1$  for proton of poly-propylene.

As to  $T_1$ , one V-shaped part of  $T_1$  versus  $1/T$  curve corresponds to one mode of internal motion, according to BPP theory (19), even if there would be a distribution of correlation time. In our experimental results, the V shaped part at higher temperatures corresponds to the segmental motion of PP, and that at lower to the internal motion of methyl groups. The data on temperature dependence of  $y_1$  supports this, since the experimental ratio of  $y_1$  at higher temperatures to that at lower was about 2:1, while this ratio is expected to be 6:3, considered from the molecular structure of PP. Our qualitative result about the internal motions in PP, which are occurring in each temperature range, is consistent with the results obtained by the steady state NMR method (14~17).

Now, we shall analyse the experimental result of the temperature dependence of  $T_1$  for internal motion of methyl groups, following BPP formula, based on "single correlation time ( $\tau_c$ )". According to it (19, 20),

$$\frac{1}{T_1} = \frac{3}{10} \frac{\gamma^4 \hbar^2}{b^6} \left\{ \frac{\tau_c}{1 + \omega^2 \tau_c^2} + \frac{4\tau_c}{1 + 4\omega^2 \tau_c^2} \right\},$$

where  $b$  is the "effective" interproton distance. Further we consider the internal motion in high polymers as an activation process, then

$$\tau_c = \tau_0 \exp\left(\frac{\Delta E}{RT}\right).$$

Considering  $b$ ,  $\tau_0$  and  $\Delta E$  as three adjustable parameters, we can analyse the data, that is, the minimum value of  $T_1$  gives  $b$ , and the temperature dependence of  $\tau_c$  gives  $\tau_0$  and  $\Delta E$ . The plots of  $\tau_c$  versus  $1/T$  are given in Fig. 6. The results of analysis are:  $b=2.2A$ ,  $\tau_0=4 \times 10^{-12}$  sec and  $\Delta E=1.9$  Kcal/mol for the internal motion of methyl groups in PP. These values are of the same order of magnitude as those obtained for alkyl groups in acryl and methacryl group high polymers (18).

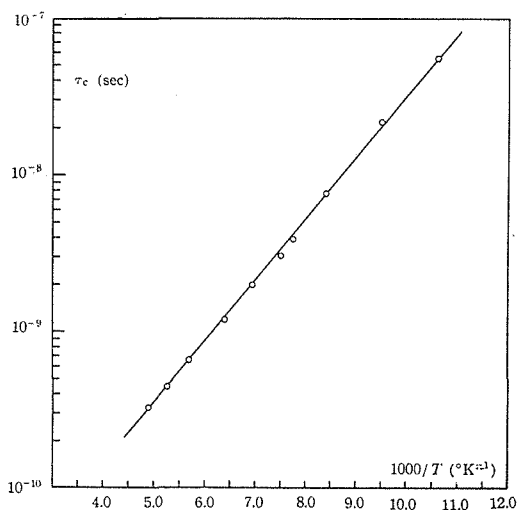


Fig. 6.  $\tau_c$  (obtained by BPP formula from data of  $T_1$ ) versus  $1/T$  for methyl group proton of poly-propylene.

As to  $T_2$ , no definite and significant conclusions could be obtained from the data. The data on  $T_2$  would be useful for such studies as on the sorbed water (2). It may be noted, however, that the value of  $T_2$  of proton in high polymers is by about one order of magnitude smaller than the value of  $T_1$  as in the case of the sorbed water (2).

The effect of crystallinity and steric configuration upon the value of  $T_1$  is not clear from our present study. We are planning to study the effect systematically by performing more accurate measurements on simpler and more refined samples.

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