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Geometry of Complex Molecular Motions of Guest Molecules in Polymers from Solid State ^{2}H NMR

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Nanoporous systems provide interesting possibilities to confine molecules to be used for specific functions, e.g., as switches, in sensorics, or in separation.[1] Such behavior partially mimics biological systems, where enzymes with specific cavities exhibit exquisite binding discrimination and reactivity.[1d,1e] Recent advances in solid-state inclusion compounds produced an extraordinary variety of cavities that encapsulate guests through noncovalent forces and can be customized through molecular design to control their solid-state properties and guest reactivity. *Crystalline polymers* offer the additional advantage of processability and alignment due to mechanical forces. In this context, the nanoporous δ and ε crystalline phases of syndiotactic polystyrene (s-PS),[2] obtained by guest removal with supercritical carbon dioxide from cocrystalline phase,[3] offer promising applications in chemical separation (mainly air/water purification), in sensorics, and optical applications.[4] In particular, the δ crystalline phase contains two identical cavities built by eight monomeric units of styrene per unit cell, which easily absorb low-molecular-mass molecules generally with single occupancy of each cavity.[2a] Moreover, high degrees of guest orientation with respect to the polymer host can be achieved.[3] For example, the location and orientation of benzene and 1,2-dichloroethane (DCE) guests in the s-PS host δ phase, determined by X-ray diffraction[3a,3b] and infrared dichroism,[3c,3d] are shown in Figure 1b along the *b* projection ($c - a \sin \gamma$ projection). By suitable procedures, guest molecules can be hosted essentially only into the δ crystalline phase, while their concentration in the amorphous phase is negligible.[3e] Moreover, s-PS films with high degree of axial[3c−3e] or uniplanar[3f] orientations of the nanoporous crystalline phase can be easily prepared by uniaxial stretching or guest induced crystallization of amorphous films.

The confinement of small molecules in nanoporous materials is not complete, however, allowing misalignment and restricted slow local molecular dynamics of the guest. In order to tailor the desired properties, this mobility should be known not only with respect to the time scale but also with respect to the geometry of the dynamics. The amplitude of the motion can be specified in terms of local dynamic order parameters well-known from liquid crystals.[5a] The information on the confinement is even more specific if oriented fibers are available. Then, as will be shown below, local dynamic order parameter and misalignment of the guest can nicely be distinguished.

Solid state ^{2}H NMR of selectively deuterated compounds[5b] provides unique information in this area. The spectra are sensitive to molecular orientation and motions on the time scale of 10^5-10^8 Hz. NMR line-shape analysis for unoriented samples, however, gives straightforward information only for rigid guests involved in simple motions. Complex reorientations of guest molecules can lead to ^{2}H solid state NMR spectra from which dynamic processes can not unambiguously be derived, as the analysis depends on motional models.[6] Much better discrimination of the dynamics can be achieved by collecting ^{2}H NMR spectra for different guest orientations with respect to the magnetic field requiring macroscopic orientation of the host. However, most host systems like zeolites, metal−organic, or organic frameworks cannot be easily macroscopically oriented.

Macroscopic orientation can be readily achieved in polymers by standard methods including sorption of deuterated molecules into stretched amorphous polymer phases.[7] Special care must be taken, however, because the alignment of the polymer chains in stretched amorphous phases generally changes the local environment of the solute molecules via the shape of their voids, thus altering their local mobility and their ^{2}H NMR line shape. This does not occur if crystalline regions of polymers are oriented. In this communication we demonstrate this different behavior of guest molecules by comparing alignment and motional processes of benzene, a small, highly symmetric guest and DCE, a less symmetric molecule dissolved in noncrystalline and crystalline regions of stretched polymers.

Figure 2 displays the ^{2}H NMR spectra of benzene-d_6 molecules (12%) dissolved in the *amorphous* phase of polyethylene films. In the unoriented sample, (Figure2a), a narrow single peak is observed, reflecting the isotropic tumbling of the benzene molecules in the isotropic amorphous polymer matrix. This narrow peak splits into two signals in axially oriented (draw ratio $\lambda \approx 4$) for film stretching direction parallel ($B_{||}$, Figure 2b) and perpendicular ($B_{\perp}$, Figure 2c) to the magnetic field. This quadrupole splitting depends on λ and local guest concentration[7c] affecting the anisotropy of the local molecular dynamics as well as the orientation in the magnetic field. In agreement with previous reports,[7b,7c] the results of Figures 2b,c indicate that the isotropic mobility of benzene molecules dissolved in polyethylene is slightly reduced by distortions of the local environment of the solute molecules, associated with polymer orientation. The resulting dynamic order parameter, however, is rather low, $\langle P_2 \rangle = 0.07$.

The central row of Figure 2 shows the room temperature ^{2}H NMR spectra of benzene-d$_6$ molecules being guest (8 wt %) in the δ nanoporous *crystalline* phase of s-PS films, being unoriented (Figure 2d) or uniaxially oriented ($\lambda \approx 3$, polymer crystalline phase orientation factor $\langle P_2 \rangle \approx 0.9$), for stretching direction parallel ($B_{||}$, Figure 2e) and perpendicular ($B_{\perp}$, Figure 2f) to the magnetic field. The ^{2}H NMR Pake pattern with quadrupolar splitting of 67 kHz of the benzene guest molecules in the unoriented sample, Figure 2d, indicates a well-defined rotation of the benzene guest about its C$_6$ symmetry axis.[8] This motion is not altered by the host orientation. In fact, already on inspection, it is apparent that the spectra for film stretching direction parallel and perpendicular to the magnetic field (Figure 2, parts e and f), correspond to the 0° and 90° components, respectively, of the Pake pattern observed for the unoriented guests (Figure 2d). This is confirmed by the simulated patterns[9] (Figure 2g−i), assuming a perpendicular orientation of the benzene ring with respect to the polymer chain axis, as generally observed for planar guest molecules of clathrate phases of s-PS.[3a−3e] The degree of orientation of the rotating benzene molecules is the only fitting

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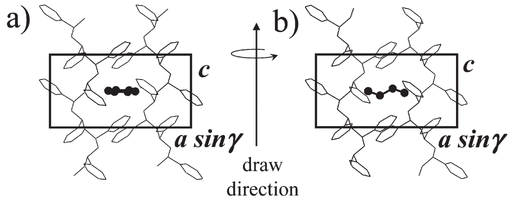

Figure 1. The along *b* projection, showing the location and orientation of benzene (a) and DCE (b) guest molecules in the cavity of the s-PS host δ phase. For clarity of presentation, only the guest molecule is represented as stick and balls.

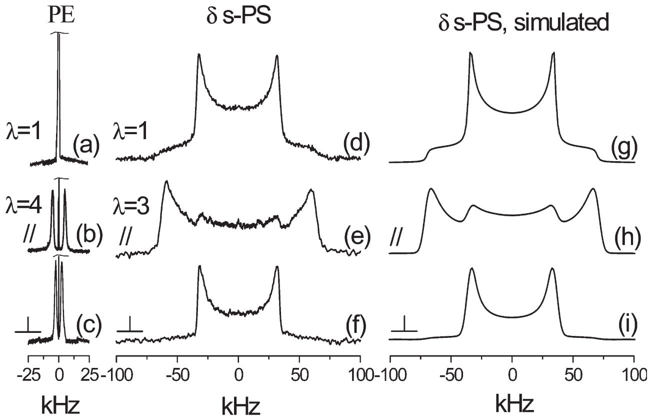

Figure 2. Solid state ^{2}H NMR spectra of benzene-d$_6$ molecules absorbed in the amorphous phase of polyethylene films unoriented (a) and uniaxially oriented (b, c) or guest of the crystalline δ-phase of s-PS films unoriented (d) and uniaxially oriented (e, f). Simulated spectra for benzene guest molecules in unoriented films (g) or in uniaxially oriented films (h, i), being nearly perpendicular to the *c* axis of the s-PS δ-phase (see text).

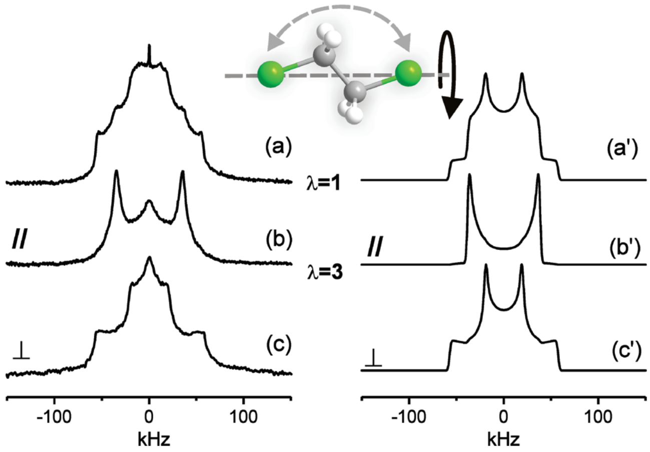

Figure 3. Solid state ^{2}H NMR spectra at 25 °C of DCE-d$_4$ molecules being guest of δ form s-PS samples: powder (a) and uniaxially stretched film for B parallel (b) and perpendicular to the stretching direction (c). Simulated spectra for DCE-d$_4$ guest molecules in unoriented films (a′) or in uniaxially oriented films (b′, c′), presenting the Cl−Cl axis being nearly perpendicular to the *c* axis of the s-PS δ-phase (see text).

parameter, yielding $\langle P_2\rangle = 0.5$. This value is significantly lower than $\langle P_2\rangle = 0.9$ of the s-PS matrix indicating additional disorder, which in good approximation can be described by a Gaussian orientation distribution of the guest molecules in the cavities. For details, see the Supporting Information.

As anticipated, the alignment of guests in oriented samples is particularly helpful to investigate the geometry of the more complex motion of a less symmetric molecule. This is demonstrated in Figure 3 showing the room temperature ^{2}H NMR spectra of DCE-d_4 molecules included (9 wt %) in the δ-form s-PS. The powder line shape does not resemble the well-known Pake pattern, characteristic of axially symmetric quadrupole tensors of aliphatic deuterons under static conditions. Rather, the complex spectrum displays three different principal values of the motionally averaged quadrupole tensor indicating a reduction of symmetry of the quadrupole coupling by molecular motion. Unfortunately, many motional models will give such spectra, as long as we do not know the orientation of the principal axes with respect to the molecule. Thus, the degree of confinement reflected in the motional narrowing cannot be derived from the powder spectrum alone.

The tensor orientation of DCE in the s-PS cavity can be determined, however, by recording orientation dependent ^{2}H NMR spectra of DCE-d$_4$ molecules in uniaxially stretched δ s-PS films ($\langle P_2\rangle = 0.9$). The ^{2}H NMR spectra collected with stretching direction parallel to the magnetic field ($B_{||}$, Figure 3b), exhibit a 70 kHz splitting, whereas the spectra acquired with the stretching direction perpendicular to the magnetic field ($B_{\perp}$, Figure 3c) show splittings of 110 and 35 kHz. It should be noted that in all spectra of Figures 3a−c a minor central peak is present, essentially independent of the orientation of the polymer crystalline phase and hence ascribed to a minor amount of mobile DCE molecules dissolved in the amorphous phase.

A unique solution for the motion can now be obtained, as shown by the simulations given in Figure 3a′−c′. The line shapes are obtained by combining the WebLab[9a] and the SIMPSON package.[9b] They result from a two step motion: large-angle Gaussian fluctuations around the Cl−Cl axis with an average amplitude of ± 40°, combined with occasional exchange of the two Cl sites (180° flips around an axis perpendicular to the Cl−Cl axis). This motional model keeps the Cl−Cl axis of each DCE-molecule fixed and is consistent with the X-ray structure. Moreover, the well-defined ^{2}H NMR line shape shows that all molecules undergo similar motions (homogeneous distribution of rotational angles). The two inequivalent C-D bond orientations derived from the crystal structure are averaged by the exchange of the two Cl site, for details see Supporting Information. The order parameter for the Cl−Cl axis of DCE in the oriented samples is $\langle P_2\rangle = 0.5$ similar to that of benzene guest molecules. Moreover, the NMR results are in good agreement with the molecular orientation of DCE molecules observed by X-ray diffraction.[3b]

It is interesting to compare the dynamics of the guests with large amplitude, yet restricted local motions within a polymer backbone, such as the phenylene flips in amorphous polycarbonate. In both cases the rotation axis is fixed. However, in amorphous polycarbonate a broad heterogeneous distribution of flip angles, about 80° in width is observed leading to a superposition of line shapes with different quadrupole tensors, even at elevated temperatures.[10a] Thus, different phenylene groups display different dynamics in *rate* and *amplitude*. For DCE as well as benzene confined in cavities of crystalline s-PS, however, the geometry of the dynamics is uniform (homogeneous) yielding NMR spectra described by a single second rank tensor. As the rate of motion is in the fast exchange limit, slight distribution of the rate of the dynamics, however, cannot be excluded. A broad distribution, covering several orders of magnitude, however, would manifest itself in the line shape.[10a] In other words, the guest molecules are dynamically equivalent, yet display a distribution of the molecular axes (C_6 axis in case of benzene, Cl−Cl axis in case of DCE) with respect to the matrix. Another comparison is the dynamic behavior of small molecules in crystals, which display nonuniform tunneling behavior, if partially deuterated.[10b]

In summary, information on the restricted dynamics of confined molecules can be easily obtained by ^{2}H solid-state NMR.

Profound differences are obtained for crystalline and noncrystalline polymers. In stretched δ crystalline polymer hosts, like s-PS, high orientation of the guest molecules can be achieved without changing their local environment. Orientation dependent NMR spectra provide means to probe the geometry of complex motions of the guest, as well as their orientation with respect to the host. While the rotation axis can be fixed, large amplitude motions can still occur, which is important information for tailoring guest–host systems for specific applications.

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Supporting Information Available: Text giving experimental details, NMR line shape analysis, ^{2}H NMR spectra of benzene-d_6 molecules in the amorphous phase of syndiotactic polystyrene oriented films and figures showing plots of averaged tensor parameters and solid state ^{2}H NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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