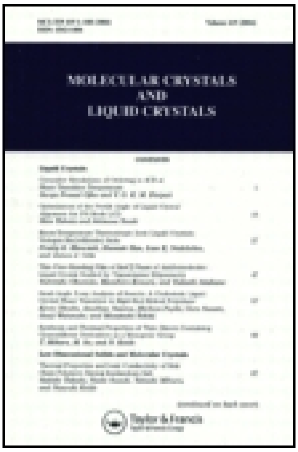

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Alfred Hagemeyer [a], Dieter Schaefer [a], Klaus Schmidt-rohr [a], Bernhard Blümich [a] & Hans Wolfgang Spiess [a]

[a] Max-Planck-Institut für Polymerforschung, D-6500, Mainz, FRG

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TWO-DIMENSIONAL SOLID STATE NMR STUDIES OF ULTRASLOW MOLECULAR REORIENTATION IN SOLID POLYMERS

ALFRED HAGEMEYER, DIETER SCHAEFER, KLAUS SCHMIDT-ROHR, BERNHARD BLÜMICH AND HANS WOLFGANG SPIESS
Max-Planck-Institut für Polymerforschung, D-6500 Mainz, FRG

Abstract Slow molecular reorientations in solid polymers have been investigated by means of two-dimensional solid state ^{2}H- and ^{13}C-NMR.

INTRODUCTION

One-dimensional (1D) NMR has proved successful in determining molecular structure and conformation.[1] For many applications ^{13}C magic angle spinning (MAS) is the method of choice, since under fast spinning conditions high resolution solid state spectra are obtained with well-resolved, sharp peaks appearing at the isotropic chemical shifts. In this way spectral overlap is avoided and liquid-like spectra can be detected by averaging out the chemical shift anisotropy (CSA). But this is not always desirable since the anisotropy of the magnetic interactions does contain valuable information about the order and motion of the molecular segment giving rise to the observed NMR resonance. The macroscopic properties of polymer materials are often supposed to be governed by the molecular motions of the chains as well as by their state of order.

By introduction of a second spectral dimension additional information becomes accessible. As far as slow molecular motions are concerned, unique geometrical information in order to distinguish between different motional mechanisms can be obtained.[2] The increase of resolution inherent in 2D techniques renders 2D-NMR on static solids increasingly attractive. ^{13}C-2D-exchange NMR can be applied to static samples containing only a few resolved carbon sites, otherwise the analysis becomes very complicated due to spectral overlap. In this case site-specifically labeled samples like selectively deuterated compounds are needed for investigation by wideline deuteron NMR.

In a static solid, the NMR frequency for ^{13}C under proton decoupling or for ^{2}H in selectively deuterated samples is dominated by an angle dependent frequency shift. The NMR frequency depends on the orientation of the molecule relative to the static magnetic field. In case of deuterons the frequency is proportional to the strength of the anisotropic interaction δ (deuteron coupling constant) and a function of the cosine of

ϑ, where ϑ is the angle the C-D bond forms with the external static magnetic field.

$$\omega = {}^{\delta}/_{2}\,(3\cos^2\vartheta - 1) \qquad (1)$$

For distributions of orientations Eq.(1) must be averaged over the orientational distribution function, which specifies the statistical weight of orientations. For isotropic distributions an inhomogeneous NMR lineshape (powder pattern) results.

The anisotropic interactions we make use of in solid state NMR are the electric quadrupole interaction in case of ^2H and the CSA in case of ^{13}C. The deuteron nucleus has spin. Therefore we have to deal with two transitions leading to mirror symmetric powder patterns, whereas ^{13}C has spin $^1/_2$ and only one transition is possible.

The 2D-exchange experiment basically consists of three time periods.[3] During evolution period t_1 each spin isochromat is labeled with its precession frequency. After mixing time t_m, during which the magnetization label is redistributed if any spin exchange has occurred, the free induction decay (FID) is acquired during the detection period t_2.[4]

^{2}H-2D-EXCHANGE NMR

In case of no exchange, the NMR frequency of a particular C-D bond remains the same during evolution and detection and only a diagonal spectrum is detected. If molecular reorientation does occur during the mixing time, t_m, then the frequencies measured during evolution and detection will be different and off-diagonal intensity will appear in the 2D frequency plane.[3,4] For an isotropic sample (powder) all orientations of C-D bonds are equally likely to occur resulting in continuous off-diagonal exchange patterns of characteristic shape.[3,4]

An example is provided by fully deuterated atactic poly(propylene) aPP $(-CD_2-CDCD_3-)_n$ (Fig. 1, T = 275 K, t_m = 25 ms). The broad featureless spectral intensity covering the whole 2D plane is indicative of diffusive reorientation, since a given C-D bond has a finite probability of being found in any orientation with respect to the magnetic field regardless of its starting position before the mixing time. The computer simulation is based on a model in which isotropic rotational diffusion over a sphere is assumed with a log-Gaussian distribution of correlation times.[5,6] By varying the mixing time t_m the dynamic evolution of the system can be studied allowing for the determination of correlation times.

On the other hand the 2D-exchange spectrum of isotactic poly(propylene) iPP (Fig. 2, T = 387 K, t_m = 150 ms) looks quite different, exhibiting sharp exchange ridges. The conventional 1D deuteron NMR spectrum appears on the diagonal. The broad signals result from the

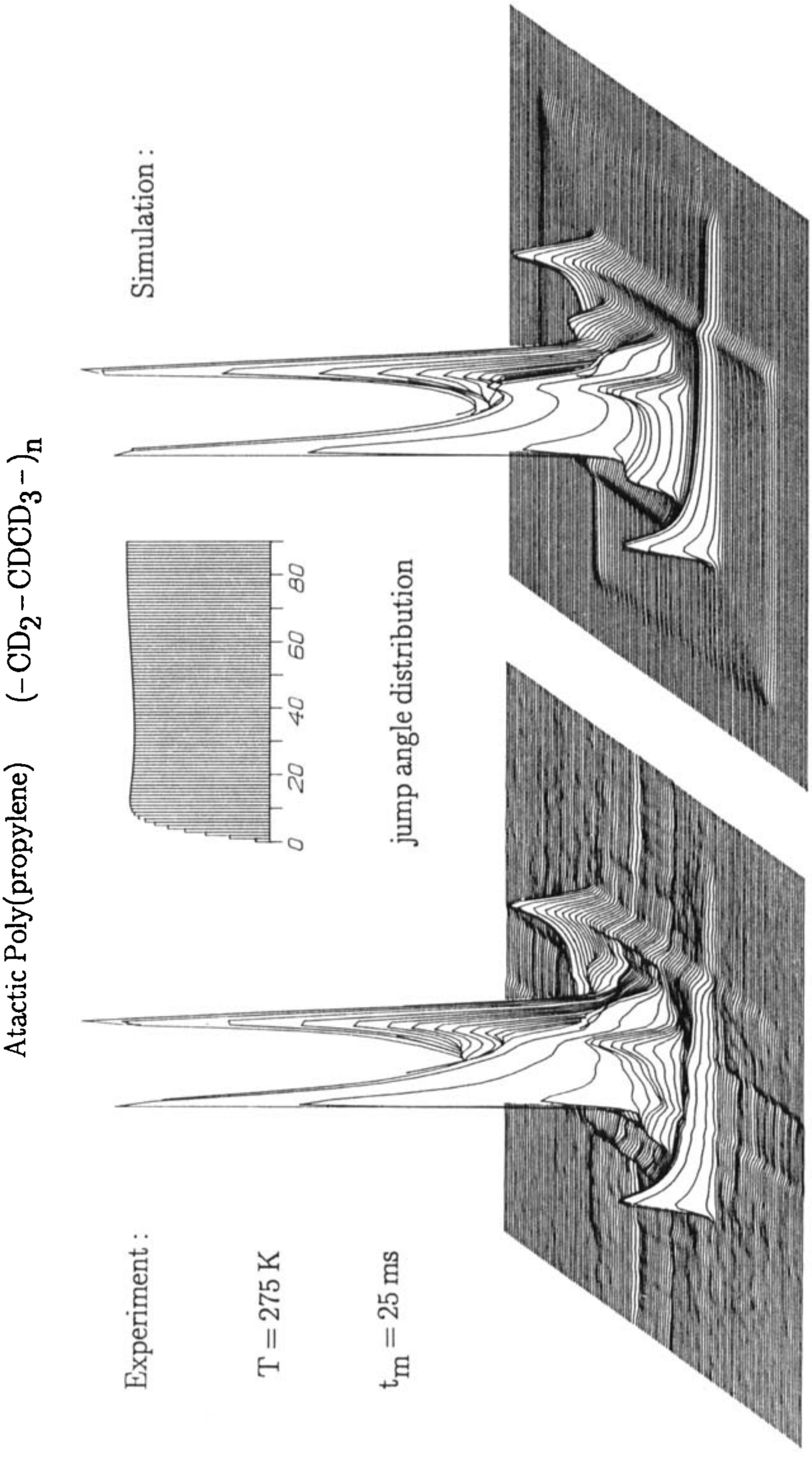

FIGURE 1 Experimental and simulated ^{2}H–2D–exchange spectra of aPP.

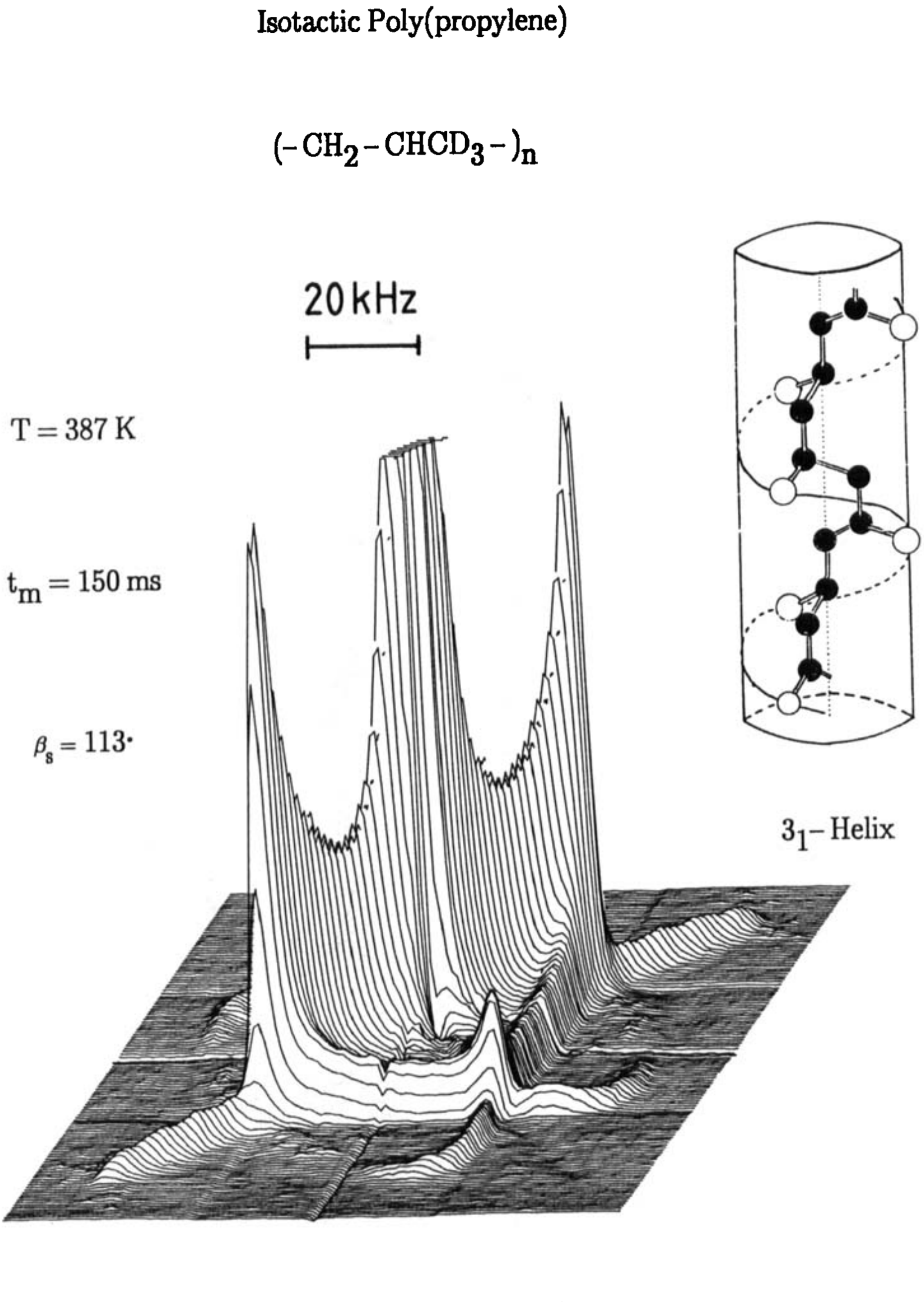

FIGURE 2 ^{2}H–2D–exchange spectrum of iPP.

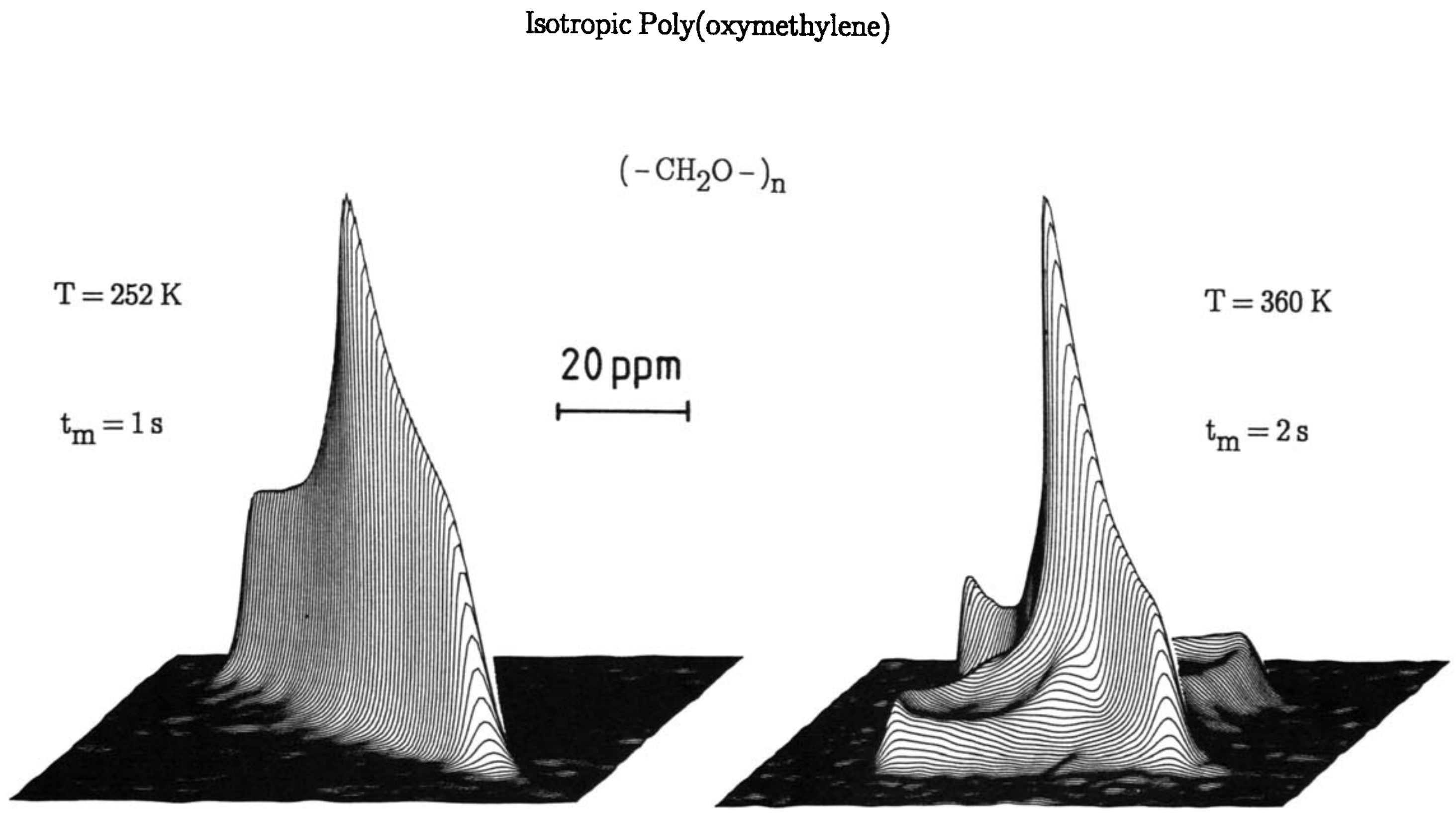

FIGURE 3 ^{13}C–2D–exchange spectra of isotropic POM.

crystalline regions of the semi-crystalline polymer and the narrow signal in the middle from the mobile amorphous regions. In the crystalline domains iPP forms a 3_1 helix. The symmetry of the helix allows a rotational jump motion of the polymer chain around the helix axis in connection with a translation so that a given monomer unit, after the jump, occupies the position of the neighboring monomer unit before the jump. When the sum over all molecular orientations is formed, the exchange signals exhibit singularities in form of an ellipse, from which the jump angle, i.e. the relative angle between the orientations of the methyl groups before and after the jump, can directly be read off as $\beta_s = 113°$. This jump angle between the methyl groups is consistent with a rotational jump motion of the helix in discrete steps of 120° about the helix axis.[7] Since the well defined helical jump motion of the iPP molecules in the crystalline regions lead to exchange singularities in form of ellipses, the jump angle can be determined without the need of interfacing a model.[3,5]

The beauty of the 2D-exchange experiment is the fact that it allows easy analysis in terms of a two-time distribution function,[5] provided pure absorption mode spectra are generated. The two-time distribution function is calculated by means of stochastic theory and allows the determination of type and time scale of slow molecular motions (on a time scale of ms up to s). Diffusive and jump-like reorientation can be discriminated simply by inspection of the 2D spectrum.

^{13}C-2D-EXCHANGE NMR

The 2D-exchange experiment can be applied to naturally abundant ^{13}C. The experimental procedures are only slightly different and the resulting spectra can be interpreted in an analogous fashion if the inhomogeneous ^{13}C resonances of different molecular segments do not overlap too strongly.[4] An example of a simple polymer is poly(oxymethylene), POM $(-CH_2O-)_n$, since there is only one carbon in the monomer unit. POM is a semi-crystalline polymer consisting of crystalline and amorphous domains. The chains in the crystalline regions form a helical conformation with nine monomer units in five turns (9_5 helix).

2D-exchange spectra of POM are shown in Fig. 3. At low temperature ($T = 252$ K, $t_m = 1$ s) a diagonal powder spectrum is observed indicating the absence of molecular reorientation on the time scale of 1 s. At elevated temperature ($T = 360$ K, $t_m = 2$ s) a pronounced exchange signal is observed in the 2D plane with a ridge-like appearance. These sharp features are characteristic of molecular jump motion. Indeed, the observed spectra can be simulated under the assumption of discrete successive 200° rotational jumps about the helix axis.[4] The jump angle of 200° is consistent with the 9_5

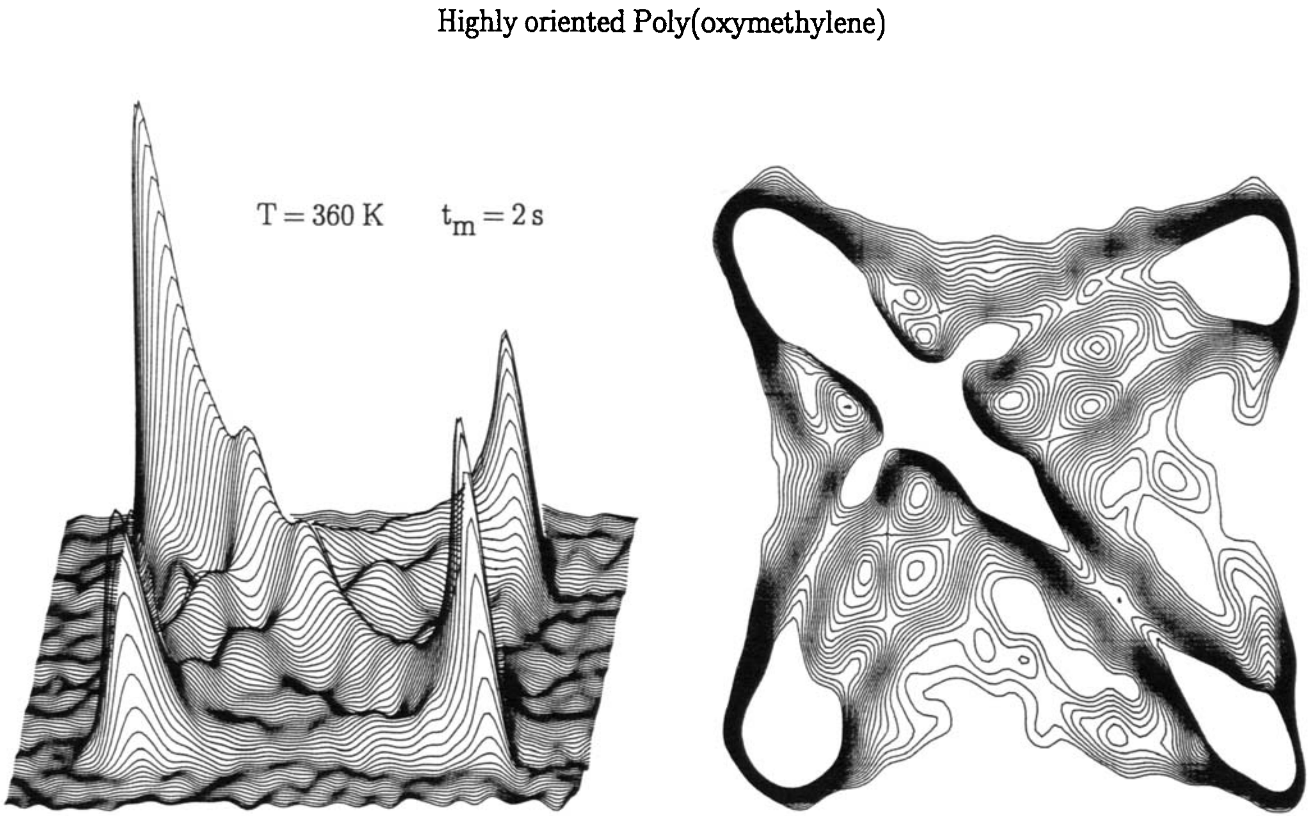

FIGURE 4 ^{13}C–2D–exchange spectrum of highly oriented POM.

helical conformation. If we take into account that a given helix can jump several times during the mixing time, then net rotation angles of 200° , 400° , etc. are possible, albeit with different populations. The geometry of the motion can even better be studied in highly ordered samples due to the even higher angular resolution. Fig. 4 displays the 2D-exchange spectrum of uniaxially ordered POM ($T = 360$ K, $t_m = 2$ s). The ridges corresponding to the 200° and 400° rotations are quite pronounced (ellipse-like patterns with long axis perpendicular and parallel to the diagonal, respectively) and even the 600° pattern is visible.[4]

The activation energy determined from exchange NMR data ($E_A = 75$ kJ/mol)[4] agrees with the activation energy for the α-process detected by mechanical and dielectric relaxation measurements. Thus the α-relaxation in POM is identified as 200° jump reorientations of the helix.

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