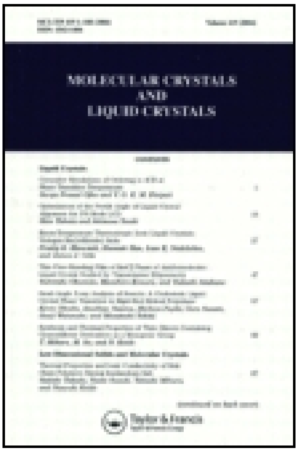

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The First Demonstration of Orientational Order in a Rigid Backbone Liquid Crystalline Polymer Using Deuterium NMR Spectroscopy

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The First Demonstration of Orientational Order in a Rigid Backbone Liquid Crystalline Polymer Using Deuterium NMR Spectroscopy

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The temperature dependence/phase behavior of the rigid main-chain copolyester (1:1) of 4-hydroxybenzoic acid and 6-hydroxy-2-naphthoic acid has been monitored using very high temperature deuterium NMR (^{2}H NMR). The results of this investigation indicate that ^{2}H NMR is able to provide, for the first time, conclusive evidence of the ability of these systems to efficiently orient in the presence of an external magnetic field.

Keywords: rigid backbone LCP, deuterium NMR, orientational order, copolyesters

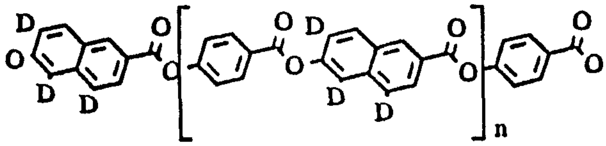
INTRODUCTION

The homopolyester of 4-hydroxybenzoic acid and its copolyesters with 6-hydroxy-2-naphthoic acid and with 4,4′-biphenol and terephthalic acid are of both commercial and academic interest.[1,2] From the application side, the interest stems from the high moduli and high temperature properties of these polymers (a result of their extremely rigid backbone) which are either available commercially or in developmental quantities. As these materials are representative of rigid main-chain thermotropic liquid-crystalline polymers, there is also considerable interest in them in terms of understanding the fundamental properties of such polymers in the mesomorphic state. One area of concern is whether these polymers will spontaneously orient in the presence of an external magnetic field, (as do *flexible* main-chain thermotropic liquid crystalline polymers)[3] a general property of non-polymeric thermotropic liquid crystals. With this in mind, we have embarked on an investigation of the molecular motions (which may lead to orientation) as a function of temperature in polymers based on the 4-oxybenzoyl unit using ^{2}H NMR spectroscopy as a probe of the dynamics. The results presented in this communication will deal only with the 1:1 copolymer of 4-hydroxybenzoic acid and 6-hydroxy-2-naphthoic acid. A more detailed study of a wide range of homo- and copolyesters will be presented in a forthcoming full paper.[4] To help identify any differences in the motions of the two monomer moieties we have specifically labelled (with deuterium) both the benzoic acid and/or the naphthoic acid monomers in the polymer. In addition we have constructed a broad-banded double-tuned high temperature NMR probe which is capable of achieving the high temperatures necessary (up to 500°C) for the study of these systems. The initial results, reported herein, indicate that ^{2}H NMR is able to provide, for the first time, conclusive evidence of the ability of these systems to efficiently orient in the presence of an external magnetic field.

RESULTS AND DISCUSSION

In Figure 1 is shown the ^{2}H NMR spectra (61.4 MHz) as a function of temperature for the copolymer deuterated in the naphthoic acid unit (**P1**). The spectrum at 25°C (Figure 1A) shows the power pattern with a splitting between the singularities (128 kHz) characteristic of a rigid solid (*i.e.* rigid on the deuterium NMR time-scale of *ca.* 0.25 MHz). As the temperature is raised above 180°C, the spectra begin to exhibit very significant deviations from the rigid Pake spectrum. The splitting of the two prominent singularities of the theoretical solid-state ^{2}H power pattern for 180° ring flips about the C_1–C_4 carbons of a benzene ring is 1/4 that of the rigid ring[5,6] (*i.e.* 32 kHz). This splitting further reduces to 1/8 of the rigid ring value (*i.e.* 16 kHz) for a ring which is freely rotating about the C_1–C_4 axis.[5,6] The barely observable splitting of *ca.* 11 kHz at 184–190°C suggests that not only are some of the naphthoic acid moieties freely rotating about their long axes, but that this motion is further augmented by fluctuations or oscillations about the rotation axis which has the effect of further reducing the observed splitting. However, the width at half height (*ca.* 24 kHz) suggests that not all of the rings are freely rotating about their long axes but rather that some are undergoing discrete 180° flips. This is more clearly seen in the spectrum at 218–228°C which appears to be a composite of rings undergoing discrete 180° degree flips and rings which are freely rotating in addition to oscillations about their long axes.

P1



The spectra from 238°C to 267°C reveal a gradual ordering of the molecules which is characterized in the spectrum at 267°C by two well defined quadrupolar split doublets with splittings of 45 and 13.7 kHz respectively. The ordering of the sample over this temperature range is consistent with the endothermic transition

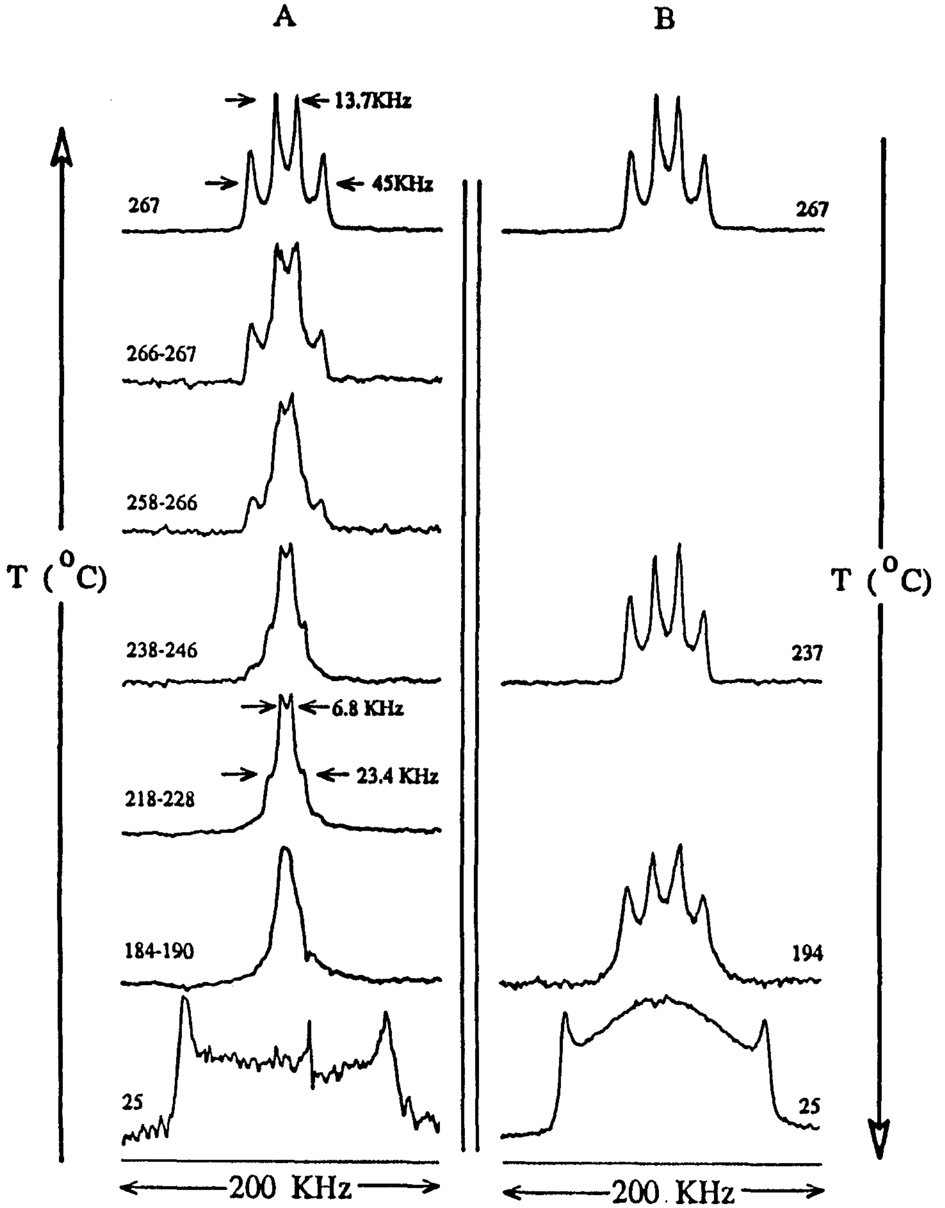


FIGURE 1 ^{2}H NMR spectra as a function of temperature for **P1**: a) The initial heating of the sample, b) The cooling of the oriented sample. At no time was the sample removed from the magnet. The arrows indicate the direction in which the temperature was changed.

from *245–255°C* observed for **P1** by differential scanning calorimetry (DSC). The quadrupolar splittings found for ordered **P1** are typical for aromatic deuterons on other non-polymeric liquid crystals and are the first to be observed for rigid main-chain thermotropic liquid crystalline polymers. It is important to note that the spectra from 238–267°C indicate that the sample does not order istelf "en mass," but rather that small domains of the sample order individually, leading eventually to the complete ordering of the sample. This ordering of small domains may be a result of the inherent molecular weight distribution found in these systems which is not present in non-polymeric liquid crystals.

The cooling of oriented **P1** is displayed in Figure 1B and clearly shows that the sample maintains its order on cooling below the "solid → liquid crystalline" (S → LC) phase transition of 245–255°C. The spectra at 237 and 194°C, although somewhat broadened at the lower temperatures, are still well characterized by the two quadrupolar doublets. As deuterium NMR spectra are completely dominated by the quadrupole coupling of the deuterium nucleus, the observed $\Delta\nu_Q$ can be described to a very good approximation by Equation 1. This feature of ^{2}H

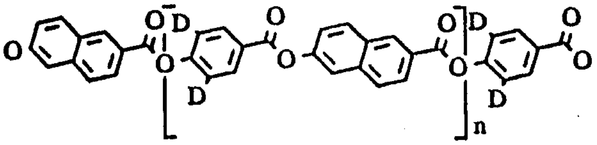
$$\Delta \upsilon = \frac{3}{4}\left[\frac{e^2qQ}{h}\right]\langle 3\cos^2\theta - 1\rangle \qquad (1)$$

NMR spectra and the fact that we can still resolve the two quadrupolar doublets for **P1** *below* the S → LC phase transition allows for the study $\Delta\nu_Q$ as a function of θ for **P1**. This is shown in Figure 3 and will be discussed subsequently. The room temperature spectrtum of oriented **P1** shows, as did the room temperature spectrum of unoriented **P1**, a static powder pattern. However there is significantly more intensity in the center of the oriented spectrum, a result of the non-random distribution of the molecules from a "freezing-in" of the liquid crystal molecular orientations.

Figure 2 illustrates the effect of rotating (at room temperature) a previously oriented sample by 90° and then observing the effect on the spectra as a function of temperature. The spectra at 217–219°C and 234–240°C were recorded *below the temperature necessary for reorientation of the polymer backbone in the field* (>245°C) and clearly show two well resolved quadrupolar doublets that are exactly 1/2 the magnitudes (22.5 and 7 kHz respectively) those previously observed for the non-rotated sample (see Figure 1). This result indicates that the long axis of the polymer chains must align parallel with the magnetic field when the sample is allowed to orient in the magnetic field and that rotation of the sample yields a system where the polymer chains are oriented approximately perpendicular to the magnetic field.

The spectra from 254°C to 287°C in Figure 2 illustrate that even a *previously* oriented sample will reorient in the presence of an external magnetic field. As in the case of the non-oriented sample, the oriented sample reorients in small domains, rather then the sample undergoing a single coherent reorientation.

P2



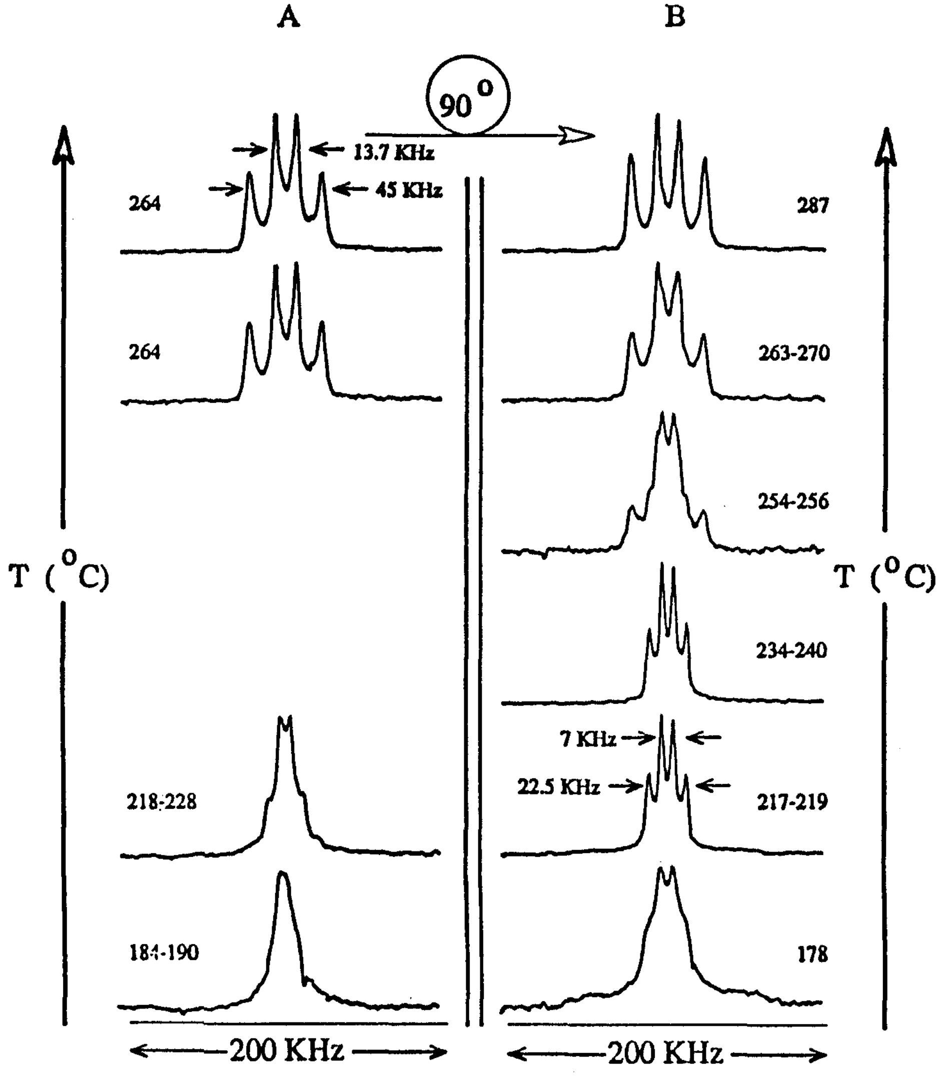


FIGURE 2 ^{2}H NMR spectra illustrating the effect of rotating an oriented sample by 90°: a) Spectra for a nonrotated sample, b) Spectra for a sample which was rotated by 90°.

The temperature dependence of the benzoic acid labelled polymer (**P2**) is shown in Figure 3. These spectra show a similarity to those obtained for **P1** with some of the rings undergoing 180° flips while others are freely rotating about their C_1-C_4 axis (see spectra at 192–197°C and 221–225°C). As was the case for the naphthoic-labelled polymer the benzoic acid moieties must also undergo additional averaging in the form of oscillations about the rotation axis in order to give the observed splitting of 8.1 kHz. However unlike **P1**, the spectra for the oriented polymer (*i.e.* above 260°C) do not show a marked difference from those observed below the S → LC phase transition. Several possibilities could account for this: 1) The smaller benzoic acid moieties may undergo more extreme conformational changes resulting

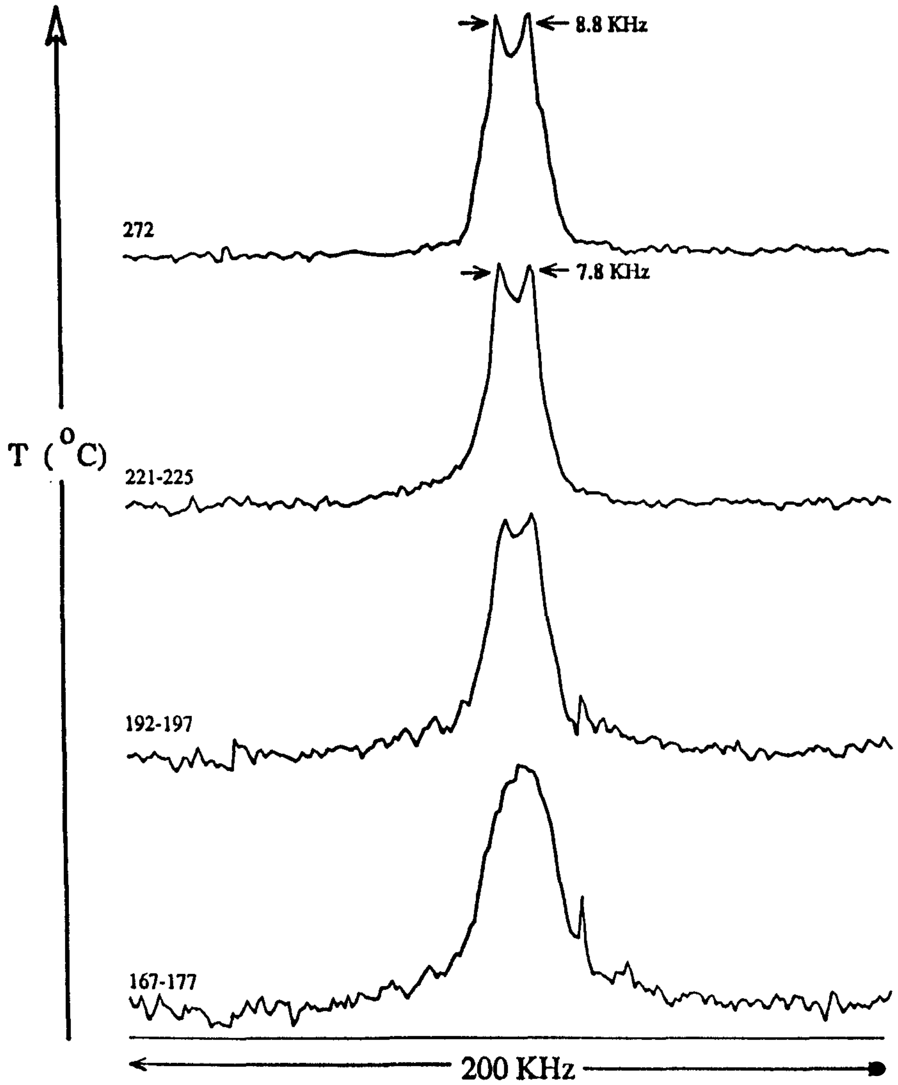
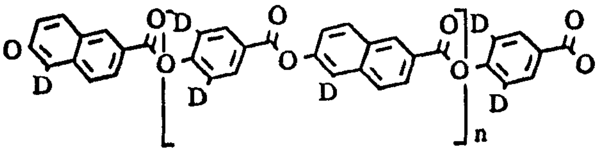


FIGURE 3 ^{2}H NMR spectra for **P2** as a function of temperature.

in a smaller observed $\Delta\nu_Q$. 2) The protons ortho to the deuterons may be broadening the observed lines *via* ^{2}H$-^1$H coupling causing them to be less well resolved. Decoupling the protons during acquisition of the signal would eliminate any broadening due to ^{2}H$-^1$H coupling and may lead to a more well defined spectrum for oriented **P2**. The results of this experiment will be forthcomming.[4]

The ratio of the two quadrupolar couplings observed for **P1** is *ca.* 2:1. This may result from the positions of the deuterium in the naphthalene ring *i.e.* position 4 and 5 must be equivalent as their C—D bond vectors are parallel, but 7 will be non equivalent to 4 and 5 with respect to the magnetic field in the oriented polymer.

P3



It is also possible that the 2:1 ratio could result from the random distribution of the monomers within the polymer chains. In an effort to distinquish between these two possibilities we have prepared and investigated polymer **P3** which contains only one deuterium on the naphthoic acid moiety, and 2 deuterium atoms on the benzoic acid moiety. The temperature dependence of the ^{2}H NMR spectra for **P3** are shown in Figure 4.

Below the S → LC phase transition the spectra are similar to those observed for **P1** and **P2**. However, above the S → LC phase transition the spectra appears to be a composite of the spectra observed for **P2** plus the inner quadrupolar doublet from the spectra observed for **P1**. The small signal with $\Delta\nu_Q = 45$ kHz is a result of a small percentage (*ca.* 10%) of deuterium in position 7 of the naphthalene ring of **P3**. These spectra clearly show that the 2:1 ratio observed for **P1** is a result of the positions of the isotopic labels and not a result of the sequencing of the monomers'within the polymer.

CONCLUSIONS

These data provide the first example of the usefulness of very-high temperature ^{2}H NMR studies for the investigation of the liquid crystalline order present in rigid main-chain copolyester polymers. Details of further results pertaining to the polymer discussed in this communication and to other polyesters will be discussed in future publications.

EXPERIMENTAL

MATERIALS: 4-Hydroxybenzoic acid (Aldrich) was used without purification. 6-hydroxy-2-naphthoic acid was a gift from Celanese Research Co., Summit N.J. The labeling of the monomers with deuterium was achieved according to reference 7. The polymers were prepared according to literature techniques.[8] Deuterium spectra were obtained using the quadrupolar-echo sequence using a Bruker MSL400 spectrometer. 90° pulse lengths were *ca.* 4μs.

NMR PROBE: The high temperature broad-banded and double tuned probe used to record the deuterium spectra was home-built and consisted of a horizontal solenoid coil encased in a furnace. The outer casing of the probe consisted of a water cooled jacket to protect the magnet and room temperature field shims from the high temperatures involved.

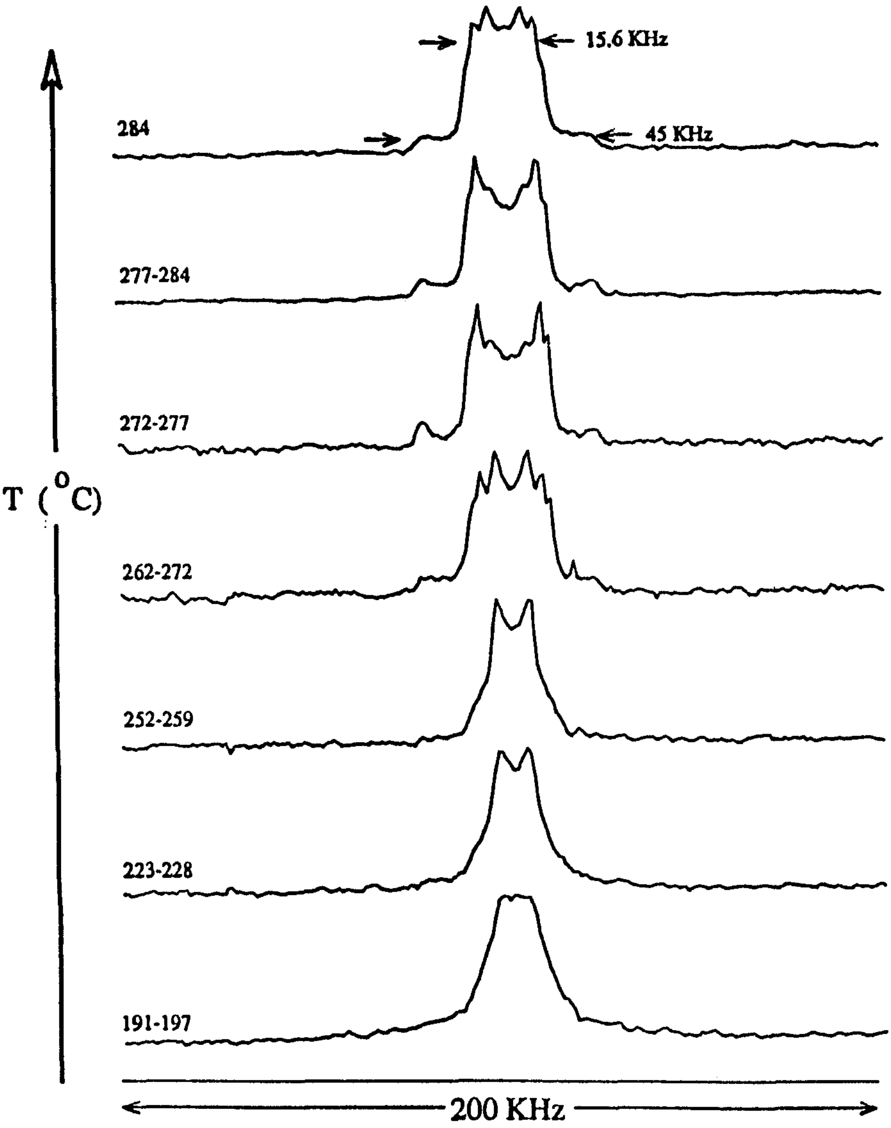


FIGURE 4 ^{2}H NMR spectra for **P3** as a function of temperature.

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