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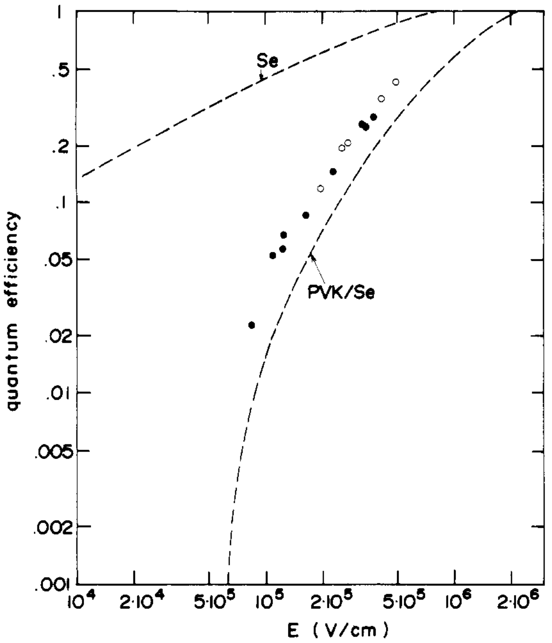

Figure 4. Apparent carrier injection efficiency from an a-Se layer into a layer of poly(2-*N*-carbazolylethyl acrylate) with the thickness of 14 (●) or 10 m (○). Xerographic gains of a-Se and 0.3-μm Se/12.5-μm PVK[30] are also shown for comparison.

disorder is smaller for the polyacrylate, in which the carbazole chromophores encounter less steric hindrance with the polymer backbone than in the polymethacrylate.

The hole injection efficiency from a-Se into the layer of the polyacrylate is depicted in Figure 4. The abrupt decrease of the apparent injection efficiency is a result of low carrier mobility of the polymer at low electric field; i.e., measurement were carried out while a transit was still proceeding in the polymer layer.[18] Compared with PVK/Se,[30] the falloff in the apparent injection efficiency occurs at a lower field, reflecting the high mobility of the present acrylate polymer.

Acknowledgment. We thank K. Fushimi and M. Tokushige for photoinduced discharge measurements.

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(14) 2-*N*-Carbazolylethyl acrylate was prepared by refluxing *N*-(2-hydroxyethyl)carbazole, acrylic acid, and a trace of *p*-toluenesulfonic acid in benzene for 3 h; yield, 88%. It was recrystallized from ethanol and further purified by silica gel column chromatography (eluant, benzene) and reverse-phase liquid chromatography (ODS-silica column, TSK-gel AT 10 μm, 2.2 × 30 cm; eluant, acetonitrile); mp 76 °C (lit. mp 75–76 °C,[15a] 74–75 °C[15b]).

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(16) Thickness was determined capacitively or by direct observation of the cross-section by photomicroscopy.

(17) The specimen was charged with a Colotron charger to an initial voltage. After a sample stage was moved into place under the surface-potential measuring probe, the decay of the voltage induced by irradiation with monochromatic light generated from a xenon tube through a monochromator was monitored with a Monroe isoelectric voltometer (Model 244), digitized with a transient converter and fed to an NEC PC-8800 microcomputer. Light intensity was adjusted sufficiently low to avoid a space-charge effect (<1 × 10^{12} photons/(cm^2 s) and the irradiation time was controlled with an electromagnetic shutter. All operations were controlled with the microcomputer. The injection efficiency (η) was evaluated from the initial photoinduced discharge rate $(\mathrm{d}V/\mathrm{d}t)_0$ by the relation $\eta = (\epsilon_0\epsilon/edI)(\mathrm{d}V/\mathrm{d}t)_0$, where ϵ_0 is the permittivity of vacuum, ϵ is the dielectric constant of the specimen (3.5), e is the electronic charge, d is the film thickness, and I is the incident photon flux.

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Ryuichi Oshima,* Toshiyuki Uryu, and Manabu Senō

Institute of Industrial Science, University of Tokyo
7-22-1, Roppongi, Minatoku, Tokyo 106, Japan

Received January 14, 1985

A 2D-Exchange NMR Study of Very Slow Molecular Motions in Crystalline Poly(oxymethylene)

In NMR information about molecular motions is usually obtained by measurements of relaxation times T_1, T_2, $T_{1\rho}$, etc. These relaxation times are sensitive to relatively fast motions (T_1, MHz motions; $T_{1\rho}$, 10–100-kHz motions; T_2, ~1 kHz motions). Very slow molecular motions (1 kHz–0.01 Hz) can be investigated by the spin alignment technique developed by Spiess.[1] This last technique, however, has the disadvantage that partly deuterated samples are needed.

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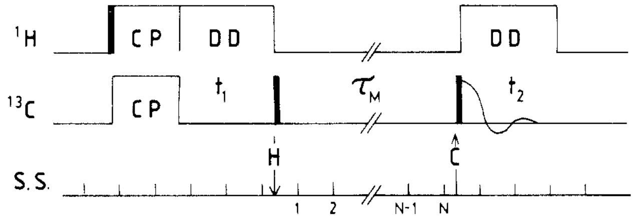

Figure 1. Pulse sequence for the 2D-exchange experiment with cross polarization (CP = 500 μs) and high-power dipolar decoupling (DD). 90° pulses (6 μs) are in black. In the case of slow magic angle spinning a synchronous mixing time is obtained with the Synchro-Spin (SS).[4] With an optical signal from the spinner, the Synchro-Spin holds the pulse programmer at point H and lets it continue after N spinner rotations.[4]

Edzes and Bernards[2] applied a 2D-exchange experiment[3] to a static powdered solid with the purpose of investigating slow (1 kHz–0.1 Hz) molecular motions in polymers via natural-abundance ^{13}C NMR. The pulse scheme for this experiment is given in the top half of Figure 1. First, transverse ^{13}C magnetization is created via cross polarization, and then the spin packets are allowed to precess freely during the evolution time. At time t_1 a $\pi/2$ pulse is applied to the system, therewith creating for each spin isochromat a magnetization vector along the z axis whose magnitude depends on the precession frequency of the isochromat during evolution. The remaining transverse magnetization dephases quickly because proton decoupling is turned off during the mixing time τ_m. At the end of the mixing period (which can be of the order of the ^{13}C T_1) a second $\pi/2$ pulse is applied and the ^{13}C FID is acquired during t_2. If during the mixing time a change in resonance frequency of a spin packet has occurred, this will manifest itself as off-diagonal intensity in the resulting 2D spectrum.

So if the experiment is applied to a static powdered sample with chemical shielding anisotropy one can detect if a change in the orientation of the chemical shielding tensor (and thus of the resonance frequency) of a particular spin has occurred during τ_m. However, it appears[2] that one cannot distinguish between ^{13}C–^{13}C spin diffusion and molecular motions. Furthermore, the sensitivity is rather low, especially with broad powder patterns. In order to overcome these problems we proposed applying the experiment to samples rotating about the magic angle with a frequency smaller than the chemical shielding anisotropy.[4] MAS will enhance the sensitivity. Furthermore, spinning at very high speeds would certainly eliminate ^{13}C–^{13}C spin diffusion.[5] For slow spinning at the magic angle the situation is less clear, and the experiment proposed here may be a technique to study ^{13}C–^{13}C spin diffusion under slow MAS conditions.

The effect of sample rotation is that the resonance frequency of each spin isochromat becomes time dependent. This causes the occurrence of spinning sidebands in a 1D spectrum.[6] As a result of the time-dependent resonance frequency the 2D-exchange spectrum not only shows diagonal spinning sidebands and centerbands but also off-diagonal peaks show up even if there are no molecular motions. However, if we choose the mixing period to be an integer multiple of the spinner period, then the off-diagonal spinning sidebands disappear (if there is no molecular motion) and the pattern along the diagonal is equivalent to the 1D spinning sideband spectrum. If molecular motions have occurred during the mixing time, this will manifest itself as off-diagonal cross peaks between the different spinning sidebands. In this experiment it is very important that the spinner is in exactly the same position at the end of t_1 and at the beginning of t_2. This is controlled with the aid of an optical signal from the rotor by a piece of equipment, called Synchro-Spin, which is added to a Bruker CXP-300 spectrometer.[4] Variations in the rotor speed will only result in a small change of the mixing time but will not cause the appearance of any cross peaks. This has been checked with hexamethylbenzene. For more details the reader is referred to ref 4. This technique offers a good method to study the nature of molecular motions ($t_1 < \tau_c < T_1$) because one can relate

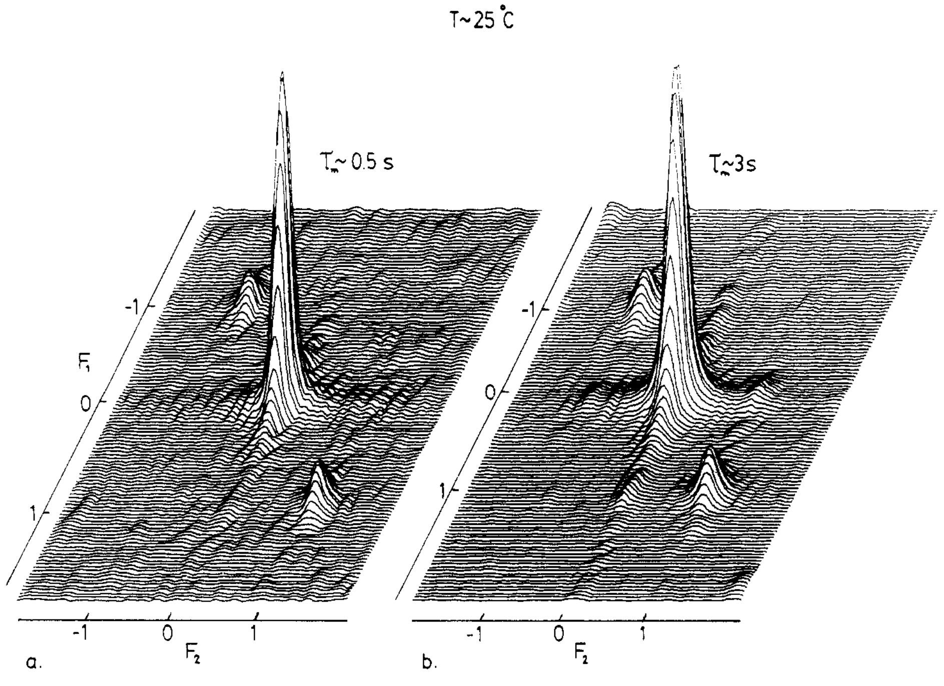

Figure 2. ^{13}C exchange NMR of poly(oxymethylene) at room temperature on a Bruker CXP-300 (^{13}C, 75.432 MHz). Numbers indicate the position of the spinning sidebands. (a) Mixing time of 750 rotor periods with a spinning frequency of 1470 Hz (64 × 750 FIDS) (27 h). (b) Mixing time of 4200 rotor periods with a spinning frequency of 1400 Hz (128 × 250 FIDS) (40 h).

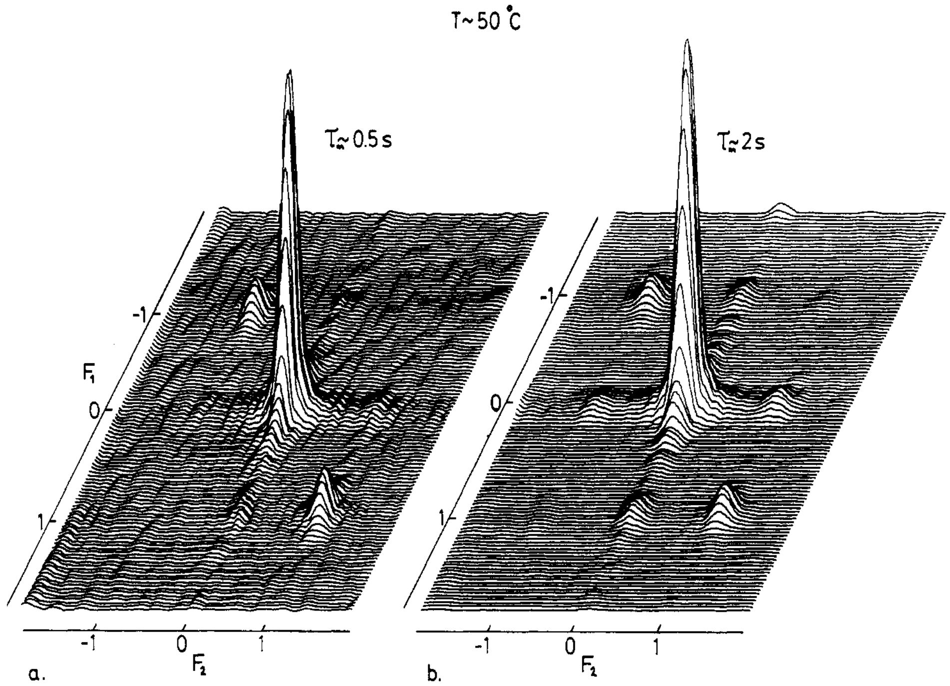

Figure 3. ^{13}C exchange NMR of poly(oxymethylene) at 50 °C. (a) Mixing time of 750 rotor periods with a spinning frequency of 1475 Hz (64 × 870 FIDs) (31 h). (b) Mixing time of 3000 rotor periods with a spinning frequency of 1520 Hz (64 × 750 FIDs) (47 h).

the orientation of the chemical shielding tensor in t_1 to that in t_2.

Here we want to report our first results on poly(oxymethylene) (commercially available Hostaform-C from Hoechst). It is known that only the crystalline part of POM gives rise to a full NMR powder pattern at room temperature. In the amorphous part the chemical shielding anisotropy is partly averaged by molecular motions so that it gives a relatively narrow line.[7] As a result we will with slow magic angle spinning only see spinning sidebands from the crystalline part of the polymer. In addition, the short T_1 of the amorphous part (amorphous T_1 = 75 ms; crystalline T_1 = 15 s at 45 MHz[8]) ensures that when the mixing time is not shorter than 0.5 s, amorphous spins only contribute to axial peaks, which are removed from the spectrum by proper phase cycling.

Figure 2 shows the results of the 2D-exchange experiment applied to poly(oxymethylene) at room temperature with a mixing time of 0.5 and 3 s at a spinning rate of approximately 1400 Hz. The τ_m = 0.5 s spectrum shows the POM signal with two spinning sidebands on the diagonal. In the τ_m = 3 s spectrum some weak cross peaks show up, indicating that the POM chains are moving slowly. At 50 °C this effect becomes more pronounced (Figure 3). Here the τ_m = 0.5 s spectrum already shows some very weak cross peaks, and with a mixing time of 2 s the off-diagonal peaks are even bigger as in the τ_m = 3 s spectrum at 25 °C. This temperature dependence clearly shows that we are dealing with molecular motions and not with spin diffusion.

Motions in POM are extensively studied by mechanical and dielectric relaxation measurements (ref 9 and references therein). Apart from the low-temperature γ and β relaxations these measurements show a low-frequency (1 Hz) loss maximum at 80–130 °C (α relaxation). Nothing is known yet about the precise character of the motions responsible for this α relaxation, although indications exist that these motions occur in the crystalline phase of the material.

Extrapolation of the α relaxation map of POM from dielectric loss data[9a] yields a frequency of ~0.1 Hz at 50 °C. In Figure 3 we see that the cross peaks are very weak after 0.5-s mixing time but become more pronounced at a mixing time of 2 s. This tells us that the observed motion must be slower than ~1 Hz. Since the relaxation times found in the dielectric loss measurements and the NMR experiment are in the same range, we believe that the motion observed in the NMR experiment should be associated with the α relaxation. As the motions responsible for the cross peaks in Figures 2 and 3 arise from polymer chains in crystalline regions, this then shows that the α relaxation process indeed takes place in crystalline poly(oxymethylene). Further, we believe that the above-reported 2D NMR method will enable us to obtain precise information about the molecular motion involved. The relative intensity of the cross peaks compared to that of the centerband depends on the change of the orientation of the chemical shielding tensor during the mixing period.[4] By assuming a certain model for the motion (e.g., chain rotation) the 2D spectrum can be simulated and compared with the experimental spectra. Investigations along these lines are in progress.

Acknowledgment. We thank J. W. M. van Os for building the Synchro-Spin and his technical assistance. This work was supported by the Dutch Foundation for Pure Research (ZWO/SON).

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A. P. M. Kentgens, A. F. de Jong, E. de Boer, and W. S. Veeman*

Department of Physical Chemistry
Faculty of Science, University of Nijmegen
Toernooiveld, 6525 ED Nijmegen, The Netherlands

Received November 26, 1984