

Polywater: Proton Nuclear Magnetic Resonance Spectrum

Abstract. *In the presence of water, the resonance of the strongly hydrogen-bonded protons characteristic of polywater appears at 5 parts per million lower applied magnetic field than water. Polywater made by a new method confirms the infrared spectrum reported originally.*

Results of research on the structure of polywater based on data from infrared and Raman spectra were reported (1). We now report the ^1H nuclear magnetic resonance (NMR) spectrum (Fig. 1) and confirmation of the infrared spectrum of polywater (2).

The NMR spectrum was observed with a homogeneous solution of polywater (200 μg) and water (100 μg) (3). The frequency of the broad resonance centered about 300 hz (5 ppm) lower field than water (4) agrees with the chemical shift expected for a proton bonded or bridged between two oxygen atoms as in structures suggested (1). A proton so bonded or so bridged would be positively charged relative to water due

to electronegativity of oxygen. In addition, the formal delocalized negative charge associated with the proposed polycyclic structure (1) would increase the positive charge of the protons. A paramagnetic shift in the resonance relative to water would be expected because of electron abstraction at the proton. For somewhat analogous reasons the acid protons of mineral acids and organic acids also resonate in a region 300 to 500 hz downfield (lower applied field) from water at 60 Mhz.

Protons around the perimeter of the polywater lattice should be exchangeable. Thus their resonance would coincide with that of water because of chemical exchange. No appreciable broadening of the water resonance was apparent.

The breadth of the polywater resonance (~ 100 hz) is also consistent with the structure proposed (1). Polymers typically have broadened resonances that are due to restricted internal molecular motion. Also, a distribution of molecular sizes contains many similar electronic environments with small relative chemical shifts. Viscosity effects from restricted molecular mo-

tion and association would also contribute to signal broadening.

Figure 2 is the infrared spectrum of polywater (5) prepared by a method different (6) from that of the polywater used for the NMR spectrum (Fig. 1). The infrared spectrum was obtained on a film cast on an Irtran (ZnS_2) plate. No expansion of scale or condensation of beam was used.

The bands at 1595, 1410, and 1360 cm^{-1} agree well with the spectrum reported for polywater (1). The region of high diamond background (2700 to 1840 cm^{-1}) was originally observed only with difficulty (1). In Fig. 2, this region is free of background and no appreciable absorption occurs in this region, as was reported (1).

A little residual water is indicated by the broad OH-stretching vibration at 3450 cm^{-1} and weak absorption at 1645 cm^{-1} . The optical density of the 3450 cm^{-1} band decreased after the Irtran plate was warmed. The band at 1110 cm^{-1} is believed to be due to an impurity arising from the method of preparation since the relative intensity of this band has been found to vary. However, it should be noted that the normal coordinate analysis of polywater predicts an infrared absorption at 1110 cm^{-1} for a puckered cyclic structure (7).

Note added in proof: After this report was submitted, polywater has been prepared in which no 1110 cm^{-1} band is observed in the spectrum (6).

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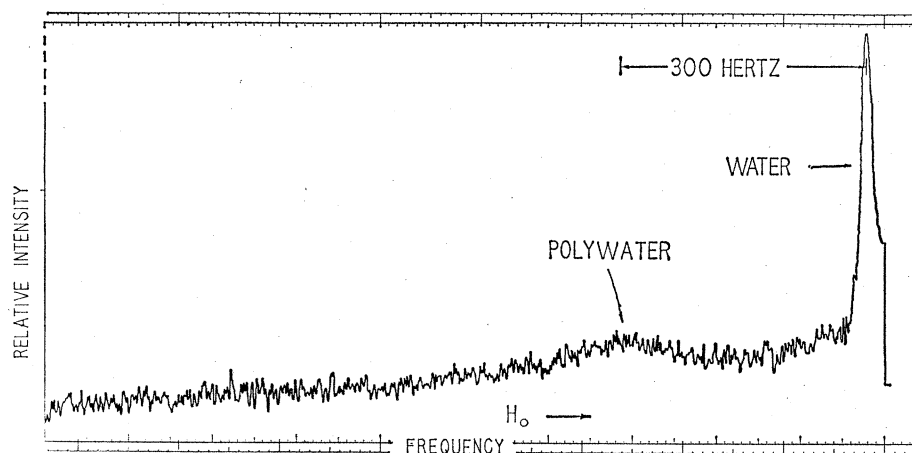


Fig. 1. The ^1H NMR spectrum of polywater at 60 Mhz (123 time-averaged scans).

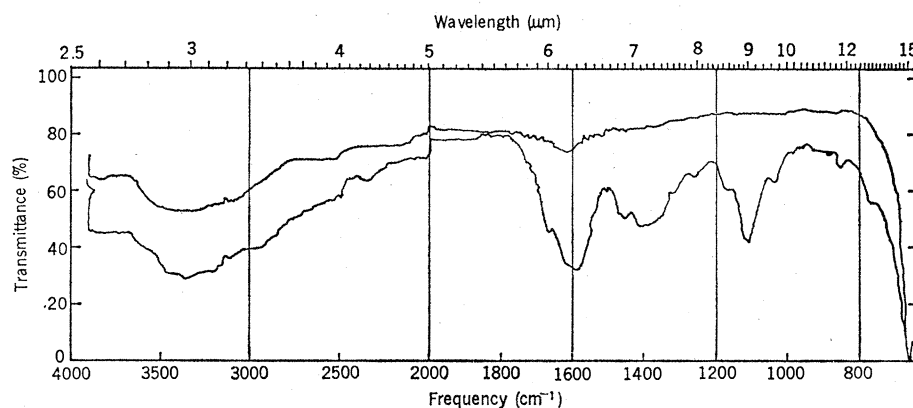


Fig. 2. The infrared spectrum of polywater. Film on Irtran (bottom); background (top).

References and Notes

1. E. R. Lippincott, R. R. Stromberg, W. H. Grant, G. L. Cessac, *Science* **164**, 1482 (1969).
2. The NMR spectrum was run on a Varian model HA-60-IL and is the average of 123 scans obtained using a Varian C-1024 time-averaging computer. The spectrum was easily observed at rapid sweep rates on a single-spectral scan and without field-frequency control. The spectrometer was locked to external hexamethyldisilane, and the spectrum was time-averaged to determine frequencies accurately. Standard experimental techniques were used.
3. The water resonance (Fig. 1) is chemically shifted 422 hz downfield from external hexamethyldisilane at 39.2°C (measured with the methanol NMR thermometer).
4. Frequency measurements relative to the internal water resonance do not require correction for magnetic susceptibility.
5. The infrared spectrum was run on a Perkin-Elmer model 521 grating spectrometer.
6. T. F. Page, Jr., in preparation.
7. J. B. Bates, E. R. Lippincott, Y. Mikawa, R. J. Jakobsen, in preparation.

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