Detection of Slow 180° Phenylene Flips in PET Fibers via ^{13}C Two-Dimensional Solid-State Exchange NMR

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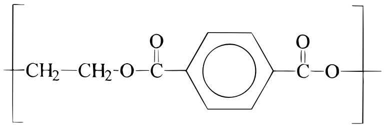
Introduction. Reflecting the importance of the semicrystalline polymer poly(ethylene terephthalate) PET, considerable scientific effort has been made to elucidate its properties. The research in connection with PET covers virtually all aspects of polymer physics such as correlation between X-ray structure and force field methods,[1,2] dielectric measurements[3,4] and their relation to mode coupling theory,[5] crystal structure, the relation between morphology and mechanical properties,[6−10] or the characterization of orientation.[11,12] Important aspects can be studied by the use of solid-state NMR spectroscopy to determine morphology,[13,14] orientation,[15−17] and mobility[18−20] in the bulk material. Previous solid-state NMR studies concerning mobility were restricted to information deduced from relaxation times or line shape analysis. Both types of measurements yield data related to motions with rates faster than several kilohertz, which at ambient temperatures originate in the amorphous regions.



A particularly important feature of PET is the fact that a simple two-phase model is inadequate to describe its morphology. Besides the crystalline and the amorphous regions, partially immobilized noncrystalline layers are present and are assumed to play an important role in determining the materials properties.[21] In drawn PET films or fibers, the chains in these noncrystalline layers are almost as highly aligned as those in the crystalline regions.[16] Therefore, in this paper we employ ^{13}C two-dimensional exchange NMR[22] to check whether slow motions with rate $k \approx 1\ \mathrm{s}^{-1}$ occur in these aligned and partially immobilized regions of bulk industrial fibers.

NMR Background. The ^{13}C-NMR chemical shift for different carbons in PET [16,23] leads to different frequencies described by[22]

$$\omega = \omega_{\mathrm{iso}} + \delta/2(3\cos^2\theta - 1 - \eta\sin^2\theta\cos 2\varphi) \quad (1)$$

Here, the angles θ and φ describe the orientation of the magnetic field $\mathbf{B_0}$ with respect to the principal axes system (PAS) of the chemical shift tensor. Every chemical shift tensor is characterized by the values of ω_{iso}, δ, and η and three Euler angles relating its PAS to the molecular frame. All protonated carbons of the aromatic ring have identical chemical shift anisotropies and the same direction of the chemical shift tensor with respect to the molecular frame; i.e. the upfield principal value ω_z is associated with the normal of the ring, and the downfield value ω_x with the C−H bond direction. The phenylene para-axis and the fiber axis are inclined by 18°. Consequently, ^{13}C solid-state NMR is able to distinguish two frequencies originating from the protonated aromatic sites, denoted as 2 and 3 in Figure 1, even if the fibers are aligned parallel to the magnetic field; vide infra.

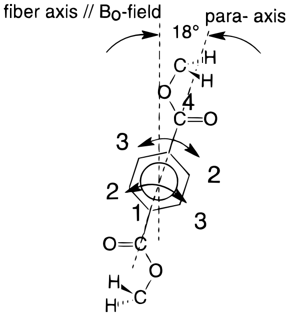


Figure 1. Sketch of repeat unit of PET. A 180° flip motion of the phenylene unit changes the orientation between the C−H bond of a protonated aromatic carbon atom and the applied $\mathbf{B_0}$ field (labeled as sites 2 and 3). Note the difference in orientation of approximately 18° between the fiber axis ($\|\mathbf{B_0}$ field) and the para-axis of the aromatic ring. The difference in orientation leads to a difference in frequency for carbon 2 compared to carbon 3 according to eq 1.

With two-dimensional exchange NMR[22] we are able to correlate the frequency ω_1 at a time $t = 0$ for one carbon site with a frequency ω_2 after a mixing time t_{m} for the same carbon site. The range for t_{m} is typically between 5 ms and 5 s and limited for long times by the ^{13}C spin−lattice relaxation time T_1. As shown in Figure 1, a 180° flip of a phenylene ring along the para-axis during t_{m} will lead to an exchange between the two sites 2 and 3 and therefore to frequencies $\omega_1 \neq \omega_2$. As a result, off-diagonal intensity in the 2D exchange NMR spectrum will appear. Thus, slow 180° flip motions of the phenylene rings in PET fibers can be detected this way.

Experimental Section. The industrial PET-fiber samples under investigation were provided by Hoechst-Celanese. Textile parameters: 8 g/denier; tensile strength of 70 cN/tex; module 8.8 N/tex; shrinkage of about 9% and 50% crystallinity. NMR measurements were carried out on a Bruker MSL 300 NMR spectrometer (7.05 T) with a static probe on a bundle of such fibers with the fiber axis parallel to the magnetic field; see Figure 1. Typical experimental parameters: repetition time 3.7 s; cross polarization (CP) time of 500 μs; 90° pulse length of 4.5−5 μs; detection in t_2 via an echo every 6 μs for 512 data points; 64 data points during t_1 and signal averaging of about 400 acquisitions per t_1 increment. The mixing time was varied in several measurements between 15 and 2000 ms at temperatures of 253, 293, and 333 K.

Results and Discussion. Spectral Assignment. The two-dimensional ^{13}C-NMR spectrum of the PET fiber in Figure 2 shows both diagonal and off-diagonal intensity. The assignment for the different sites along the *diagonal* spectrum is done by calculating the frequencies using eq 1 for the known values and orientation of the chemical shift anisotropy.[16,23] Moreover, protonated and nonprotonated carbons are discriminated by variation of the CP time. In Figure 3 the calculated 1D diagonal spectra for all sites are shown for a uniaxially oriented sample with a Gaussian

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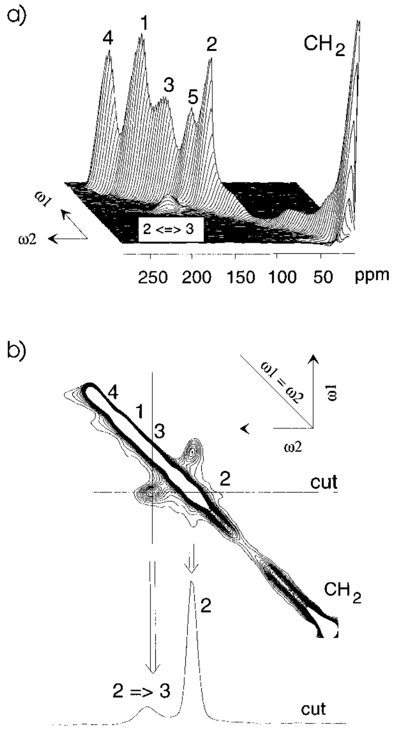

Figure 2. (a) ^{13}C two-dimensional solid-state NMR spectra of a bundle of oriented, industrial PET fibers. The diagonal peaks are labeled according to Figure 1. The spectrum was acquired at 293 K with a mixing time of 1 s. The 180° phenylene motion about the para-axis is reflected in the sharp exchange peak between positions 2 and 3. The high intensity along the diagonal is due to carbon atoms which have not changed their position and therefore not changed frequency during the mixing time t_m. (b) Contour plot of the spectrum shown in (a). The 20 linearly spaced lines between 1.5 and 17% of the maximum height of the spectrum indicate clearly the 180° flip motion. In addition, a cut through the spectrum at peak 2 is shown. The integration of the exchange peak intensity for different t_m leads to the rate distribution for this motion as shown in Figure 4a.

distribution full width half-maximum (fwhm) of 20°.[16] For such a distribution Legendre order parameters are $\langle P_2\rangle = 0.93$ and $\langle P_4\rangle = 0.79$. Figure 3 shows that in such oriented samples the spectral intensities are contracted to narrow bands, resulting in a strong increase in signal-to-noise ratio (S/N). Peak 5 in Figure 2 is related to rapid 180° flip motions of phenylene rings, interchanging the protonated aromatic carbons 2 and 3[19] with rates higher than the frequency differences for the two sites. Peak 5 also comes from oriented material. Its intensity increases with temperature. This indicates correlation times in the tens of kilohertz region at ambient temperatures.

The *off-diagonal* exchange peak connects carbon sites 2 and 3; see the contour plot in Figure 2b. This exchange peak thus also originates from the 180° flip motion along the para-axis of the phenylene ring, as described above, however, with much longer correlation times, comparable to the mixing time t_m. The spectral width of peaks 2 and 3 is reduced through the orientation by a factor of about 10, as shown in Figure 3. The exchange intensity in the two-dimensional spectral plane is therefore increased by about 100 in the fibers compared with unoriented samples. This explains why the slow 180° flip has not yet been detected before by ^{13}C solid-state NMR of unoriented PET samples.

Integration of the exchange intensity yields the fraction of the phenylene rings which have flipped an odd number of times during t_m. If a phenylene ring does not move or flips an even number of times during t_m, the orientations at $t = 0$ and $t = t_m$ coincide. Hence, for these rings $\omega_1 = \omega_2$ and they contribute to the diagonal intensity in the 2D spectrum.

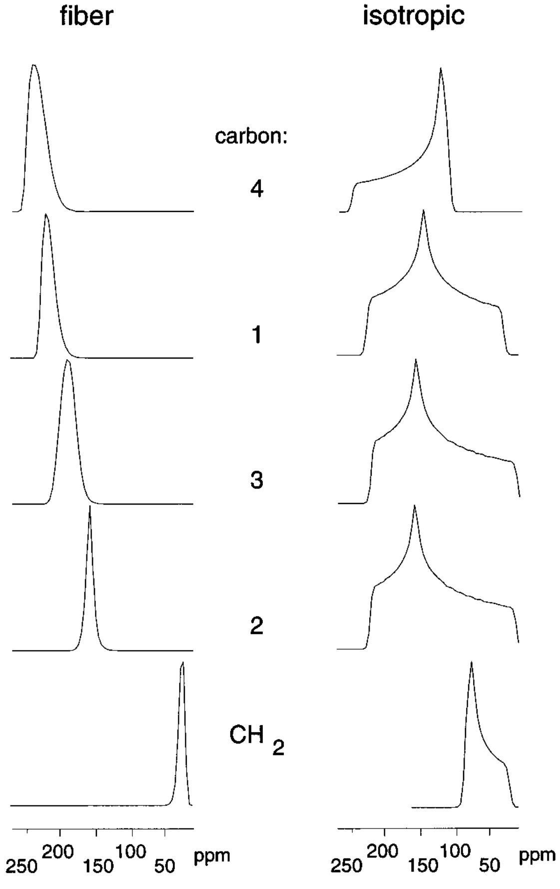

Figure 3. Simulated 1D spectra for the five different carbon sites in PET. The simulation was done under the assumption of a Gaussian distribution (fwhm = 20°) and a uniaxial distribution of the molecular axis, left. For comparison, powder spectra for isotropic samples are plotted at the right. The simulation provides the basis for the spectral assignment of Figure 2. All spectra are scaled to the same height.

Flip Rate. The variation of the mixing time t_m yields the buildup of the exchange intensity plotted in Figure 4a, which is found to be highly nonexponential. If the motion would occur inside a crystallite, a single exponential would be expected. Furthermore, only highly oriented molecules can give rise to sharp exchange peaks; see above. Thus we conclude that the slow flip motion detected here indeed takes place in the immobilized, highly oriented noncrystalline parts of the semicrystalline polymer fiber.

For a quantitative analysis we describe the increase of the exchange intensity with t_m, by a Kohlrausch–Williams–Watts (KWW) function[24] $I_{(tm)} = 1 - \exp\{-(kt_m)^{\beta}\}$. For $T = 293$ K the fit (see Figure 4a) yields a mean rate $k = 1.52$ s^{-1} and $\beta = 0.34$, indicating a wide distribution of jump rates. It is interesting to note that the wings of such a distribution extend into the tens of kilohertz region for which motional averaging (peak 5) is observed. Since those spectral features were not taken into account explicitly in our fit, the distribution of motional rates in the highly oriented regions will actually be even wider.

Similar experiments were carried out at $T = 253$ K and $T = 333$ K. In Figure 4b the flip rates determined by ^{13}C 2D exchange NMR are compared with those

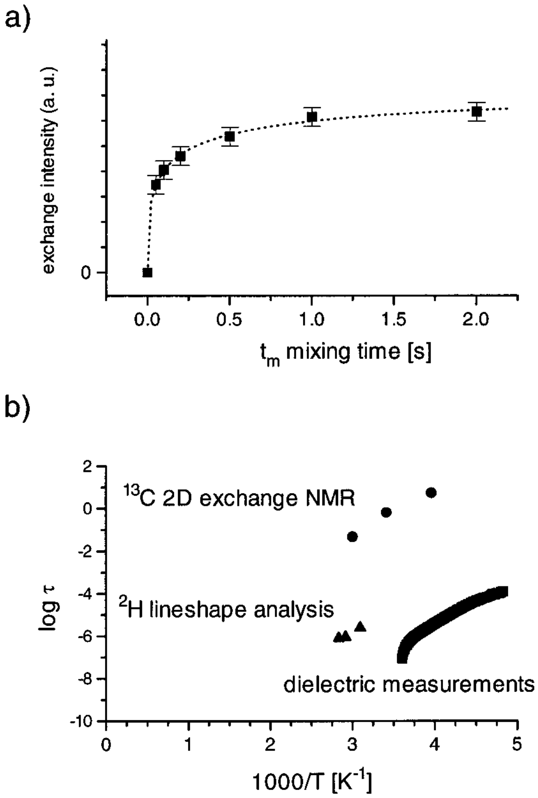

Figure 4. (a) Exchange intensity for the 180° flip motion of the phenylene ring in PET fibers as a function of mixing time t_m, measured at 293 K. Nonexponential behavior for the exchange intensity $I_{(\mathrm{tm})}$ is evident. A fit with a KWW distribution of correlation times according to $I_{(\mathrm{tm})} = 1 - \exp\{-(kt_m)^{\beta}\}$ yields the mean rate for the motion $k = 1.52\ \mathrm{s}^{-1}$ and $\beta = 0.34$. This corresponds to a distribution width of about 3 decades full width half-maximum, characteristic of a noncrystalline environment. (b) Activation plot of correlation times in PET determined from dielectric relaxation,[25] ^{2}H-NMR [18] and ^{13}C 2D exchange NMR.

obtained by dielectric relaxation of the same fibers[25] and ^{2}H NMR line shape analysis of a phenylene deuterated isotropic sample.[18] Both methods yield significantly shorter mean correlation times consistent with rapidly flipping rings in the mobile amorphous regions.

Thus, to our knowledge the slowly flipping phenylene rings in the more rigid, highly oriented amorphous regions are detected here for the first time. The fraction of phenylene rings undergoing these slow motions can be judged from the intensity of the exchange peak, as compared to the diagonal peak which is dominated by the crystalline regions; see Figure 2. This shows that about 20% of the phenylene groups which do not undergo fast motions are flipping with such low rates. Thus, our 2D NMR study shows that the packing in these ordered noncrystalline layers leads to a motional behavior of the phenylene rings different from that of the amorphous and the crystalline regions. This is particularly relevant since the noncrystalline immobilized regions are assumed to play a crucial role in determining the properties of PET fibers.[21]

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