

35-CL NQR Spectroscopy of Polychloral

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INTRODUCTION

High resolution 1-H and 13-C NMR spectroscopies have revolutionized structure determinations of high polymers in solution. More recently, with the development of magic angle spinning techniques, NMR spectroscopy has been extended to the study of polymers in the solid state. Under favorable conditions, the degree of resolution achieved by solid state NMR spectroscopy can approach that of solution measurements.

On the other hand, nuclear quadrupole resonance spectroscopy (NQR) has been used much less extensively. The nuclei commonly detected by this solid state technique include 35-Cl and 14-N. To date, most work has involved crystalline, low molecular weight compounds (BRAME,1973, SMITH,1971, SEMIN, ROBAS,1966). Work on polymers has been restricted by extensive line broadening (KHOTSYANOVA et al,1967, SEMIN et al,1975) and by the difficulties of finding the proper signals in the scale of operation. The first NQR spectrum of a polymer was that of poly(vinylidene chloride) (BABUSHKINA et al,1964). Later, polychloroprene was also studied (BABUSHKINA et al,1981).

As with other spectroscopic techniques, NQR can yield information regarding the structural changes between monomer and polymer. NQR spectroscopy can also provide information about the structure of the polymer chain and its stereochemistry. Furthermore, because the NQR technique is concerned with solid samples, polymer chain interactions can also be measured (SEMIN et al,1975, BABUSHKINA et al,1964, SEMIN et al,1967, BABUSHKINA et al,1971).

Polychloral is a semicrystalline polymer (VOGL,1969, VOGL et al,1972, KUBISA et al,1976), which is completely isotactic according to infrared spectroscopy (NOVAK, WHALLEY,1959), X-ray diffraction (KUBISA, VOGL,1980), and most recently, solid state magic angle 13-C NMR spectroscopy (HARRIS et al,1983). The isotacticity of polychloral could finally be proven: Chloral could be polymerized with chiral anionic initiators to an isotactic, optically active polymer. Optical activity arises from the formation of one helical screw sense, i.e. from macromolecular asymmetry (CORLEY, VOGL,1980b).

It was the objective of this work to show how ^{35}Cl NQR spectroscopy can contribute to the structure determination of polychloral, and to demonstrate that NQR spectroscopy, a valuable but little used technique, can be generally used to characterize polymers.

EXPERIMENTAL PART

Polychloral was prepared by cryotachensic polymerization of chloral in n -hexane solution (30 percent monomer) with 0.2 mole percent lithium tertiarybutoxide as the initiator (KUBISA, VOGL,1977). Polychloral was stabilized by treating the raw polymer with methanolic hydrochloric acid (CORLEY, VOGL,1980a), a process which converted all living alkoxide to the more stable hydroxy endgroups.

All ^{35}Cl NQR spectra were measured at 77°K on a ISSH-2-13 pulse NQR spectrometer-relaxometer (made by SKB IRE AN SSSR). The frequency range covered was from 30 to 130 MHz, and the signals were detected by the spin echo technique; the spin echo signal was created by the two usual RF pulses of 90° - 180° .

The spectra were recorded by means of a signal accumulator. The spectrum of the chloral monomer had been recorded previously (SEMIN et al, 1975, SEMIN et al,1967); it had three peaks at 38.794, 39.172 and 39.291 MHz, respectively.

RESULTS AND DISCUSSION

The NQR spectrum of chloral (Figure 1a) (SEMIN et al,1975, SEMIN et al, 1967) consists of three narrow lines of equal intensity; these lines relate to the average position of the three chlorine atoms in the solid state of chloral (which has a m.p. of 114°K). One can assume that the two higher frequency lines which are closer together can be attributed to the chlorine atoms situated on both sides of the molecular plane and are characteristic of the free molecule in the crystal.

Polymerization of the chloral monomer (KUBISA, VOGL,1980) gives a polymer which consists of a polyacetal backbone of isotactic structure whose conformational restrictions places the polymer chain in a helical structure (Figure 1b).

The polymer NQR spectrum has a very broad asymmetric line (Figure 2), that can be separated into two broad peaks. The ratio of the integrated intensities of these lines is 1:3.5 with the centers of the peaks at 39.585 MHz and 39.785 MHz (Figure 1b); the line widths of the deconvoluted peaks are 300 KHz and 270 KHz, respectively, and the accuracy of measurement is 0.4%.

A comparison of the line widths (assuming Gaussian shape) shows that the disorder of the chlorine atoms with respect to the nearest neighbors of the two types of ^{35}Cl NQR signals, as judged by the line widths, is about the same. The line splitting seems to be due to intermolecular interactions. The ratios of the integrated intensities 1:3.5 of the two chlorine peaks appear to indicate that

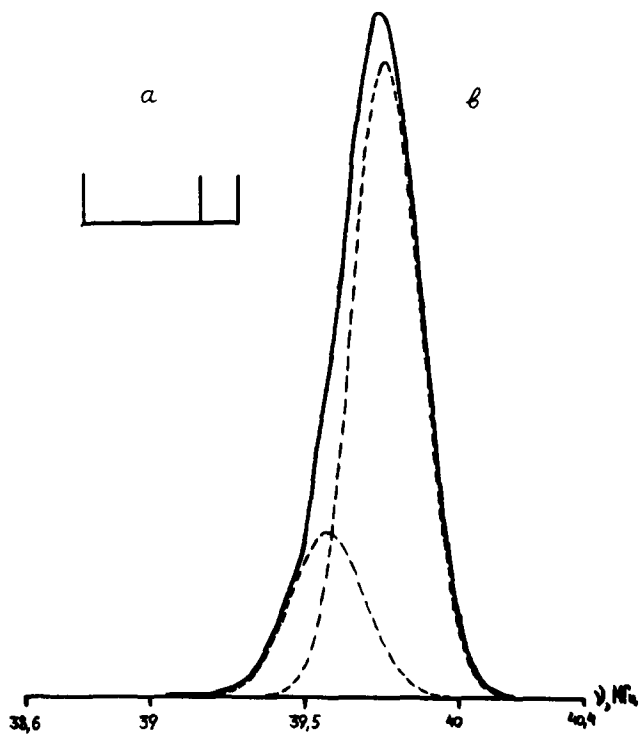


FIGURE 1: a.) Schematic Representation of the ^{35}Cl NQR Spectrum of Chloral.
 b.) ^{35}Cl NQR Spectrum of Polychloral with the Line Separation in the Unresolved Doublet.

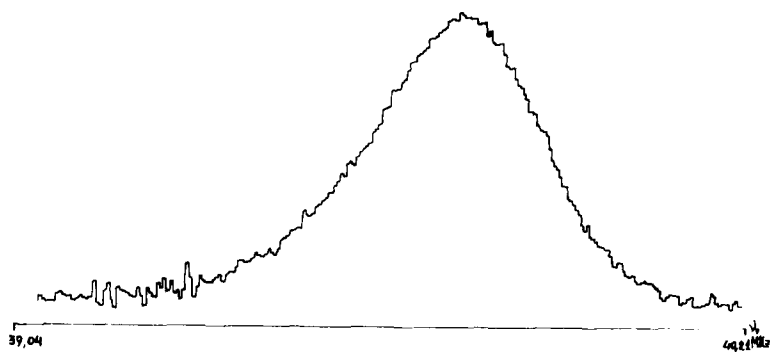


FIGURE 2: Actual Recording of the ^{35}Cl NQR Spectrum of Polychloral.

there exists a difference in the population of the positions corresponding to two different environments of nearest neighbors. This result implies that there is a limited number of possible combinations confirming the helical structure and it is also consistent with polychloral being a helical polymer with 3.5 monomers per helix repeat unit.

The high frequency shift of the polymer as compared to the monomer can be explained by considering two factors:

- 1) Accumulation of the substituent CCl_3 groups, and;
- 2) A rather loose packing of the polychloral due to low crystallinity, which according to (KHOTSYANOVA et al,1967, SEMIN et al,1978) must result in a high frequency shift.

Because of the large line width, no precise measurement of T_1 was possible. However, a comparison of the saturation rates of the observed lines with the analogous values for molecular crystals and for more ordered, crystalline polymers indicates that there is some mobility of the CCl_3 groups in polychloral; this does not imply, however, free rotation. The acetal oxygen provides "hinges" in the chain for permitting limited mobility than is less likely with carbon linkages in the polymer chain.

The large line width of the polychloral ^{35}Cl NQR spectrum is caused by statistical representations of the CCl_3 groups in the polymer chain followed by a disorder in the individual positions of the CCl_3 groups in the macromolecule. The line widths of the ^{35}Cl peaks in the polychloral spectrum are typical for disordered crystals or amorphous organic materials bonded by van der Waals forces (BABUSHKINA et al,1967, SEMIN et al,1979).

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