

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

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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 , τ_0 and ΔE were determined to be 2.2 Å, 4×10^{-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

typical example of the study by using the NMR pulse apparatus.

2. Construction of improved apparatus

The whole block diagram of the improved apparatus is given in Fig. 1, where improved parts are shown by double boxes. Other parts are the same as reported in I. For measurements of T_1 and T_2 , the 90° - 90° pulse method was used (7). All experiments were performed at 25 Mc/sec, which corresponds to about 6000 gauss for proton. A detailed description of the improved parts are given below.

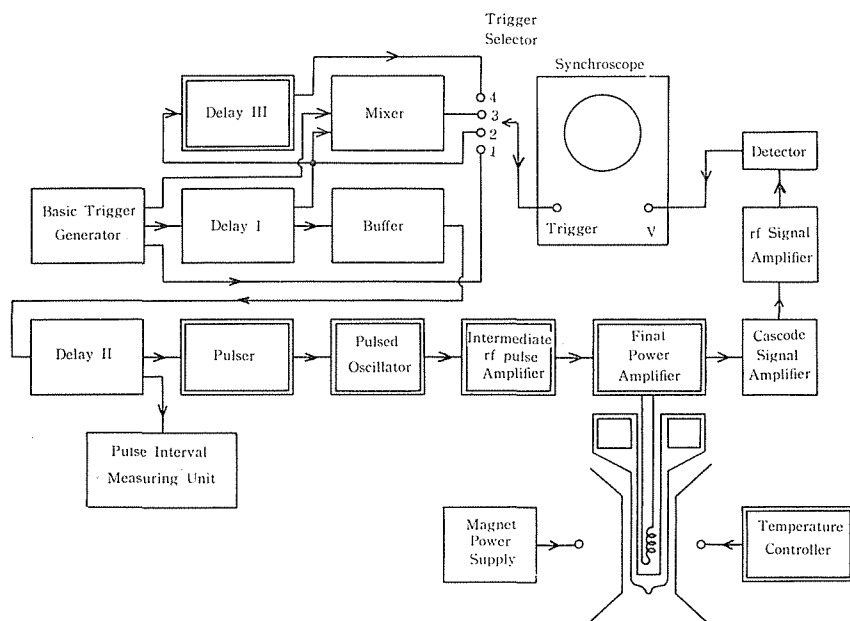


Fig. 1. Block diagram of the whole apparatus, where the improved parts are shown by double boxes.

(A) *Pulser and pulsed oscillator*

The circuit diagram is shown in Fig. 2. For pulser, a plate coupled monostable multivibrator with plate catching diode (8) is used, since it provides better performance than the previous one for narrow pulses. By proper choice of R and C elements, an appropriate pulse width for 90° pulse was obtained. Negative gate pulse from this pulser initiates oscillation of the next Hartley type pulsed oscillator (9). The rf pulse of small amplitude thus obtained is then amplified by the following amplifier stage.

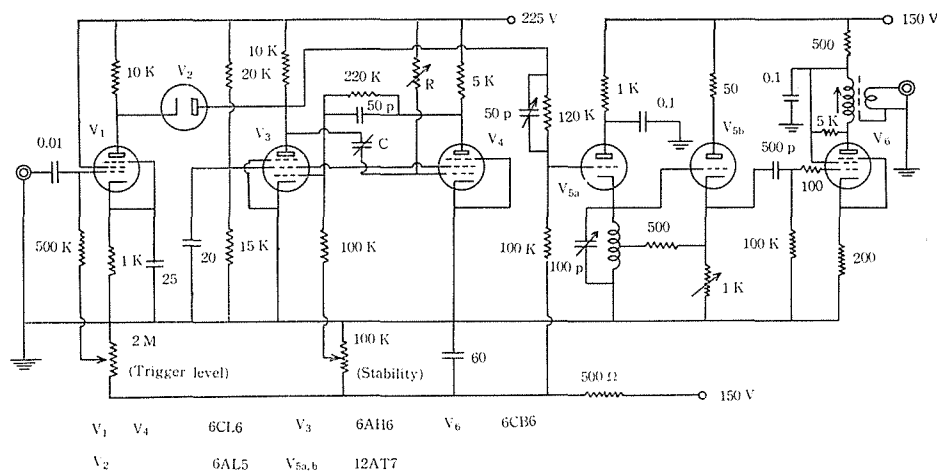


Fig. 2. Circuit diagram of pulser and pulsed oscillator.

(B) *Intermediate rf pulse amplifier*

Fig. 3 shows the circuit diagram. In this stage, the rf pulse of small amplitude from pulsed oscillator is amplified to drive the next final power amplifier. The stability and the wide band width are important in this stage, the overall band width being about 1 Mc/sec.

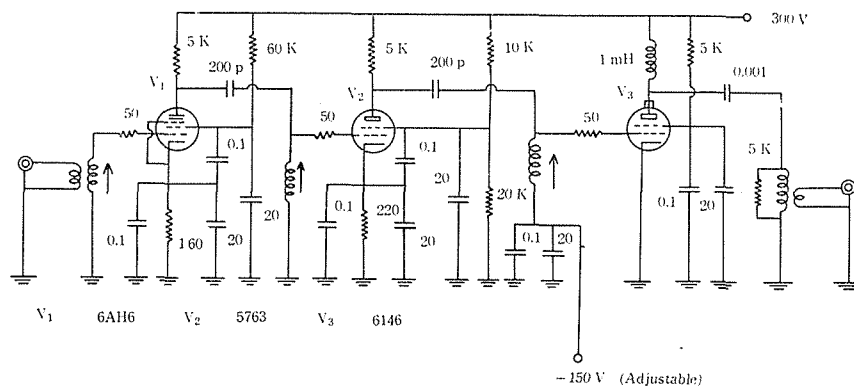


Fig. 3. Circuit diagram of intermediate rf pulse amplifier.

(C) *Final power amplifier and associated circuits*

Fig. 4 shows the circuit diagram. The previously used gas flow type cryostat was replaced by the Gutowsky type (10). The sample coil is composed of 12 turns of BS 16 enamelled copper wire 1.1 cm in inside diameter and 1.6 cm long, to which are shunted the capacity of rigid coaxial line included in Dewar jar,

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 5μ sec.

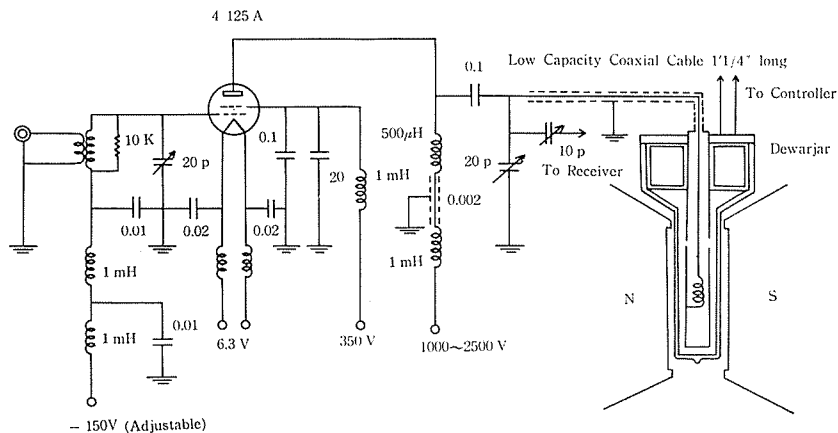


Fig. 4. Circuit diagram of final power amplifier and associated circuits.

(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 τ , the spin echo signal appears after the time interval 2τ 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 τ .

(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° pulse (t_w) is not so narrow and the receiver recovery time (t_{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 $2/\gamma \cdot 4H_{1/2}$ (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 $t_w = 5\mu\text{sec}$, $t_{\text{dead}} = 15\mu\text{sec}$ and $4H_{1/2} = 10$ 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° 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°C, where no spin echo signal appears. The temperature dependence of y_1 is also shown in Fig. 5 in linear arbitrary scale.

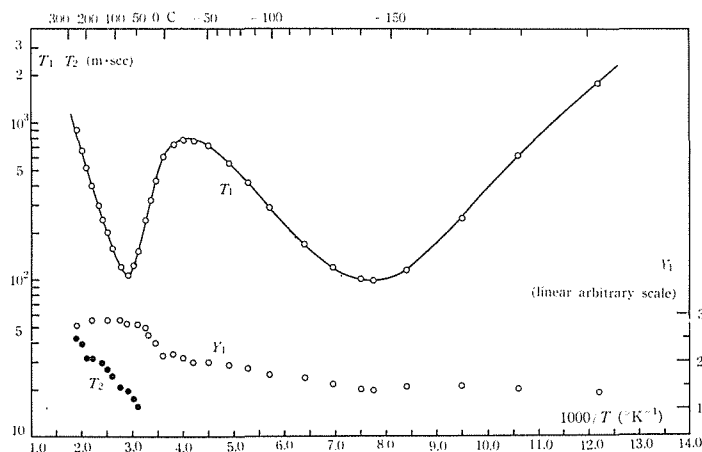


Fig. 5. Experimental data of temperature dependence of T_1 , T_2 and y_1 for proton of poly-propylene.

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 (τ_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

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

Considering b , τ_0 and ΔE as three adjustable parameters, we can analyse the data, that is, the minimum value of T_1 gives b , and the temperature dependence of τ_c gives τ_0 and ΔE . The plots of τ_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).

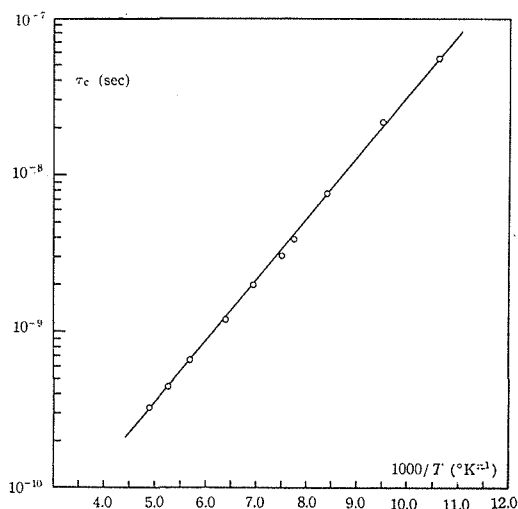


Fig. 6. τ_c (obtained by BPP formula from data of T_1) versus $1/T$ for methyl group proton of poly-propylene.

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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