

Conformation of Poly(ethylene oxide)–Hydroxybenzene Molecular Complexes Studied by Solid-State NMR

D. J. Harris,^{*,†} T. J. Bonagamba,^{†,‡} M. Hong,[§] and K. Schmidt-Rohr^{*,†,§}

Polymer Science and Engineering Department, University of Massachusetts, Amherst, Massachusetts 01003, Universidade de São Paulo, Instituto de Física de São Carlos, PO Box 369, 13560-970, São Carlos, São Paulo, Brazil, and Department of Chemistry, Iowa State University, Ames, Iowa 50011

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ABSTRACT: The conformation of poly(ethylene oxide), PEO, in molecular complexes with resorcinol (RES) and *p*-nitrophenol (PNP) was investigated by solid-state NMR. The two-dimensional double-quantum NMR spectrum shows that all OC–CO bonds in the PEO/RES molecular complex are gauche with $\psi = 74 \pm 9^\circ$ and a torsion angle distribution with a width $\sigma < 10^\circ$. The spectra of the PEO/PNP complex, however, show that $33 \pm 8\%$ of the OC–CO bonds are trans with $\sigma < 7^\circ$. The fraction of trans bonds was also confirmed by ^{13}C CODEX experiments. The gauche torsion angle of $70 \pm 9^\circ$ differs significantly from the value of 60° assumed in some models. Magic-angle-spinning ^{13}C INADEQUATE NMR, the CODEX data, and ^2H – ^{13}C REDOR NMR allowed assignment of the two observed PEO ^{13}C NMR peaks. Both carbons on the trans bond, characterized by minimal dipolar broadening in the INADEQUATE spectrum, have chemical shifts of 69.2 ppm. The downfield gauche carbon at 71.4 ppm is $3.2 \pm 0.2 \text{ \AA}$ from the *d*-PNP OD deuteron, while the upfield 69.8 ppm gauche carbon is estimated to be at a 1.13 ± 0.06 times larger distance, or $3.6 \pm 0.3 \text{ \AA}$, from the deuteron.

Introduction

Poly(ethylene oxide), PEO, is a relatively nonpolar polymer but contains ether oxygens that are capable of forming hydrogen bonds and coordinating with alkali metal ions. The chains have no large side groups and are thus easily distorted by intermolecular interactions. Understanding the effects of hydrogen bonding on the conformation of this biocompatible polymer is important and will help to both predict and analyze the structure of PEO in other systems, such as polymer electrolytes.

The structures of both amorphous and crystalline PEO have been previously studied. The conformational statistics in amorphous PEO has been calculated on the basis of stress-temperature coefficients and electric dipole moments.¹ According to the rotational isomeric state (RIS) model, the OC–CO bonds are predominately gauche, but $\sim 20\%$ are trans. A majority of the CC–OC bonds are trans, but $\sim 27\%$ are gauche. We previously studied PEO intercalated in clay and MoS_2 with double-quantum solid-state ^{13}C nuclear magnetic resonance (DQ-NMR) spectroscopy, and 90% of OC–CO bonds were found to be gauche.²

The conformation of the bonds in crystalline PEO has been studied^{3,4} by wide-angle X-ray diffraction (WAXD), infrared (IR), and Raman spectroscopic methods. Crystalline PEO is a 7_2 helix with a TTG sequence: all OC–CO bonds are gauche, and all CO–CC bonds are trans. However, the helix is distorted to improve intermolecular interactions. The WAXD pattern⁵ suggests that the OC–CO torsion angles have discrete values ranging from 49° to 92° with a mean of 68° , and the CO–CC torsion angles range from 180° to 204° with a mean of

186° . A distorted structure is also suggested by the ^{13}C cross-polarization/magic-angle spinning (CP-MAS) spectrum. At low temperatures, sufficiently high spinning rates, and strong proton decoupling fields, the spectrum has four maxima with frequencies ranging from 71 to 75 ppm.⁶

The conformation of PEO when complexed with various small molecules, such as alkali metal salts,⁷ urea,⁸ thiourea,⁹ and mercuric halides,¹⁰ is changed from the TTG sequence found in crystalline PEO. Recently, there has been much interest in the complexes of PEO with *p*-dihalogenobenzenes^{11,12} and hydroxybenzenes including resorcinol (RES)^{13–19} and *p*-nitrophenol (PNP).^{13,19–24} WAXD and IR data suggest that the conformation of the PEO in many of the complexes with *p*-dihalogenobenzene or RES is only slightly distorted from the original 7_2 helix. The conformation of the chains in these systems remains TTG, but the periodicity of the helix changes slightly.¹⁴

Contrary to the PEO/RES complex, the conformation of the chains in PEO/PNP complexes is very different from the 7_2 helical conformation.¹¹ IR and WAXD analyses suggest that $1/3$ of the OC–CO bonds are in the trans conformation. The hydrogen bonding between the host and guest molecules is believed to induce the chain to adopt a TTGTTGTTT TTGTTGTTT structure.²¹ It should be noted that up to now this "unusual" conformation was not further confirmed. Another unusual property of the PEO/PNP complex is that there are two broad ^{13}C peaks at 71.4 and 69.4 ppm,²⁴ compared with a median of 72 ppm for neat PEO. The relative integrated intensities of these peaks are equal to 1:2. In this complex, there are two PNP molecules for every three ethylene oxide repeat units so the 67% peak was attributed to the carbons adjacent to an ether oxygen with a hydrogen bond with the OH of the PNP.¹⁹

In this work, the OC–CO conformation of PEO in PEO/PNP and PEO/RES is determined using ^{13}C homonuclear undecoupled and decoupled DQ-NMR.^{25,26} DQ-

[†] University of Massachusetts.

[‡] Universidade de São Paulo.

[§] Iowa State University.

* To whom correspondence should be addressed. K. Schmidt-Rohr: Tel (515) 394-3521, Fax (515) 294-0105, E-mail srohr@iastate.edu. D. J. Harris: Tel (413) 577-2466, Fax (413) 545-0082, E-mail wolfgang@iskra.pse.umass.edu.

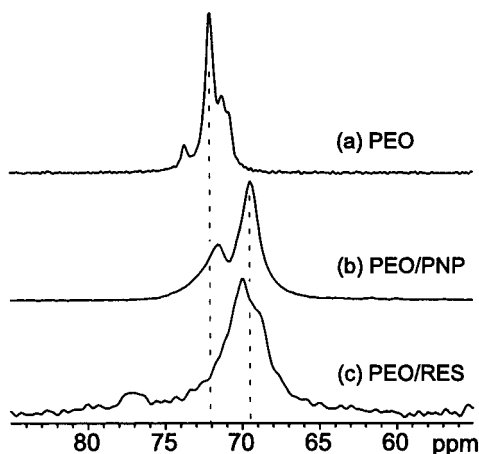


Figure 1. PEO resonances in the ^{13}C CP/MAS NMR spectra of (a) neat PEO, (b) PEO/PNP, and (c) PEO/RES. All spectra were measured at 75.5 MHz. The PEO was measured at 213 K with a spinning rate of 6 kHz. The PEO/PNP was measured at 245 K with a spinning rate of 5 kHz, and the PEO/RES was measured at 245 K with a spinning rate of 4 kHz.

NMR yields two-dimensional (2D) spectra in which the first dimension shows the sum of the orientation-dependent ^{13}C chemical shifts, while the second dimension shows the individual anisotropic chemical shifts and ^{13}C – ^{13}C dipolar couplings. The relative orientation of the coupled sites, i.e., the torsion angles, can be determined from simulations of these 2D spectra. Trans conformations are easily identified by a diagonal ridge with a slope of two. In addition to torsion angle determination, the information content of the isotropic chemical shifts in the PEO/PNP complex is also studied. A ^{13}C CODEX experiment^{27,28} with spin diffusion is employed to identify the trans and gauche peaks. The assignments are confirmed by the line widths in a magic-angle-spinning INADEQUATE ^{13}C NMR experiment with recoupling of ^{13}C – ^{13}C interactions by the CMR7 sequence,^{29–31} which also yields the connectivities of the ^{13}C peaks of PEO in the complex. A ^2H – ^{13}C rotational-echo double-resonance (REDOR) NMR experiment^{32,33} is used to determine the distances between the hydroxyl deuteron in d-PNP and the ^{13}C nuclei in the PEO.

Experimental Section

A. Materials. Synthesis of (^{-13}C – ^{13}C –O–) PEO. Doubly ^{13}C labeled PEO was synthesized by anionic polymerization in THF.² The monomer was a mixture of 3.5 g (79 mmol) of unlabeled ethylene oxide gas and 0.5 g (11 mmol) of ethylene- $^{13}\text{C}_2$ oxide gas. The reaction flask containing 20 mg (0.5 mmol) of potassium metal and 100 mg (0.78 mmol) of naphthalene was filled with 70 mL of anhydrous and O_2 -free THF. After polymerizing for 72 h at ambient temperature, the PEO was precipitated in hexanes, redissolved in THF, and reprecipitated in hexanes. The molecular weight was determined by gel permeation chromatography with a light-scattering detector and using CH_2Cl_2 as the eluent. The instrument determined $M_n = 27\,000$ g/mol and $M_w = 30\,000$ g/mol (PDI = 1.10). A ^1H NMR spectrum showed that 13% of the ethylene oxide units are ^{-13}C – ^{13}C –O–.

Complexation with Hydroxybenzenes. RES and PNP (both from Aldrich) were used as received. The molecular complexes of the labeled PEO and the hydroxybenzenes were prepared by heating a stoichiometric mixture at 120 °C for 24 h under nitrogen and then recrystallizing. The molar ratio of PEO monomeric units and the PNP was 3:2 (68 wt % PNP), and the ratio for RES was 2:1 (55 wt % RES). The ^{13}C CP-MAS NMR spectra of the complexes, Figure 1, were similar

to previous reported spectra²⁴ with peaks at 71.4 and 69.4 ppm for the PEO/PNP complex and 69.7 ppm for the PEO/RES complex. Differential scanning calorimetry (DSC) showed melting endotherms at 93 °C for PEO/PNP and 98 °C for PEO/RES and a weak melting endotherm at 50 °C which corresponds to about 5% uncomplexed PEO crystalline phase in the samples. WAXD confirmed that little uncomplexed crystalline PEO phase was present in the samples, and the correct complexed phases had been formed. The uncomplexed crystalline PEO will not contribute to the DQ-NMR spectra due to its high chain mobility that results in short ^{13}C T_2 and ^1H $T_{1\rho}$ relaxation times.

B. Sample Characterization. Wide-Angle X-ray Diffraction. WAXD was performed using a Siemens D500 instrument with Ni-filtered $\text{Cu K}\alpha$ radiation source in transmission mode.

Differential Scanning Calorimetry (DSC). DSC measurements were performed with 10 mg samples loaded in Al pans on a DuPont Instruments DSC 2910. Samples were heated at 10 °C/min from 25 to 130 °C.

Static DQ-NMR. The static 2D DQ-NMR spectra were recorded on a Bruker MSL-300 spectrometer at a ^{13}C resonance frequency of 75.5 MHz in a 4.5 mm diameter coil of a static variable-temperature probe. The proton 90° pulse length was ca. 3.1 μs , corresponding to a radio-frequency field strength of 80 kHz during cross-polarization. For decoupling, the field strength was increased to ~ 100 kHz. Typical carbon 90° pulse lengths were 2.6 μs . A cross-polarization time of 500 μs and a signal-acquisition time of 2.6 ms were used.

In all static double-quantum spectra, the signals from amorphous regions of PEO were suppressed by a T_1 filter, where the magnetization generated by cross-polarization was immediately rotated to the $+z$ and $-z$ axes in alternating scans.^{25,34} During the ensuing 1.3 s delay, the magnetization of the amorphous phase relaxes to the $+z$ direction. Flipping the crystalline-phase magnetization back to its original transverse direction results in the cancellation of the amorphous-phase signal in every other scan. After the T_1 filter, the double-quantum sequence is started.

In the t_1 dimension, 40 slices with increments of 20 μs were acquired. In the t_2 dimension, the dwell time was 10 μs , and the number of data points was 256 for the ^{13}C uncoupled spectra and 80 for the decoupled spectrum. The double-quantum excitation and reconversion delay was $2\tau = 280$ μs .²⁵ A combination of phase cycling and off-resonance evolution was used to reduce artifacts in the spectra. All of the pulses were applied on-resonance, but the frequency was switched by 5.5 kHz during the evolution time,³⁵ which separates zero- and single-quantum artifacts from the true double-quantum spectrum. The phase cycle had 128 steps, which varied the phases of the cross-polarization, double-quantum excitation, double-quantum reconversion, and the z -filter pulses. The recycle delay for the PEO/PNP complex was 5 s, while the delay for the PEO/RES complex was 20 s. The spectra of the PEO/PNP complex were obtained at 293 K and those of PEO/RES at 255 K. The PEO/PNP spectra and the PEO/RES spectrum were taken with 512 and 128 scans per t_1 slice, respectively. The measuring time for each two-dimensional double-quantum spectrum was ca. 30 h.

The simulated 2D spectra were calculated directly in the frequency domain by averaging the \mathbf{B}_0 orientation over all directions.^{36,37} For each orientation and the given torsion angle, the program calculates the sum of the ^{13}C anisotropic chemical shifts (ω_1 dimension), the individual ^{13}C anisotropic chemical shifts, and the ^{13}C – ^{13}C dipolar coupling (ω_2 dimension). The double-quantum generation as well as the dipolar/chemical shift frequencies and intensities was calculated according to the exact formulas.^{2,38} Realistic line broadening was generated by convolution with suitable Gaussian curves oriented parallel and perpendicular to the line of slope two.

Dipolar/CSA Correlation Experiment. In our experiments, the ^{13}C chemical shift anisotropy (CSA) is used as a probe of segmental orientation. The orientation of the chemical shift tensor relative to the bonds is dependent on the electronic environment around the nucleus and has to be determined

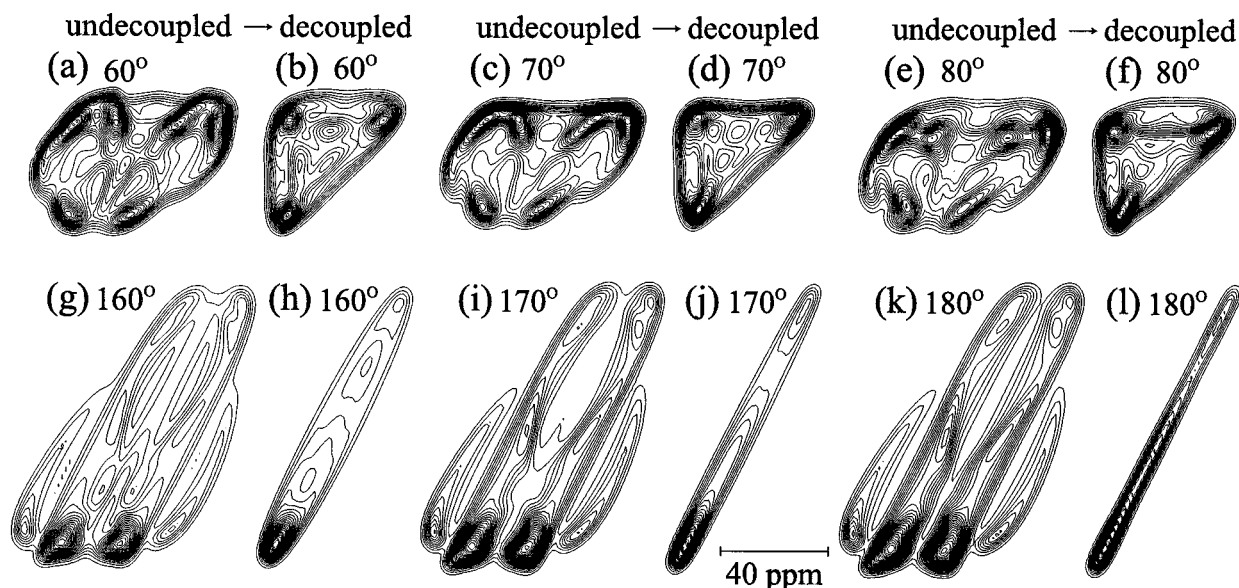


Figure 2. Simulated static double-quantum ^{13}C NMR spectra of ^{13}C - ^{13}C labeled PEO with and without ^{13}C dipolar decoupling for torsion angles of (a/b) 60° , (c/d) 70° , (e/f) 80° , (g/h) 160° , (i/j) 170° , and (k/l) 180° . The tensor parameters are those of the gauche component as given in the caption of Figure 3.

experimentally. Therefore, the orientations of the CSA tensors of the ^{13}C - ^{13}C -O- units in PEO/PNP relative to the C-C bond were measured by a C-C/CSA correlation experiment.^{39,40} Since both the C-C dipolar coupling and the pure chemical shift anisotropy are independent of the torsion angle, the spectral line shape depends only on the chemical shift tensor orientation relative to the C-C bond. The ^{13}C - ^{13}C dipolar couplings were decoupled during detection using a decoupling sequence with a 10-pulse cycle.^{26,39} The spectrum was measured on the Bruker MSL-300 spectrometer. The number of slices in the t_1 dimension was 32, and 196 scans were averaged per slice to obtain the 2D spectrum. The recycle delay was 7 s, and the total experiment time was 12 h.

Chemical Shift Tensors. Three slightly different chemical shift tensors were used in the simulations of the PEO/PNP spectra, since the experimental spectra show clear differences in the principal values. In the static double-quantum ^{13}C decoupled spectrum, the right edge of the trans pattern is 6 ppm upfield from that of the gauche pattern. The MAS ^{13}C double-quantum experiment for PEO/PNP (see below) shows different isotropic chemical shifts of 71.4 and 69.8 ppm²⁴ for the gauche and of 69.2 ppm for the trans conformations. On this basis, the principal values of the chemical shift tensors for the two gauche components were obtained as $\sigma_{11} = 93$ ppm, $\sigma_{22} = 84$ ppm, and $\sigma_{33} = 36$ ppm ($\sigma_{\text{iso}} = 71$ ppm) and $\sigma_{11} = 91$ ppm, $\sigma_{22} = 82$ ppm, and $\sigma_{33} = 34$ ppm ($\sigma_{\text{iso}} = 69$ ppm). The trans component was simulated with a chemical shift anisotropy of $\sigma_{11} = 92$ ppm, $\sigma_{22} = 87$ ppm, and $\sigma_{33} = 28$ ppm ($\sigma_{\text{iso}} = 69$ ppm). On the basis of the dipolar/chemical shift anisotropy (CSA) correlation experiment, the polar coordinates of the C-C bond in the chemical-shift principal-axis system (PAS) were $\alpha = -60^\circ$ and $\beta = 120^\circ$ for the gauche components and $\alpha = -60^\circ$ and $\beta = 117^\circ$ for the trans component. The effective distance between two adjacent carbons was set equal to 1.56 Å. Examples of simulated spectra obtained for torsion angles of 60° , 70° , 80° , 160° , 170° , and 180° are shown in Figure 2.

Solid-State Dipolar ^{13}C INADEQUATE Spectroscopy under MAS. A dipolar-mediated INADEQUATE NMR experiment²⁹ using the dipolar recoupling sequence CMR⁷³⁰ to excite the double-quantum coherence under MAS was applied to determine the connectivities of the carbon peaks in PEO/PNP. The experiment was performed on a Bruker DSX-300 spectrometer at a frequency of 75.5 MHz in a 7 mm ZrO₂ rotor. The spinning rate was 5 kHz, and the temperature was 293 K. The ^1H decoupling field was ~ 80 kHz. The 90° pulse lengths were 4 μs for ^{13}C and 4.1 μs for ^1H . The recycle delay was 5 s, and the number of scans was 128. A total of 96 t_1 -slices were acquired. The total experiment time was 16 h.

^{13}C CODEX Experiment. To identify the gauche and trans peaks in the PEO/PNP spectrum, a ^{13}C CODEX experiment^{27,28} with ^{13}C spin diffusion in the mixing time was performed, and the normalized peak intensities in the resulting spectra were plotted as a function of the spin-diffusion time. For the two sites on a trans bond, the anisotropic chemical shift is the same; thus, spin diffusion does not result in a frequency change and does not dephase the signal. For gauche bonds, we have a two-site exchange process. Exchange in the long-time limit results in a frequency change for half the magnetization, while the other half still resides in the initial site. Therefore, dephasing reaches an asymptote of 50%. The ^{13}C CODEX experiment was carried out on a Bruker DSX spectrometer at a ^{13}C resonance frequency of 75.5 MHz using a 4 mm double-resonance MAS probe. The ^{13}C and ^1H 90° pulse lengths were 2.3 and 3.3 μs , respectively. A cross-polarization time of 500 μs , a signal acquisition time of 10 ms, and a recycle delay of 4 s were used. The spectra were acquired with a spinning frequency of 10 kHz at room temperature.

REDOR ^2H - ^{13}C Distance Determination Experiments. The hydroxyl hydrogen in PNP was exchanged with deuterium by dissolving in CH₃OD and then drying under vacuum. This deuterated PNP was used to prepare PEO/d-PNP. A ^2H - ^{13}C REDOR experiment^{32,33} was performed, and the dipolar recoupling-time-dependent peak intensities in the resulting spectra were used to determine ^{13}C - ^2H distances. The NMR experiments were performed at a frequency of 75.5 MHz on a Bruker DSX-300 spectrometer using a 4 mm triple-resonance MAS probe. The ^1H decoupling field strength was 80 kHz. The 90° pulse length was 3.5 μs for ^{13}C and 2.1 μs for ^2H . A ^1H - ^{13}C CP time of 500 μs was used. The spectra were acquired with a spinning frequency of 4.7 kHz at room temperature. The acquisition time was 38 ms, and the number of scans was typically 6000. ^2H - ^{13}C dipolar recoupling times of 0.43, 0.85, 1.28, and 2.13 ms were used.

Results and Discussion

Dipolar/CSA Correlation. This 2D experiment was used to analyze the orientations of the CSA tensor by correlating it with the C-C bond direction. The experimental spectrum is shown in Figure 3a and compared with the best-fit simulated spectrum in Figure 3b. The orientations of the gauche and trans chemical shift tensors were allowed to be slightly different. The best-fit simulation, which was also consistent with the DQ-NMR spectra, required a trans tensor orientation of α

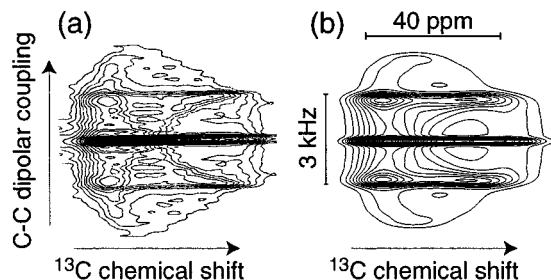


Figure 3. ^{13}C CSA dipolar coupling correlation NMR spectrum (a) of PEO/PNP complex at 293 K. (b) Best-fit simulation using a trans:gauche ratio of 1:2. The tensor orientation (C–C bond in the PAS) was $\alpha = -60^\circ$ and $\beta = 117^\circ$ for the trans component with principal values of ($\sigma_{11} = 92$ ppm, $\sigma_{22} = 87$ ppm, $\sigma_{33} = 28$ ppm) and of $\alpha = -60^\circ$ and $\beta = 120^\circ$ with principal values of ($\sigma_{11} = 93$ ppm, $\sigma_{22} = 84$ ppm, $\sigma_{33} = 36$ ppm) and ($\sigma_{11} = 91$ ppm, $\sigma_{22} = 82$ ppm, $\sigma_{33} = 34$ ppm) for the gauche components.

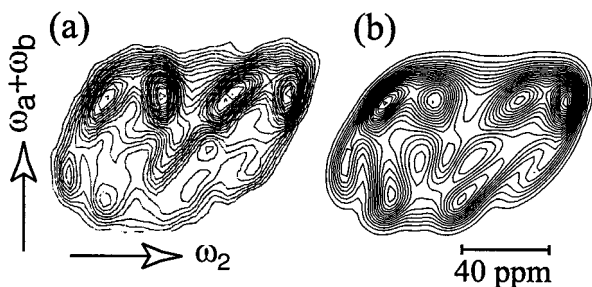


Figure 4. Static double-quantum ^{13}C NMR spectrum of labeled PEO/RES without ^{13}C homonuclear dipolar decoupling (a) measured at 75.5 MHz and 250 K. The best simulation (b) has an average gauche angle $\psi = 74 \pm 9^\circ$ with a distribution of width $\sigma = 7^\circ$.

$= -60^\circ$ and $\beta = 117^\circ$ and a gauche tensor orientation of $\alpha = -60^\circ$ and $\beta = 120^\circ$. The uncertainty in the more important angle parameter β is $\pm 5^\circ$; that in α is $\pm 30^\circ$. These results are similar to previous measurements on PET^{39,40} and consistent with C–H/CSA correlation results on PEO.⁴⁰

The effect of α is seen mostly on the left-hand side of the pattern. From the local symmetry of the CH_2 group, $\alpha = 0^\circ, \pm 90^\circ$, or 180° would be expected. However, the $\alpha = 0^\circ$ value is excluded by measurements on oriented samples.⁴⁰ For $\alpha = -90^\circ$, reduced agreement with the experimental dipolar/CSA spectrum is observed. In addition, better fits of the double-quantum spectra are obtained with $\alpha = -60^\circ$. Nevertheless, overall the differences between $\alpha = -90^\circ$ and $\alpha = -60^\circ$ double-quantum patterns are small and do not change the torsion angle determination significantly.

These orientations were used as parameters for the static double-quantum ^{13}C NMR simulations. The undecoupled double-quantum spectra, which reflect both chemical shift and dipolar coupling in the ω_2 dimension, provide additional confirmation of the validity of this tensor orientation.

Static Double-Quantum ^{13}C NMR Measurements. The observed and simulated C–C undecoupled static double-quantum spectra of PEO/RES are shown in Figure 4. The observed spectrum shows that all of the OC–CO torsion angles are gauche. The simulation suggests that the average torsion angle is $\psi = 74 \pm 9^\circ$ with an angle distribution width of $\sigma < 10^\circ$. Other effects, such as insufficient ^1H decoupling or slow chain motion, may broaden the spectrum and result in an apparently broadened torsion angle distributions in the

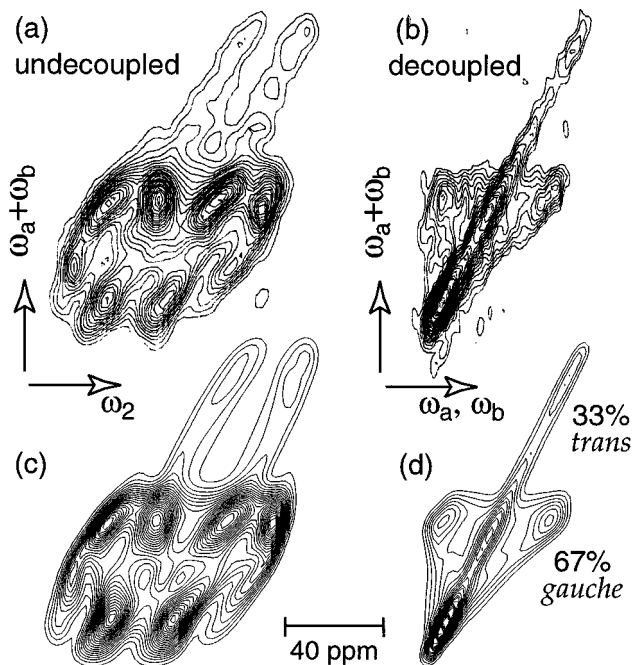


Figure 5. Static double-quantum ^{13}C NMR spectra of labeled PEO/PNP measured at 75.5 MHz and 293 K. (a) Without ^{13}C homonuclear decoupling and (b) with decoupling. The best simulations of both the undecoupled (c) and decoupled (d) spectra use a trans:gauche ratio of 1:2. The average gauche angle is $\psi = 70 \pm 9^\circ$ with a Gaussian width of $\sigma < 10^\circ$; a value of $\sigma = 5^\circ$ was used in the shown simulation. As seen from Figure 2j, significant deviation from 180° results in broad diagonal ridges which was not experimentally observed. The narrow diagonal ridge indicates that the Gaussian width of the trans torsion angle distribution is $\sigma < 7^\circ$.

simulations. On the other hand, torsional librations that are fast on the NMR time scale of $\sim 100 \mu\text{s}$ should be invisible to the experiment and not be taken into account in the quoted width of the distribution.

The observed and simulated undecoupled and decoupled static double-quantum spectra of PEO/PNP are shown in Figure 5. The spectra show a strong slope-to diagonal ridge due to trans OC–CO bonds. The simulations of the observed spectra were produced by factoring 0.33 for trans and 0.67 for gauche conformers. Both the undecoupled and decoupled static double-quantum spectra are consistent with one-third of OC–CO bonds of the PEO/PNP in the trans conformation ($\psi = 180^\circ$, $\sigma < 7^\circ$) and two-thirds in the gauche conformation ($\psi = 70 \pm 9^\circ$, $\sigma < 10^\circ$).

Dipolar ^{13}C INADEQUATE Spectroscopy under MAS. The 2D INADEQUATE MAS spectrum of PEO/PNP is shown in Figure 6. Three peaks, a doublet and a singlet, are observed in the spectrum. Signals at the same ω_1 value belong to a ^{13}C – ^{13}C pair, and the chemical shifts of the two ^{13}C 's in the pair can be read off in the ω_2 dimension. In addition, due to special magic-angle spinning effects, the line broadening makes it possible to identify which peaks belong to gauche or trans conformations: a broadening arises if the two dipolar-coupled ^{13}C nuclei have different CSA orientations, as is the case for a gauche conformation. In that case, the dipolar coupling is not completely removed by MAS, since the sum of chemical shift difference Hamiltonian and the dipolar coupling Hamiltonian, which have to be considered together, does not commute at different rotor orientations. In other words, the sum of the chemical shift difference and the dipolar coupling

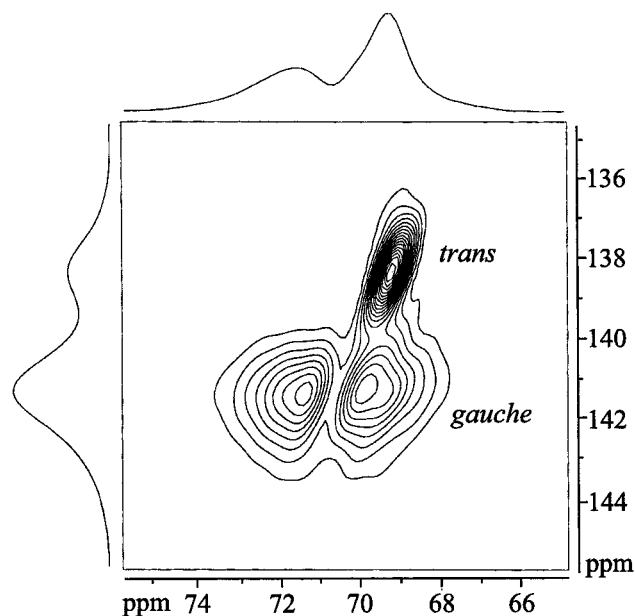


Figure 6. 2D MAS ^{13}C double-quantum solid-state NMR spectrum of PEO/PNP. The spectrum was obtained at 293 K with a spinning rate of 5 kHz. There are peaks at (71.4, 141.3 ppm) (g_a) and (69.8, 141.3 ppm) (g_b) which correspond to the carbons of the gauche OC–CO bonds. The narrower peak at (69.2 ppm, 138.4 ppm) belongs to the magnetically equivalent carbons of the trans OC–CO bond.

represents a homogeneous Hamiltonian that produces broadened MAS peaks.⁴¹

The doublet of broad peaks at (71.4, 141.3 ppm) and (69.8, 141.3 ppm) correspond to two bonded ^{13}C nuclei with inequivalent chemical shifts. The strong broadening of the peaks shows that they are connected by a gauche bond. The singlet peak at (69.2, 138.4 ppm) is much sharper, which means that it must be due to a ^{13}C spin pair around a trans bond. The peak position shows that the isotropic chemical shifts of both ^{13}C nuclei of the trans bond are 69.2 ppm. This equivalence suggests that the chain structure is point-symmetric around the trans bond. The integrated area of the two gauche peaks is $73 \pm 5\%$, and the area of the trans peak is $27 \pm 5\%$. The slight deviation from the 66:33 ratio may be due to background from noncrystalline segments in the broad gauche signal.

The conformational effects on the chemical shift of PEO have previously been considered on the basis of NMR spectra of alkyl chains. The ^{13}C chemical shift for alkyl chains is predominantly affected by conformational effects rather than packing effects.^{42,43} Gauche bonds in alkyl chains result in γ -gauche effects which lower the chemical shifts of adjacent carbons by approximately 4 ppm. Studies of the temperature dependence of the chemical shift of PEO in water^{44,45} have suggested that the gauche conformation of PEO also results in a lower chemical shift than the trans conformation. The gauche and trans chemical shifts were estimated to be 71.58 and 73.83 ppm, respectively. However, the INAD-EQUATE spectrum for PEO/PNP shows that there may not be a simple relationship between C–C bond conformation and chemical shift. In fact, the signal in crystalline PEO, where all OC–CO bonds are gauche and all CC–OC bonds trans, shows peaks separated by several ppm,⁶ which suggests that packing effects can result in significant chemical shift differences. Also, γ -gauche effects are not expected to occur in PEO/RES and PEO/

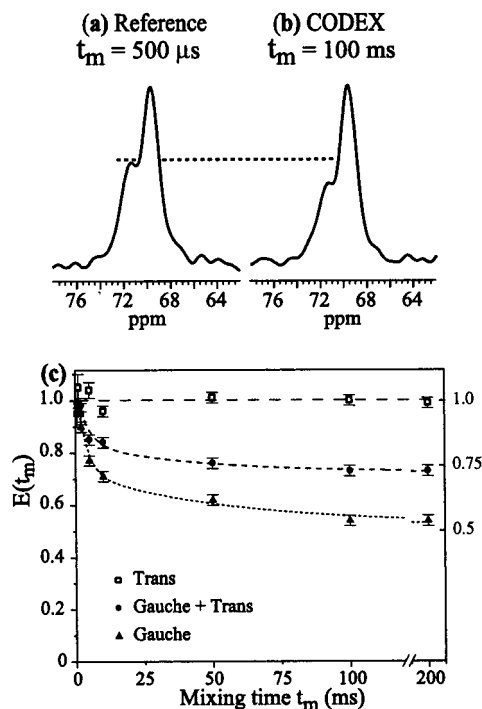


Figure 7. ^{13}C CODEX spectra used to determine the trans–gauche ratio in PEO/PNP. (a) Reference spectrum with a mixing time of 0.5 ms and (b) CODEX spectrum with a mixing time of 100 ms. The right peak was scaled to equal height to enable comparison of the relative intensities. The decay of the peak intensities in (c) shows that the downfield peak at 71.4 ppm is gauche while the upfield 69.4 ppm line is 50% gauche and 50% trans.

PNP because only CC–OC bonds are relevant for γ -gauche shifts in PEO, and they are all trans.

^{13}C CODEX Experiment. The assignment of the peaks to gauche and trans conformations is confirmed by the ^{13}C CODEX experiment with exchange by spin diffusion. As observed in Figure 1, the PEO/PNP 1D ^{13}C spectrum consists of two broad peaks. The ^{13}C CODEX spectrum obtained with a mixing time of 100 ms, and the reference spectrum obtained with the same pulse sequence but a mixing time of only 0.5 ms, are presented in parts b and a of Figure 7, respectively. The spectra are scaled to equal heights of the 69.4 ppm line to highlight the greater effect of the spin diffusion on the 71.4 ppm line. To understand this difference, it has to be noted that spin diffusion between trans sites is not detectable because it does not introduce a change in the frequency of the involved ^{13}C nuclei; thus, a spin-diffusion-induced decay is observed only for the two gauche sites. In Figure 7c, the mixing-time dependence of the CODEX spin diffusion is plotted for both peaks. The relative intensity of the 71.4 ppm gauche signal for long mixing times (>100 ms) decays to a constant value of $E_\infty \sim 0.5$. Meanwhile, the relative intensity for the other peak decays to approximately 0.75, as expected since the peak has a trans and a gauche component. The same plot also shows the decay for the pure trans conformation, obtained by determining the difference between the intensities of the left and the right line and taking the ratios of the differences obtained from reference and spin-diffusion CODEX spectra. This ratio is very close to unity, as expected for the trans conformation. From the values of the relative intensities obtained at $t_m = 200$ ms for both lines, Figure 7c, the gauche–trans ratio is estimated to be two, which

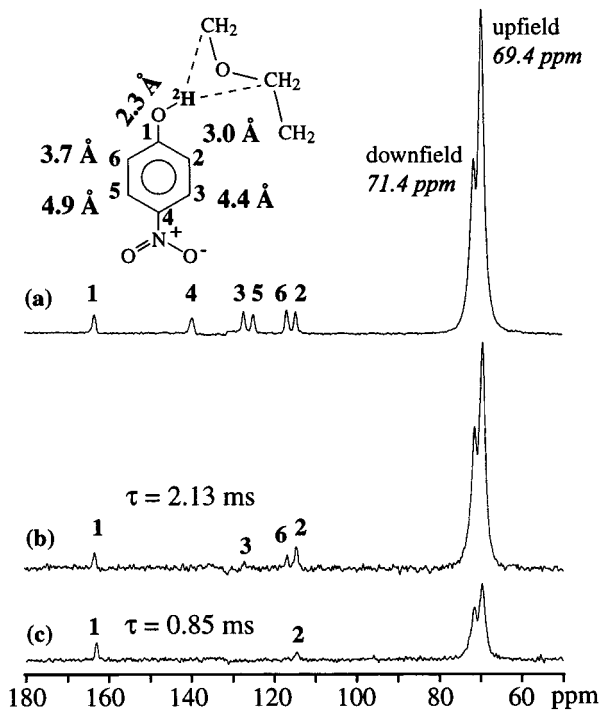


Figure 8. ^2H - ^{13}C dipolar recoupling NMR spectra to determine the distances between the deuterated-PNP OD deuteron and the PEO carbons in the PEO/PNP complex. The CP/TOSS spectrum (a) is compared with the intensities of the peaks after recoupling times of (b) 2.13 ms and (c) 0.85 ms (spectra scaled to equal height of peak 1). The relative intensities of the 71.4 ppm peaks are greater than the peaks near 69.4 ppm when compared to the CP/TOSS spectrum. The intensity buildups of the PNP peaks were used as references to determine internuclear distances.

confirms the result obtained from the double-quantum spectra, where $1/3$ of the OC-CO torsion angles are trans and $2/3$ are gauche.

^2H - ^{13}C Distance Estimates from REDOR. Information on PNP-PEO hydrogen bonding is obtained by measuring distances between OD deuterons and PEO carbons. Known carbon-deuteron distances within the d-PNP molecules are used as internal references. The ^2H - ^{13}C difference spectra with recoupling times of 2.13 and 0.85 ms are shown in parts b and c of Figure 8. The spectra are scaled to equal heights of peak 1. For reference, the CP/TOSS-MAS spectrum is shown in Figure 8a. The PEO peak at 71.4 ppm has a relatively higher intensity than that at 69.4 ppm when compared with the CP-MAS spectrum. The CP-MAS reference spectrum has a ratio of 1:1.90 for the intensities of the 71.4 ppm:69.4 ppm peaks. At a short recoupling time of 0.85 ms, this ratio is 1:1.46, and in the spectrum with a longer recoupling time of 2.13 ms, it is 1:1.60. This suggests that the 71.4 ppm gauche carbon is closer to the OD group of d-PNP than the combination of the trans and gauche carbons in the 69.4 ppm peak. The carbon-deuteron distances can be estimated by comparison with the signal buildup of the various d-PNP sites. At shorter recoupling times, the signal of carbon 1, which is at only 2.3 Å from the deuteron, is much stronger than that of the other aromatics. At intermediate mixing times, the signals of carbon 2 (at 3.0 Å from the ^2H), carbon 6 (at 3.7 Å), and partly carbon 3 (at 4.4 Å) are also observed. The REDOR buildup curves for the important peaks are shown in Figure 9. Using the intensity buildup of the d-PNP peaks as references, the distances of the carbons in the PEO chain for the

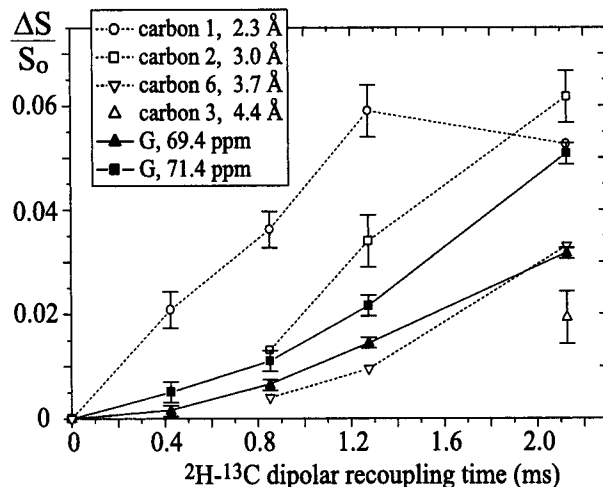


Figure 9. Normalized REDOR difference signal intensities ($\Delta S/S_0$) of the four carbons of PNP and the two observed peaks from the PEO chain was used to determine internuclear distances. The PEO peak at 69.4 ppm was assumed to be composed of two components: a trans carbon that is equally distant from the deuteron as the 71.4 ppm gauche peak and a gauche carbon that is more distant. The value of $\Delta S/S_0$ for the 69.4 ppm peak was calculated to be $[\Delta S(69.4) - \Delta S(71.4)]/[S_0(69.4) - S_0(71.4)]$. The ^2H - ^{13}C distances were calculated to be 3.2 ± 0.2 Å for the 71.4 ppm gauche peak and 3.6 ± 0.3 Å for the 69.4 ppm gauche component.

deuteron were estimated. Thus, the distance from the ^2H to the ^{13}C with the chemical shift of 71.4 ppm (g_a) was determined to be 3.2 ± 0.2 Å. The observed REDOR buildup curves are steeper than simulated curves (not shown), which may be due to the high abundance of deuterons in the system.

The distances for the gauche and trans carbons with chemical shifts near 69.4 ppm can be estimated using the REDOR spectra and the predicted crystal structure of PEO/PNP, shown in Figure 10. If there is strong hydrogen bonding between the OD of the d-PNP and the ether oxygens as indicated in Figure 10, carbons labeled g_b are further from the OD groups. The distance between the deuterons and the gauche carbons g_a was assumed to be approximately equal to the distance between the deuterons and the trans carbons t . Using this assumption, the intensity of the 71.4 ppm peak was subtracted from the 69.4 ppm peak in the REDOR spectra. The resulting intensity was used to estimate that the distance from the deuteron to the carbon g_b is 1.13 ± 0.06 times larger than that to the carbon g_a ; this yields a value of 3.6 ± 0.3 Å.

Conclusions

We have employed five state-of-the-art solid-state NMR techniques to study the chain conformation, hydrogen bonding, and chemical shifts of ^{13}C -labeled PEO in complexes with hydroxybenzenes. A two-dimensional double-quantum spectrum confirmed that the OC-CO torsion angles in PEO/RES are all gauche. In contrast, one-third of the OC-CO torsion angles in PEO/PNP are trans, with $\psi = 180 \pm 7^\circ$, and two-thirds are gauche, with $\psi = 70 \pm 9^\circ$. This confirms the previously suggested structure.²¹ The solid-state INAD-EQUATE spectrum and spin-diffusion CODEX experiments of PEO/PNP show that the carbons in the gauche OC-CO bonds have different chemical shifts of 71.4 and 69.8 ppm, while the carbons in the trans OC-CO bonds

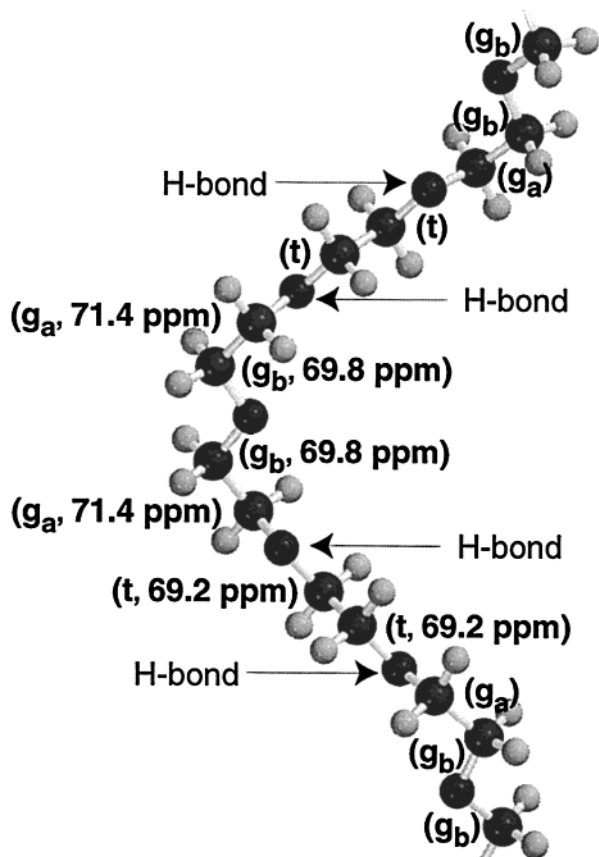


Figure 10. Crystal structure of PEO/PNP with assignment of chemical shifts. The structure shown has the OC–CO gauche torsion angles of $\pm 70^\circ$ determined here and reproduces the 1.56 nm repeat period determined by X-ray diffraction, with $\pm 5^\circ$ deviations of the CC–OC torsion angles from exact trans. The assignment is based on the ^2H – ^{13}C dipolar recoupling NMR spectra and the 2D MAS ^{13}C double-quantum solid-state NMR spectrum of PEO/PNP. The two different types of gauche carbons in the crystal structure are expected to have different distances from the OH group of the PNP. The carbons g_a , which have a chemical shift of 71.4 ppm, are close to the d-PNP deuteron while the carbons g_b are more distant and have a chemical shift of 69.8 ppm.

both have a chemical shift of 69.2 ppm. The ^2H – ^{13}C REDOR experiments showed that the hydroxyl group of the PNP is closer to the 71.4 ppm gauche carbon than the 69.4 ppm carbons, with a distance of $3.2 \pm 0.2 \text{ \AA}$. This is inconsistent with the previous hypothesis that hydrogen bonding was responsible for the upfield shift of the 69.4 ppm peak. Instead, the chemical shift differences is attributed to packing effects, which in crystalline PEO were found to result in shifts of several ppm. The combination of all the information obtained allows chemical shift assignment for the three types of conformationally inequivalent carbons in the PEO/PNP complex.

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