creasing the craze fibril drawing stress. This toughening mechanism should occur in any system where an incompatible low molecular weight rubbery polymer is finely enough dispersed in a glassy polymer matrix. It may even be a factor in normal rubber-toughened polystyrene where there could be a significant low molecular weight sol fraction dissolved in the rubber particles. In this context it is relevant to note that craze fibrils and craze interfaces are stained dark by exposing the samples to OsO_4. This phenomenon has been ascribed to the reaction of OsO_4 with (1) double bonds produced as decay products of the radicals created by the chain scission inherent in the crazing process[10-12] and/or (2) unknown molecular heterogeneities[11] on the surface of fibrils. The first hypothesis does not explain why the craze staining in the PB-modified PS is much stronger than that in crazes in pure PS. The extra staining observed in high-impact polystyrene (HIPS) may then be the staining of the low molecular weight unsaturated rubber fraction which diffuses out from the rubber particles along the craze–matrix interfaces during craze growth.

Acknowledgment. The experiments at Cornell were supported in part by the Cornell Materials Science Center which is funded by the DMR-MRL division of NSF. The research of A.S.A., R.E.C., and O.S.G. has been supported by the NSF/MRL under Grant DMR 84-18718 through the CMSE at MIT.

Registry No. PS, 9003-53-6.

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Received July 15, 1988;
Revised Manuscript Received November 29, 1988

Order-Exchange Correlated Two-Dimensional NMR Study of Slow Molecular Motion in Highly Oriented Crystalline Poly(oxymethylene)

Two-dimensional (2D) NMR spectroscopy has become a valuable method for the study of molecular order or dynamic processes such as those resulting from chemical exchange, molecular motion, and spin diffusion.[1-10] In those experiments, the new signals due to molecular order or exchange are introduced by means of an additional spectral frequency dimension. In heterogeneous solids, e.g., glassy polymers, the type and the time scale of molecular motion may depend on the degree of molecular order. Therefore, experiments are desirable which can *correlate* molecular order and dynamics in partially oriented materials. One obvious way to correlate order and exchange for a partially oriented polymer sample is provided by 3D NMR.[11] Recently, we have developed a new rotor synchronized magic angle spinning (MAS) NMR method which can detect the correlation of molecular order and dynamics in partially ordered materials in two dimensions already.[12]

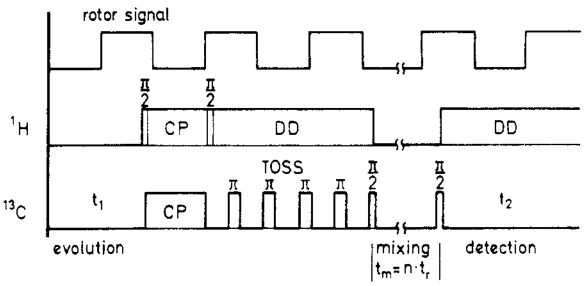

Figure 1. Two-dimension rotor synchronized ^{13}C MAS NMR pulse sequence for the correlation of molecular order and spin exchange.

The technique and the analysis of the sideband patterns are described in ref 12. It is the purpose of this paper to demonstrate its potential in polymer science by giving a preliminary report of a study of the chain mobility in highly oriented poly(oxymethylene) (POM).

The technique is based on three concepts: (i) By synchronization of the data acquisition with the rotor position in MAS-NMR of partially ordered polymers, a 2D sideband pattern can be obtained for each resonance, where the sidebands in the ω_1-dimension reflect the degree of molecular order.[7,8] (ii) Sidebands can be suppressed by applying the TOSS sequence[13-15] (total suppression of spinning sidebands). (iii) When combining TOSS with the exchange experiment,[1a] suppressed sidebands reappear in the presence of ultraslow dynamic processes during the mixing time.[16]

By combination of these three concepts, i.e., rotor-synchronized TOSS with insertion of a mixing time to allow for exchange, a 2D experiment can be designed,[12] where most of the sidebands occur only if the residue giving rise to the signal is involved in *both* molecular order and dynamics.

The pulse scheme for this experiment is given in Figure 1. After the pulse programmer is triggered by the rotor signal, the evolution period t_1 is inserted, being incremented in 16 steps of Δt_1 equal to one-sixteenth of one rotor period t_r. Transverse ^{13}C magnetization is created via cross-polarization (CP). After CP we apply the conventional TOSS pulse sequence consisting of four π-pulses the pulse spacings of which have been tabulated by Dixon.[14] For isotropic samples thereby the total suppression of spinning sidebands is achieved, whereas the sidebands are not suppressed for ordered samples, vide infra. At the point when the acquisition begins in a standard TOSS experiment, the transverse magnetization is stored parallel to the magnetic field by a 90° pulse, and a mixing period of an integral number of rotor periods starts. The remaining transverse magnetization dephases quickly because proton decoupling its turned off during the mixing time t_m. At the end of the mixing period the magnetization is rotated back into the transverse plane of the rotating

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frame for detection of the signal under proton dipolar decoupling (DD).

When the experiment is applied to an *isotropic sample*, the signal detected is independent of the rotor position and the TOSS sequence can suppress all the sidebands. In the absence of spin exchange, the spin packets will experience the same NMR frequencies at the beginning and at the end of the mixing time and a 2D centerband only will be detected. If spin exchange does occur, the delicate spin state prepared by TOSS will be disturbed by the resulting frequency changes,[16] which introduces sidebands confined to a center line parallel to the ω_2-axis (see Figure 2 of ref 12).

If the experiment is applied to an *ordered sample* (with the order axis not parallel to the rotor axis), under the TOSS condition the centerbands corresponding to each crystallite are in-phase and do not change with the rotor position, but the sidebands which depend on the rotor position are phase modulated. The phase angle increment of the sideband for two different rotor positions is proportional to the order of the sideband. Therefore, in the absence of dynamics only the diagonal peaks are observed.[12] Additional off-diagonal sidebands occur only if the corresponding residue is involved in *both* order and dynamics, which can therefore be correlated in heterogeneous systems. This has been checked with polyethylene. For more details the reader is referred to ref 12.

Here we want to report our first results of applying this technique to highly oriented crystalline POM, kindly provided by Prof. I. M. Ward. It is known that only the crystalline part of POM gives rise to a full NMR powder pattern at room temperature. The amorphous part gives a relatively narrow peak only, because the chemical shift anisotropy is partly averaged by fast molecular motion.[17] POM is a highly crystalline polymer. The unit cell consists of chains in a helix conformation with nine monomers in five turns of the helix.[18] This model has been refined by Uchida and Tadokoro[19] to 29 units in 16 turns; such small refinements, however, bear no significance for the present study. Within a crystal all helices are parallel and have the same form. The principal values of the chemical shift tensor are $(\sigma_{xx}, \sigma_{yy}, \sigma_{zz}) = (67, 86, 111 \text{ ppm})$.[20] The orientation of the chemical shift tensor is determined by the local tetrahedral symmetry of the CH_2O_2 unit; i.e., the *Z*-axis is perpendicular to the O–C–O plane, forming an angle of 55° with the helix axis. The *Y*-axis lies within the O–C–O plane and bisects the O–C–O angle. The *X*-axis is of course perpendicular to the *Y*- and *Z*-axes.

The experiments were performed on a Bruker MSL 300 spectrometer, operating at a ^{13}C NMR frequency of 75.47 MHz. Parts a and b of Figure 2 show the results for POM at 320 K with a mixing time $t_m = 0$ and 4 s, respectively, at a spinning rate of 630 ± 1 Hz. The $t_m = 0$ spectrum generated without a mixing time shows only the diagonal peaks with positive and negative amplitudes. From this spectrum we can get the order parameters by using the method developed by Harbison.[8] We fitted the spectra to sixth order of subspectra, but the highest order parameter $\langle P_6 \rangle$ is somewhat unreliable because of the small size of the ^{13}C-shielding tensor in POM, which generates a small number of sidebands only. The order parameters for the helix axis, $\langle P_2 \rangle$ and $\langle P_4 \rangle$, are 0.70 and 0.69, respectively. The $t_m = 4$ s spectrum, on the other hand, gives all the 2D sidebands. As mentioned before[12] the sum of their intensities parallel to the ω_2-axis gives only the information about molecular order: $\langle P_2 \rangle = 0.98$ and $\langle P_4 \rangle = 1.0$ for the helix axis. The difference between the two experiments can be attributed to the short T_1 of the amorphous part.[21] The $t_m = 0$ spectrum contains the contribution of both amorphous and crystalline parts, where the mobile amorphous regions contribute mainly to the centerband. The $t_m = 4$ s spectrum contains only the contributions of long T_1 components (crystalline part and/or highly oriented amorphous part), and the short T_1 spins only contribute to axial peaks which have been removed from the spectrum by proper phase cycling. The high $\langle P_2 \rangle$ and $\langle P_4 \rangle$ values of the spectrum of $t_m = 4$ s indicate that all the helices are very highly oriented along the draw direction.

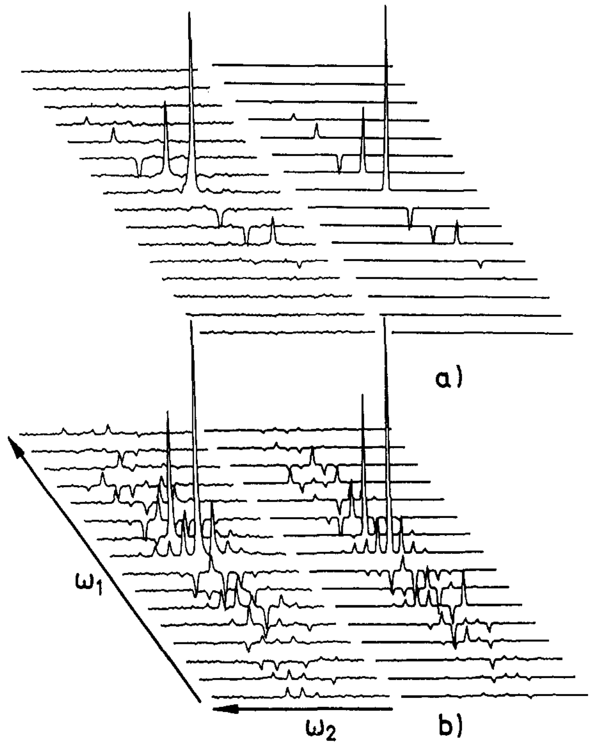

Figure 2. Experimental and theoretical pure absorption mode ^{13}C 2D rotor synchronized TOSS MAS spectra at 75.47 MHz of highly oriented crystalline POM at 320 K and a spinning rate $\omega_r/2\pi = 630 \pm 1$ Hz. Slices in ω_1 are $2\pi \times 630$ Hz apart; the scale in ω_2 is defined accordingly by the sidebands observed. (a) Spectra with zero mixing time. (b) Spectra with a synchronous mixing time of 4 s. The theoretical spectrum of (a) was calculated by using the order parameters obtained from the experimental spectrum, and the theoretical spectrum of (b) was calculated by using the jump model proposed by Kentgens.[20] Perfect order was assumed in the calculation of spectrum b.

The ultraslow molecular motion in crystalline POM has been studied by measurements of relaxation times[21] and by application of the 2D-exchange experiment.[20,22] The motional model proposed is that the helical polymer chains make 200° jumps around the helix axis. We believe that our spectrum will be sensitive to the details of the motional mechanism because we observe pure absorptive 2D sidebands with positive and negative intensities. The simulated spectra in Figure 2 were calculated according to eq 5 of ref 12, using the motional model described above, which has previously shown by Kentgens[20] to account for the 2D-exchange sideband patterns of isotropic POM. The agreement between experimental and calculated spectra of an ordered sample (Figure 2b) nicely confirms this model. The off-diagonal signals are rather strong because there is complete correlation of order and mobility since the helix axis not only is the preferred direction for the molecular order but also is the axis about which the rotational motion occurs. In principle the slow motion in the highly oriented amorphous region is also accessible to the experiments. But in our spectrum of $t_m = 4$ s the signal from the oriented amorphous region, with lower values of

$\langle P_2 \rangle$ and $\langle P_4 \rangle$, is not observed. This also indicates that the T_1 value of the spins in the oriented amorphous region is shorter than 1 s.

Acknowledgment. The highly oriented POM sample studied here was kindly provided by Prof. I. M. Ward, Leeds University, UK, which is gratefully acknowledged. A.H. thanks the "Stiftung Volkswagenwerk" and the "Fonds der chemischen Industrie" for a Kekulé stipend.

Registry No. POM, 9002-81-7.

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Received August 31, 1988;
Revised Manuscript Received November 8, 1988

Spontaneous Formation of Long-Range Order in Actin Polymer Networks

Actin is a major protein constituent of cells and, in the filament form, not only helps to define the structure and mechanical properties of cytoplasm but also plays a role in many aspects of cellular motility, as well as in muscle contraction. Our understanding of the details of structure/function relationships in cellular processes is in its infancy, although a large body of knowledge on the interactions of the many actin-binding proteins with actin from in vitro experiments[1-6] has been assembled. These experiments have shown quite complex and varied mechanisms control the polymerization state of actin.

Purified actin forms a network of filaments when polymerized in vitro with salt. The mechanical properties of this network and the diffusion of individual actin filaments or of added probes within the network have been studied by several groups by viscoelastic[7-11] and fluorescent photobleaching methods.[12-15] There are conflicting interpretations in the literature as to whether or not individual actin filaments in the network form noncovalent cross-links in the absence of added actin-binding proteins which are known to form a cross-linked gel with actin.[1-6]

We have recently reported on dynamic light scattering measurements of the diffusion of inert spherical probes within actin solutions at concentrations below about 1 mg/mL.[16] These measurements found a progressive decrease in the diffusion of the probes at increasing actin concentrations for a fixed probe radius or with increasing probe radius at fixed actin concentrations. In attempting to extend this work to higher actin concentrations and lower scattering angles, we observed a new type of behavior which is the subject of this report.

Actin was extracted from rabbit muscle acetone powder and purified according to published procedures using a final column purification step.[16] Monomeric actin was filtered into optical cuvettes and monodisperse polystyrene latex spheres (PLS) were added, to serve as local microviscosity probes, at concentrations which ensured that the diffusion coefficients determined were those of the probe.[16] The probes have been shown to act as inert, non-actin-binding spheres.[16] Prior to polymerization of the actin with either 1 mM $MgCl_2$ or 100 mM KCl, 50 μM Mg-EGTA was added and the sample was incubated for 5 min. Diffusion coefficients were determined by dynamic light scattering with a previously described system.[16-18] Experiments of typically 20-s duration determined the average diffusion coefficient of the probes, the average scattered intensity, and the second cumulant parameter, which is a measure of the polydispersity of local microviscosity in this case. At concentrations of actin above about 1 mg/mL, after an incubation time of 20–90 min (depending upon the salt) a series of dynamic light scattering measurements were made at varying scattering angles (in the range 15° to 90°). When these experiments had been performed at actin concentrations below about 1 mg/mL, the results were reproducible, in the sense that fluctuations in the scattered intensity of light and in the measured diffusion coefficients of the probes were small.[16] At higher concentrations, we observed the onset of large (up to factors of 5) and slow (several minute) fluctuations in the intensity of scattered light and corresponding large fluctuations in the measured diffusion coefficients so that a record of repeated 20-s experiments gave seemingly erratic results (see Figure 1). These results clearly indicate the presence of large spatial inhomogeneities in the PLS probe concentration. When the average diffusion coefficients of the PLS, average scattered intensities during the duration of the experiment, and "polydispersity" measure indicating the range of different local microviscosity environments were cross-correlated in successive experiments, a very strong correlation was found as shown in Table I.

For these same samples, at lower scattering angles, we viewed on a screen a quasi-stationary diffraction pattern (see Figure 2), which had the following characteristics. The pattern consisted of a set of diffraction maxima, randomly arrayed with a circular trend due to the optical arrangement, which had persistence times of several minutes. At higher concentrations or with larger PLS probes, the