412 © *1983 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, ***56***, *412—415 (1983)* [Vol. 56, No. 2

# A Simple Pressurized High-temperature Proton NMR Apparatus for the Thermal Degradation of Polymers[†]

Shigezo Shimokawa,* Eiji Yamada, and Kazuo Makino[††]
*NMR Laboratory, Faculty of Engineering, Hokkaido University, Sapporo 060*
[††]*Department of Applied Chemistry, Faculty of Engineering, Hokkaido University, Sapporo 060*

(Received August 17, 1982)

A simple pressurized, externally heated, high-temperature proton NMR apparatus for the temperature range from 293 to 823 K and pressure range from 0.1 to 40 MPa is reported. The sample cell has a capillary opening and the vessel is pressurized by inert gas. An application of this apparatus to the thermal degradation of poly(vinyl chloride) is presented.

Some of polymers in the molten state at high temperature are in an equilibrium where competitive reactions such as the decomposition, polymerization and polycondensation are balanced. And there are some ordered states such as liquid crystalline phases (mesophase) in the molten state under growing temperature.[1)] Previously we showed[2)] that the thermal decomposition of poly(vinyl chloride) (TD-PVC) is a good model to study such a molten state at high temperatures. It was found[3)] that high-temperature high resolution proton NMR provided a useful tool to detect the dynamic structure of molten polymers at high temperature.

However, such an atmospheric pressure experiment gives sometimes insufficient information, because the escape of gaseous products causes much loss of the liquid residue product. It is well known that a pressure vessel for thermal reaction is almost black box which is used only for the detection of thermal change.[4)]

There is dangerous and difficult procedure for us to increase the pressure, keeping high temperature in the static magnetic field. Several studies[5–11)] of high-temperature and high-pressure NMR only focused on pure liquid materials, for example, water or molten metals. As far as we know, there is no example of application of NMR under pressure to the process of thermal reaction at high temperature. Recently we developed an internally heated high-temperature and high-pressure C-13 NMR apparatus for direct measurements of pyrolysis of polymers.[12)] In this report, the design of an externally heated high-temperature and high-pressure proton NMR apparatus and its application to thermal degradation process of TD-PVC have been presented.

## Design of Apparatus

We constructed a heat and pressure resisting vessel for NMR study at high temperature of 823 K under high pressure of 40 MPa. Figure 1 shows the block-diagram of the homemade apparatus used in this study. The apparatus consists of a high resolution magnet, an externally heated high pressure vessel, a pressurizing system with inert gas, and an external field frequency lock system. A wide gap (6 cm) electromagnet of modified JEOL 3H type was used. The electromagnet was equipped with homogeneity current shim coils, a flux stabilizer and an external $^1$H field frequency lock system in order to keep the good homogeneity and stability of the magnetic field. The basic spectrometer

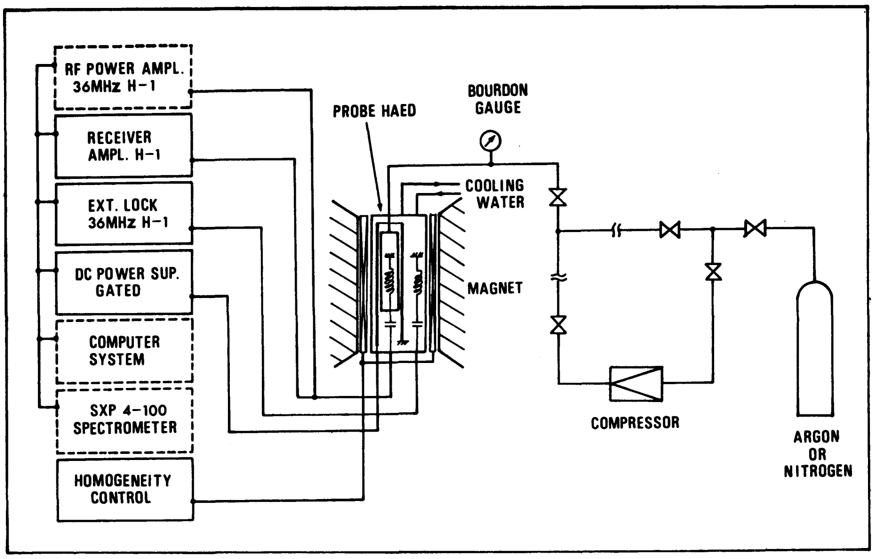

Fig. 1. Block-diagram of a simple pressurized high-temperature proton NMR apparatus, ------ denotes Bruker spectrometer units.

---

[†] Presented at the 19th Symposium on NMR, Sapporo, September, 1980.

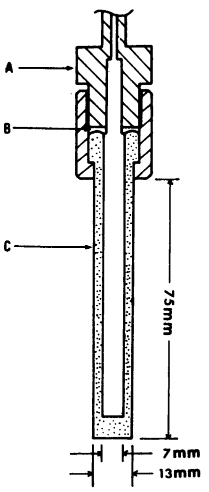

Fig. 2. High-pressure vessel of titanium alloy.
A; SUS 316 stainless steel, B; copper sealing washer, C; titanium alloy vessel.

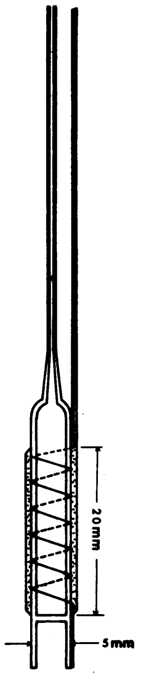

Fig. 3. Sample cell with a capillary opening.

used was a Bruker SXP 4-100 high power pulse spectrometer with Nicolet BNC-12 computer system.

Figure 2 shows the high pressure vessel made of titanium alloy (KS-130A, supplied by Kobe Steel Co. Ltd.). The vessel was externally heated. The tensile strength of the titanium alloy was 11600 kg cm$^{-2}$ over extended periods (10000 h) at 673 K. The maximum working pressure of the vessel was reached over 40 MPa, but in this study the working pressure was restricted to 30 MPa, because of the limiting pressure of the Bourdon gauge and valves. Figure 3 shows a simple sample cell. The cell was made of heat resisting glass and it consists of three parts, *i.e.*, the bottom of the cell, the body of coil and the capillary. The bottom of the cell, which was needed for homogeneity of $H_1$ field for relaxation measurement. The sample cell was simply inserted into the vessel. 0.2 g of powder sample can be put into the cell. After introduction of the sample, the top of the cell was made in the form of capillary. Resonance coil for each sample cell was wound and fixed on the cell by heat resisting cement (Sauereisen cement No. 8). Rf lead wire was insulated by 1 mm ceramic tube. The sample cell was always renewed after each experimental run and tuning for probe balance was readjusted easily. The top of the vessel which contained the closure plug and nuts with rf terminals was cooled by a water jacket: The sealing was made by copper washer and an rf lead wire was insulated by ceramic tubes. The outlet of the rf lead wire was sealed and insulated by Teflon cone, which was located away from the vessel. One of the terminals of the lead wire was grounded to the vessel. The escape of the sample from the sample cell as gaseous products at high temperature was much reduced by use of capillary. Very small amount of eluted gas caused slight contamination of the inner wall of the vessel as well as outer surface of the sample cell. This did not, however, give any trouble to get a good signal from the sample.

A high temperature probe assembly was made of aluminum block. A pure Nichrome wire noninductively wound on a quartz tube (25 mm o.d.). The temperature on the surface of the bottom of the titanium vessel was monitored by a YEW 2575 digital thermometer using an Alumel/Chromel thermocouple. Cooling water of controlled temperature was flown through the aluminum jacket. There was no dissipation of heat to the magnet and to external lock probe even at temperature above 823 K. 150 W of the electric power was used to elevate temperature up to 823 K. Readjustment of the field homogeneity control was necessary for each setting of the power supply. The resolution of signal for water proton of 5 mm sample cell in this vessel was about 10 Hz at 293 K, 1 MPa without sample spinning. Line width of 10 Hz is considered to be good enough for measurements of the thermal decomposition process of polymers in the molten state, because at high temperature proton spectra of molten polymer are usually complicated by superposition of various signals and line widths become much broader due to thermally produced radicals.

## Results and Discussion

Figure 4 shows the proton spectra of TD-PVC at various temperatures and pressures. Assignment of the two peaks was made by comparing them with the peaks of pure ethylbenzene. The chemical shift difference of the two peaks was 5.5 ppm (200 Hz). Because TD-PVC was thermally pretreated to liberate HCl at 623 K under atmospheric pressure, only hydrocarbons were considered in the residue of the thermal degradation PVC. It is known[2)] that the TD-PVC melts at about 673 K. Then, liquid crystalline phases were formed in the TD-PVC under growing temperature.[3)] This formation of liquid crystalline phases depended on heating rate. The heating rate was 2 K min$^{-1}$ in further experiments. From the temperature and pressure dependence of the spectra given in Fig. 4, it is

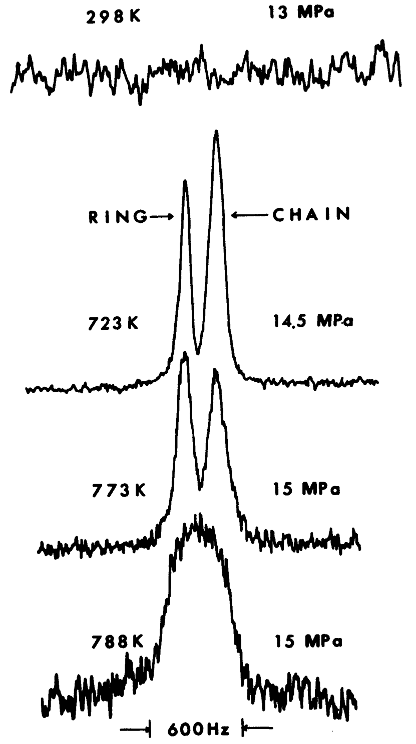

Fig. 4. Temperature and pressure dependence of proton spectra for TD-PVC.

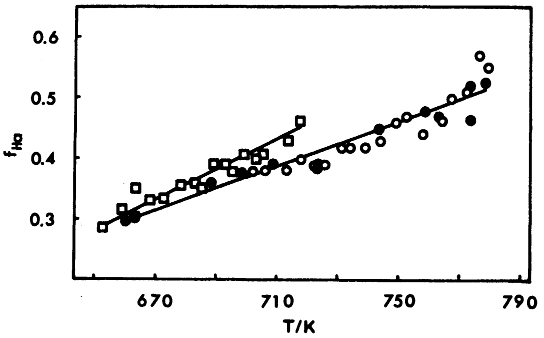

Fig. 5. Temperature dependence of proton aromaticity of TD-PVC.
□: Atmospheric pressure; pressurized condition. ●: (13 to 15 MPa), ○: (23 to 31 MPa).

found that the ring formation already occurs in the residue of TD-PVC at 723 K. At this temperature, aromatic protons are 30% of total protons. On further heating, the line width of the two peaks is broadened. At 815 K and 15 MPa, the spectrum shows an early stage of growing of liquid crystalline phases. The formation of the liquid crystalline structure was confirmed by the observation of polarized light-microscopy of quenched samples from this temperature.

It is very important to compare the present results with the data on the same material under atmospheric pressure. We define the hydrogen aromaticity as

$$f_{\rm Ha} = H_{\rm aroma}/(H_{\rm alipha}+H_{\rm aroma}), \qquad (1)$$

where $H_{\rm aroma}$ and $H_{\rm alipha}$ are the integral intensities of signals for aromatic and aliphatic protons, respectively. At atmospheric pressure the hydrogen aromaticity ($f_{\rm Ha}$) became 0.5 at 723 K but the same aromaticity was attained at 773 K under the pressurized condition, as shown in Fig. 5. The difference in the observed aromaticity for the atmospheric and pressurized conditions can be explained by the fact that the data at atmospheric pressure did not give a correct aromaticity, because the experiment at atmospheric pressure was made allowing an elusion of hydrocarbon gases from degradated TD-PVC residue. It was found that the pressure dependence of the aromaticity was not detected in the pressure range from 15 to 30 MPa.

It is known that free radicals are generated in the dehydrochlorinated PVC at high temperature.[2] The concentration of the unpaired electrons in the TD-PVC residue quenched from 673 K was found to $\approx 10^{18}$ spins$\cdot$g$^{-1}$ from ESR measurements. The TD-PVC melt at 683 K takes a polyene-like structure and the unpaired electrons are delocalized in the aromatic ring and polyene chains. Although there are two possible mechanisms for proton spin-lattice relaxation, *i.e.*, proton-proton dipolar interaction and proton-electron interaction, the latter is reasonably assumed to be predominant. We examined the spin-lattice relaxation time, $T_1$, of two kinds of protons. The values of $T_1$ measured by partially relaxed Fourier transform method at 733 K and 17 MPa were 151 and 153 ms for the ring and chain protons, respectively. These values of $T_1$ are larger by a factor of about 1.5 than those obtained at atmospheric pressure and 693 K.[3] We suppose that the existence of free radicals is suppressed in the pressurized condition by the remaining lower molecular weight fraction. This corresponds to the observed longer relaxation times in the pressurized condition at 733 K.

## Conclusion

A simple pressurized high-temperature proton NMR apparatus was constructed and applied to the study of thermal degradation process of TD-PVC up to 823 K and 30 MPa. From the temperature and pressure dependence of the observed proton spectra, correct values of hydrogen aromaticity were obtained as a function of temperature. This result was also supported by spin-lattice relaxation measurements. This apparatus can also be used for investigation of thermal reaction processes of various organic compounds at high pressures, which are ordinarily carried out in autoclaves.

We greatly appreciate the encouragement of the work by Mr. Yuichi Kanda, Dr. Toshio Sato, and Professor J. Sohma and the financial support of Nishin Soft Science Foundation.

### References

1) J. D. Brooks and G. H. Taylor, *Carbon*, **3**, 185 (1965).

2) S. Shimokawa, Y. Ohno, J. Sohma, H. Hirano, and K. Endoh, *Nippon Kagaku Kaishi*, **1973**, 2016.

3) S. Shimokawa and E. Yamada, *Am. Chem. Soc., Div. Polym. Chem. Prepr.*, **20**, 685 (1979); T. Yokono, K. Miyazawa, Y. Sanada, E. Yamada, and S. Shimokawa, *Fuel* **58**, 237 (1979); K. Miyazawa, T. Yokono, Y. Sanada, T. Chiba, E. Yamada, and S. Shimokawa, "Advances in Chemi-

stry Series 192, Coal Structure," ed by M. L. Gorbaty and K. Ouchi, Am. Chem. Soc., Washington (1981), pp. 59—71; S. Shimokawa and E. Yamada *Bull. Facul. Eng. Hokkaido University*, **102**, 155 (1981).

4) A. Sawaoka and S. Saito, "Shin Jikken Kagaku Koza," ed by the Chemical Society of Japan, Maruzen, Tokyo (1977), Chap. 10, pp. 536—539.

5) G. B. Benedek, "Magnetic Resonance at High Pressure," Interscience publishers, New York (1963).

6) D. W. G. Smith and J. G. Powles, *Mol. Phys.*, **10**, 451 (1966).

7) J. G. Powles and M. C. Gouch, *Mol. Phys.*, **16**, 349 (1969).

8) J. Jonas, *Rev. Sci. Instr.*, **43**, 643 (1972).

9) T. H. DeFries and J. Jonas, *J. Magn. Reson.*, **35**, 111 (1979).

10) W. J. Lamb and J. Jonas, *J. Chem. Phys.*, **74**, 913 (1981).

11) U. El-Hanay and W. W. Warren, Jr., *Phys. Rev. Lett.*, **34**, 1276 (1975).

12) S. Shimokawa and E. Yamada, *J. Magn. Reson.*, **51**, Jan. (1983), in press.