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Two-dimensional solid-state NMR studies of crystalline poly(ethylene oxide): Conformations and chemical shifts

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Abstract

The torsion angles of the OC–CO bonds in crystalline poly(ethylene oxide), PEO, were investigated by solid-state nuclear magnetic resonance (NMR). Two-dimensional double-quantum (DOQSY) spectra indicate that the OC–CO bonds are all *gauche* with an average torsion angle of $\psi = 74 \pm 4°$ and a narrow torsion-angle distribution, $\sigma_\psi < 8°$. This is contradictory to the wider range of *gauche* torsion angles in the distorted helical structure previously proposed based on X-ray fiber diffraction. The low-temperature magic-angle-spinning (MAS) ^{13}C NMR spectrum of unlabeled PEO contains four maxima and several shoulders, over a range of 3.1 ppm. Deconvolution of this spectrum, together with two-dimensional ^{13}C INADEQUATE NMR and exchange MAS spectra, suggests a possible assignment of chemical shifts to the 14 carbons in the 7_2 helical repeat unit. The small line widths of the individual peaks indicate that the helical repeat unit is accurately replicated throughout the crystals. The results show that packing effects or small conformational differences can change chemical shifts by amounts that had previously been ascribed only to *trans*/*gauche* differences.

Keywords: PEO; Torsion angles; Chemical shift

1. Introduction

Poly(ethylene oxide), PEO, exhibits surprising conformational disorder in its crystallites, in spite of the lack of configurational or other chemical disorder, and of bulky sidegroups. Studies by infrared, Raman, and X-ray techniques show that the chains adopt 7_2 helical conformations with *trans* CO–CC and *gauche* OC–CO bonds [1–3], but a detailed analysis of the X-ray diffraction peak intensities suggested that the helix is highly distorted with the OC–CO bonds having discrete torsion angles of 57.0, 67.8, 74.2, 49.0, 91.8, 60.2, and 79.1° [3] Static 2D exchange ^{13}C NMR spectra, which are sensitive to orientational changes after helical jumps [4,5], and corresponding simulations confirmed that the chains are distorted, but concluded that the X-ray analysis overestimated the variation of torsion angles in the 7_2 helix [4]. Neither study, however, determined the OC–CO torsion angles in PEO directly, and thus questions remain about the torsion angle distribution.

A related unresolved issue is the origin of multiple isotropic chemical shifts of ^{13}C carbons in crystalline PEO. At low temperatures, sufficiently high spinning frequencies, and strong proton decoupling fields, the ^{13}C cross-polarization/magic-angle-spinning (CP-MAS) NMR spectrum has four maxima with frequencies spreading over a 3.5-ppm range [6,7]. Packing effects and/or different torsion angles are likely responsible for the inequivalent chemical shifts in crystalline PEO, thus making this polymer a useful model system. The origin of the multiple chemical shifts or the connectivity of the carbons with the observed chemical shifts has not been determined.

In this work, the distortion of the crystalline PEO helix is analyzed by measuring the OC–CO torsion angles using double-quantum solid-state ^{13}C nuclear magnetic resonance (DOQSY-NMR) spectroscopy [8–11]. The average torsion angle and an upper limit for the distortion of the OC–CO bonds are determined from simulations of the static

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homonuclear (^{13}C–^{13}C) decoupled and undecoupled DOQSY-NMR spectra.

The chemical shifts of the 14 carbons in each 7_2 helix are determined by deconvolution of a high-resolution ^{13}C CP-MAS spectrum, obtained at low temperature and with strong ^{1}H decoupling using the two-pulse phase modulated (TPPM) sequence [12]. Furthermore, a possible assignment of the chemical shifts to the helical repeat unit is determined from both a solid-state dipolar ^{13}C INADEQUATE-CMR7 spectrum [13–15] and a 2D ^{13}C exchange spectrum under MAS [16]. The INADEQUATE spectrum determined the chemical shift of the bonded pairs of carbons while the 2D exchange NMR technique provides the chemical shifts of the carbons in the adjacent monomer units, on the basis of helical jumps that move a given segment into its neighboring site.

2. Experimental section

2.1. Synthesis of (–^{13}C–^{13}C–O–) PEO

Doubly ^{13}C labeled PEO was synthesized by anionic polymerization in tetrahydrofuran (THF) [10]. The monomer was a mixture of 3.5 g (79 mmol) unlabeled ethylene oxide gas and 0.5 g (11 mmol) of doubly labeled 1,2-^{13}C (99%) ethylene oxide gas (from Cambridge Isotope Laboratories, Inc.). 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. The eluent was freshly distilled CH_2Cl_2. The instrument determined M_n = 27,000 g/mol and M_w = 30,000 g/mol (PDI = 1.10). A ^{1}H NMR spectrum showed that 13% of the ethylene oxide units are doubly labeled (–$^{13}CH_2$–$^{13}CH_2$–O–).

2.2. Static DOQSY-NMR

The 2D DOQSY-NMR spectra with full decoupling [9] and ^{13}C–^{13}C coupling [8] were both 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 sample was cooled to 220 K to remove distortion of the line shape due to helical jumps. The proton 90° pulse length was 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. The 90° pulse length was 2.6 μs. A cross-polarization time of 500 μs and a signal-acquisition time of 2.6 ms were used. In both static double-quantum spectra, the signals from amorphous regions of PEO were suppressed by a 0.5-s T_1-filter [8,17]. 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 undecoupled and 80 for the decoupled spectra. The double-quantum excitation and reconversion delay was $2\tau = 280$ μs [8]. A combination of phase cycling and off-resonance evolution was used to eliminate artifacts from the DOQSY spectra. All of the pulses were applied on-resonance, but the frequency was switched by 5.5 kHz during the evolution time, which separates zero- and single-quantum artifacts from the true double-quantum spectrum [18]. 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 was 7 s. The measuring time for each two-dimensional double-quantum spectrum was approximately 20 h.

The simulated 2D DOQSY powder spectra were calculated directly in the frequency domain by averaging the $\mathbf{B}_0$ vector over all directions [4,19]. For each orientation and given torsion angle, the program calculates the sum of the ^{13}C anisotropic chemical shifts (ω_1 dimension), as well as 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 were calculated according to the exact formulas [20,21]. Realistic line broadening was generated by convolution with suitable Gaussian curves oriented parallel and perpendicular to the line of slope two. The effective distance between two adjacent carbons was set equal to 1.54 Å. The principal values of the chemical shift tensor used in the simulations were $\sigma_{11} = 95$, $\sigma_{22} = 86$, and $\sigma_{33} = 38$ ppm ($\sigma_{iso} = 73$ ppm) and the polar coordinates of the OC–CO bond in the chemical-shift principal-axis system (PAS) were $\alpha = -90°$ and $\beta = 120°$. This orientation of the PAS differs from the values of $\alpha = -60°$ and $\beta = 120°$ previously used to simulate DOQSY-NMR spectra of noncrystalline PEO [10]. The $\alpha = -90°$ value is expected based on local symmetry of the CH_2 unit and was necessary for matching some details near the down-field end of the ^{13}C–^{13}C decoupled DOQSY-NMR spectrum. The choice of α has little effect on the upper limit of the width of the torsion angle distribution obtained from the simulations.

2.3. ^{13}C CP-MAS spectrum

The CP-MAS spectrum was measured on a Bruker DSX-300 spectrometer with a ^{13}C resonance frequency of 75.5 MHz. A cylinder of unlabeled 100 K molecular weight PEO and a piece of high-density polyethylene were placed in a 4-mm ZrO_2 rotor. The temperature was 208 K and the spinning frequency 5 kHz. A combination of a 10-ms $T_{1\rho}$-filter and a Hahn spin-echo with $2\tau = 10$ ms was used to suppress the faster relaxing amorphous phase, and TPPM ^{1}H decoupling [12] to minimize line width. The chemical shifts were calibrated to the internal reference of polyethylene at 32.8 ppm. The 90° ^{13}C and ^{1}H pulse lengths were 3.2 and 3.6 μs, respectively. The TPPM ^{1}H decoupling field strength, the dwell time, and the number of data points were 110 kHz, 29 μs, and 2048, respectively. The spectrum was acquired with 1024 scans. The chemical shift of the crystalline peak of the polyethylene reference was calibrated to be 32.8 ppm.

2.4. ^{13}C exchange NMR spectrum

A 2D exchange spectrum of the unlabeled PEO sample was recorded under similar conditions as the CP-MAS spectrum, except that the temperature was 225 K, and the spinning frequency 4 kHz. A 10-ms $T_{1\rho}$ filter was again used, but the Hahn spin-echo before detection was shortened to $2\tau = 46$ μs. The mixing time was 0.6 s. The dwell time in t_1 was 160 μs, the number of slices, 160. Twenty-four scans were recorded for each of the slices, resulting in an experiment time of 8 h.

2.5. Solid-state dipolar ^{13}C INADEQUATE-CMR7 spectroscopy under MAS

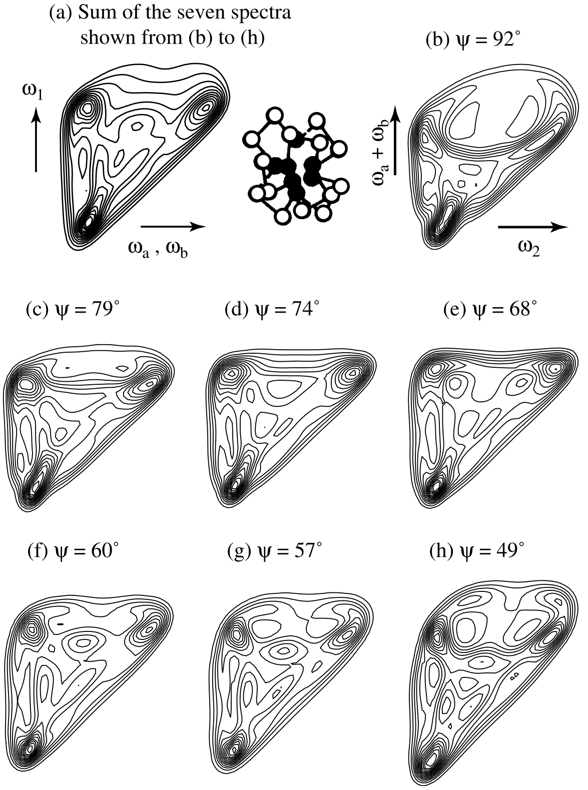
A dipolar-mediated INADEQUATE NMR experiment [13] using the dipolar recoupling sequence CMR7[14] to excite the double-quantum coherence under MAS was applied to determine the connectivities of the carbon peaks in the ^{13}C–^{13}C–O labeled PEO. The spinning frequency was 5 kHz and the temperature was 203 K. The 90° ^{1}H and ^{13}C pulse lengths were 4.0 and 4.1 μs, respectively. The ^{1}H decoupling field was approximately 80 kHz. The recycle delay was 5 s, the number of scans 128, and the number of slices in t_1 dimension 96; the total experiment time was 16 h.

3. Results and discussion

3.1. Torsion angle distribution in crystalline PEO

Simulated static ^{13}C–^{13}C decoupled DOQSY-NMR spectra for each of the seven torsion angles suggested by the previous X-ray study [3] are shown in Fig. 1(b)–(h). The mean torsion angle is $\psi = 68°$, corresponding to *gauche* conformations, and the standard deviation is $\sigma_\psi = 14°$. The sum of the seven spectra is shown in Fig. 1(a). The highest and lowest torsion angles, 92 and 49°, result in significant intensity in the upper region of the 2D spectrum and also do not have the depression and small peak in the center. These features are used to confirm or reject the hypothesized conformation and to set limits on the width of the torsion angle distribution.

The experimental spectra, Fig. 2(a) and (b), show that all of the OC–CO torsion angles are *gauche*: there is no evidence of *trans* conformations, which would result in a straight, narrow ridge with a slope of two, down to levels of 1/14 of the total intensity [10,11]. Furthermore, the observed spectra show that large deviation of torsion angles from 74° is not possible because there is no intensity in the upper region as predicted by the simulations using the torsion angles suggested by the X-ray results, Fig. 2(e) and (f). Another indication that the standard deviation of the torsion angle distribution must be less than $\sigma_\psi = 14°$ is the presence of the peak and depression in the center region of the triangular pattern. A consistent simulation for the experimental spectra was produced using an average angle of $\psi = 74°$ and a relatively narrow Gaussian distribution, $\sigma_\psi = 5°$, Fig. 2(c) and (d). The confidence interval of the mean value is $\psi = 74 \pm 4°$. Outside this interval, the central peak and depression disappear. The confidence interval for the width of the torsion angle distribution is more difficult to quantify: other effects such as the multiple chemical shifts, insufficient ^{1}H decoupling, and chain motion broaden the spectrum and may result in an overestimate of the width of the torsion-angle distribution in the experimental spectrum. Thus, only an upper limit to the distribution width can be determined: $\sigma_\psi < 8°$.


(a) Sum of the seven spectra shown from (b) to (h)

(b) ψ = 92°

(c) ψ = 79°

(d) ψ = 74°

(e) ψ = 68°

(f) ψ = 60°

(g) ψ = 57°

(h) ψ = 49°

Fig. 1. Simulated static DOQSY-NMR spectra with ^{13}C–^{13}C dipolar decoupling for torsion angles of the structure suggested by X-ray analysis [3]. The sum spectrum is shown in (a), while the spectra due to the seven individual torsion angles are shown in (b) 92°, (c) 79°, (d) 74°, (e) 68°, (f) 60°, (g) 57°, and (h) 49°. The principal values of the chemical shift tensor used in the simulations were $\sigma_{11} = 95$ ppm, $\sigma_{22} = 86$ ppm, and $\sigma_{33} = 38$ ppm ($\sigma_{iso} = 73$ ppm) with the polar coordinates of the OC–CO bond in the chemical-shift principal-axis system (PAS) of $\alpha = -90°$ and $\beta = 120°$.

The mean torsion angle of $\psi = 74 \pm 4°$ is significantly larger than the value of $\psi = 68°$ suggested previously by the X-ray results [3]. Also, the torsion angle distribution, $\sigma_\psi < 8°$, is narrower than the reported value of $\sigma_\psi = 14°$. Note that these NMR spectra cannot be used to determine the mean or distribution of the CO–CC torsion angles. The X-ray structure proposed [3] that these torsion angles have an average value of $\psi_{OC} = 186.0°$ and a narrow torsion angle distribution, $\psi_{OC} = 7.6°$. Variation of these angles by ±8° makes it possible to reproduce the fiber period of PEO with ψ around 74°, between 66° and 82°, as determined by NMR.

3.2. Isotropic ^{13}C chemical shifts

The CP-MAS spectrum of the crystalline component of unlabeled PEO, shown in Fig. 3, has four distinct peaks and three discernable shoulders. The resolution is better than in the previously published spectra [6,7] due to lower temperature,

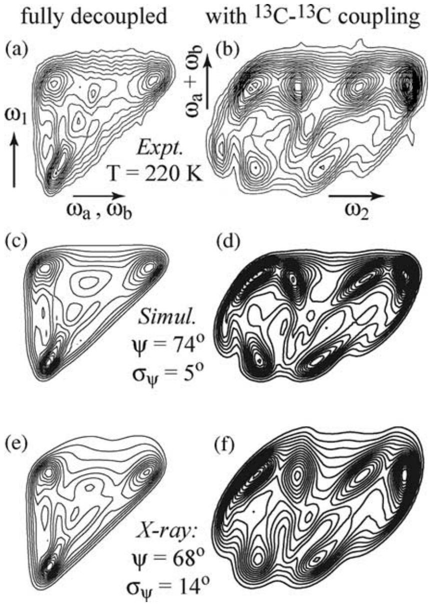


Fig. 2. Static DOQSY-NMR spectra of ^{13}C–^{13}C labeled PEO measured at 75.5 MHz and 220 K: (a) fully decoupled ^{13}C–^{13}C homonuclear and (b) with ^{13}C–^{13}C coupling. The best simulations of both (c) the fully decoupled and (d) with ^{13}C–^{13}C coupling spectra use a Gaussian torsion angle distribution with a mean *gauche* angle of $\psi = 74°$ with a Gaussian width of $\sigma_\psi = 5°$. The uncertainty of ψ is $\pm 4°$ and the maximum allowable Gaussian width which does not produce obvious deviations from the observed spectra is $\sigma_\psi < 8°$. Comparison with the simulations based on the previously suggested X-ray structure, (e) and (f), shows that the variation in OC–CO torsion angles is not as large as predicted by the X-ray based model.

higher decoupling field strength, and the $T_{1\rho}$ and Hahn-echo filters used to destroy magnetization in the amorphous and mobile regions. The high ^1H decoupling field strength of $\gamma B_1/2\pi = 110$ kHz, is critical for obtaining highly resolved spectra of CH_2 groups [6,22]. The TPPM decoupling pulse sequence [12] provided a significant reduction in ^{13}C line width compared with a spectrum obtained with continuous-wave ^1H decoupling.

The integrated area of the well-resolved peak at 74.7 ppm, labeled as peak number 7 in Fig. 3, is approximately 1/14th of the total area. This suggests that the signal arises from one of the 14 carbons in the repeat unit of the 7_2 helix. The probable chemical shifts of the other 13 carbons in the helical repeat unit were obtained by manually deconvoluting the spectrum assuming that areas of all peaks are equal. The lineshapes were 40% Lorentzian and 60% Gaussian with typical full widths at half maximum of 22 Hz. The best-fit of the experimental spectrum used chemical shifts of 74.7, 73.4, 73.1, 73.0, 73.0, 73.0, 72.9, 72.7, 72.7, 72.3, 72.1, 72.0, 71.6, and 71.6 ppm. The chemical shifts were found to be slightly temperature dependent: the shifts of the peaks varied by ±0.1 ppm between 225 and 200 K. This temperature dependence causes some small discrepancies in the assignment of the 2D exchange spectrum, discussed later, which was obtained at 225 K in order for the helical jumps to be sufficiently fast. The observation of distinct peaks with small widths typical of well-defined sites in crystalline polymers such as polyethylene or annealed polypropylene confirms that PEO takes a well-defined structure in its crystallites. Note that most (13/14) of the spectral intensity in the CP-MAS spectrum falls within a 2-ppm range. Therefore, the effects of the isotropic shift dispersion on the DOQSY spectra, which reflect the chemical-shift anisotropy of $\Delta\sigma = 57$ ppm, is quite small.

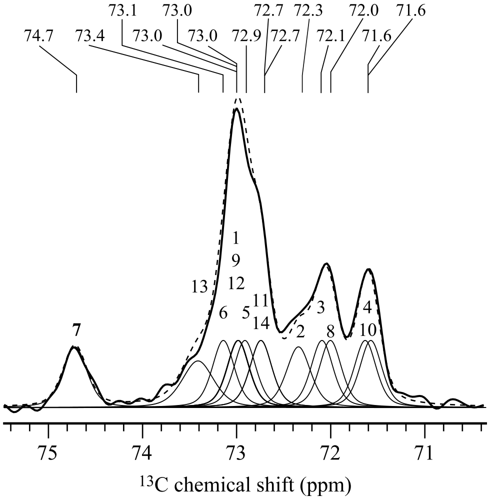


Fig. 3. Deconvolution of the ^{13}C CP-MAS NMR spectrum of the crystalline components in unlabeled PEO. The spectrum was measured at 75.5 MHz. The temperature was 208 K and the spinning frequency was 5 kHz. The spectrum used a combination of a 10-ms $T_{1\rho}$-filter and a $\tau = 5$-ms Hahn-echo to suppress the amorphous phase, and high-power TPPM ^1H decoupling to minimize line width. The chemical shift was referenced to the internal polyethylene standard that is assigned a chemical shift of 32.8 ppm. The 14 peaks in the deconvoluted spectrum have equal areas, and typical line widths of 22 Hz. The sum of simulated peaks is shown by the dashed curve.

3.3. Assignment of bonded ^{13}C sites

For assignments of the various peaks in the CP-MAS spectrum, it is useful to identify the bonding partner of a given CH_2 group. This can be achieved in the ^{13}C–^{13}C labeled PEO by 2D solid-state INADEQUATE MAS NMR with dipolar recoupling. The 2D INADEQUATE-CMR7 spectrum of the crystalline component in the labeled PEO at 203 K is shown in Fig. 4(a). In the spectrum, signals at the same ω_1 value belong to a ^{13}C–^{13}C pair, and the chemical shifts of each ^{13}C in the pair can be read off in the ω_2 dimension. Cross sections at 146.7, 146.0, 144.8, and 143.9 ppm are shown in Fig. 4(b). The spectrum and the cross section slices resolve six maxima. The peaks listed in this figure are labeled 1–14 on the basis of one possible interpretation of the results of this spectrum and both the ^{13}C CP-MAS and 2D exchange spectra. Three pairs of peaks are easily identifiable in the INADEQUATE-CMR7 spectrum: carbons **7** and **8** (74.7/72.0, 146.7 ppm), carbons **9** and **10** (73/71.6, 144.6 ppm), and carbons **3** and **4** (72.1/71.6, 143.7 ppm). The numbering scheme will be justified below. There is a large peak centered at (73.0/73.0, 146.0 ppm) which is due to the proximal pairs of peaks later assigned to carbon 5, 6 and 11, 12. Another set of chemical shifts was determined from the relatively high intensity at 144.6 ppm: thus, carbons 1 and 2 were assigned a sum shift of 145.3 ppm (73 and 72.3 ppm, respectively). Finally, the lack of intensity at 146.4 ppm

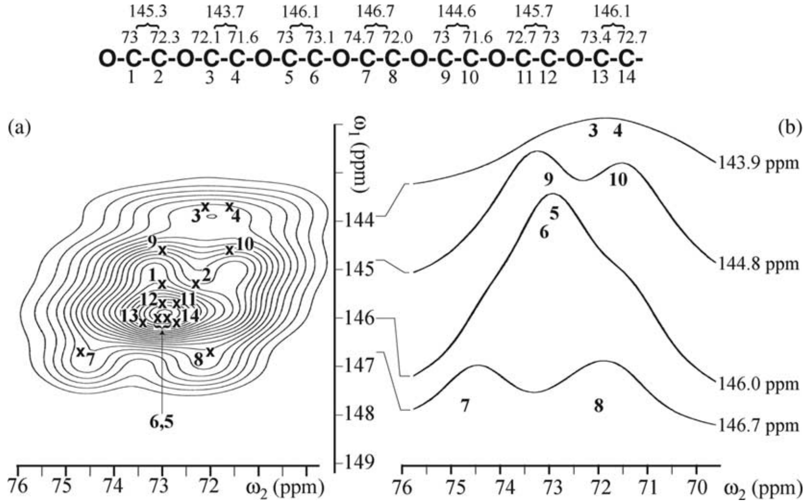


Fig. 4. (a) 2D MAS ^{13}C INADEQUATE-CMR7 solid-state NMR spectrum of crystalline ^{13}C–^{13}C labeled PEO. The spectrum was obtained at 203 K with a spinning frequency of 5 kHz. The contour levels start at 10% and are separated by intervals of 4%. The expected peaks from the assignment of chemical shifts to the helical repeat unit are labeled. The assignment is derived from the results of this INADEQUATE spectrum, the deconvolution of the ^{13}C CP-MAS spectrum shown in Fig. 3, and the exchange spectrum presented in Fig. 5. (b) Cross sections at 146.7, 146.0, 144.8, and 143.9 ppm. The peaks are broader than in the spectrum of Fig. 3 due to the ^{13}C–^{13}C dipolar and *J*-couplings in the ^{13}C–^{13}C labeled sample.

suggests that the neighbor of the 73.4-ppm carbon cannot have a chemical shift of 73.0 ppm, and, therefore, the pair 13 and 14 was assigned to the coordinates (73.4/72.7, 146.1 ppm).

Detailed simulation of the 2-D spectrum to confirm the assigned peaks is difficult. Line broadenings arise because the dipolar-coupled ^{13}C nuclei have different orientations and thus different instantaneous chemical shifts, due to the *gauche* conformation of the O^{13}C–^{13}CO fragment. Therefore, the dipolar coupling is not completely removed by MAS [23]. This broadening was previously experimentally observed for the ^{13}C–^{13}C carbons connected by a *gauche* bond in the PEO–*p*-nitrophenol molecular complex [11]. The observed peak shapes of the carbons in the *gauche* OC–CO segment were non-Gaussian, confirming the complexity of the spin system.

3.4. Identification of neighboring repeat units

Assignment of neighboring monomer units in PEO is possible due to the process of helical jumps in PEO crystallites [5]. In an individual jump, a given monomer unit moves into the position and orientation previously taken by its neighbor. Therefore, in a two-dimensional exchange spectrum that correlates the frequency of a given monomer unit before and after a mixing time t_{m}, cross-peaks will be observed between neighboring repeat units. In order to reduce peaks from multiple jumps in sequence, relatively short t_m-values are used ($t_m < \tau_c$, where τ_c is the correlation time). Cross peaks from two consecutive jumps are smaller than the one-jump peaks by approximately the same factor that relates diagonal and one-jump peak intensities, and are, therefore, visible at low contour levels.

The exchange spectrum of the crystalline component in unlabeled PEO and a possible assignment of chemical shifts to the helical repeat unit are shown in Fig. 5. The spectrum shows the many exchange peaks that occur due to the helical jumps. A total of 28 one-jump exchange peaks are possible: 20 are resolvable and labeled in the spectrum, while the other eight are merged with other exchange peaks or the diagonal ridge.

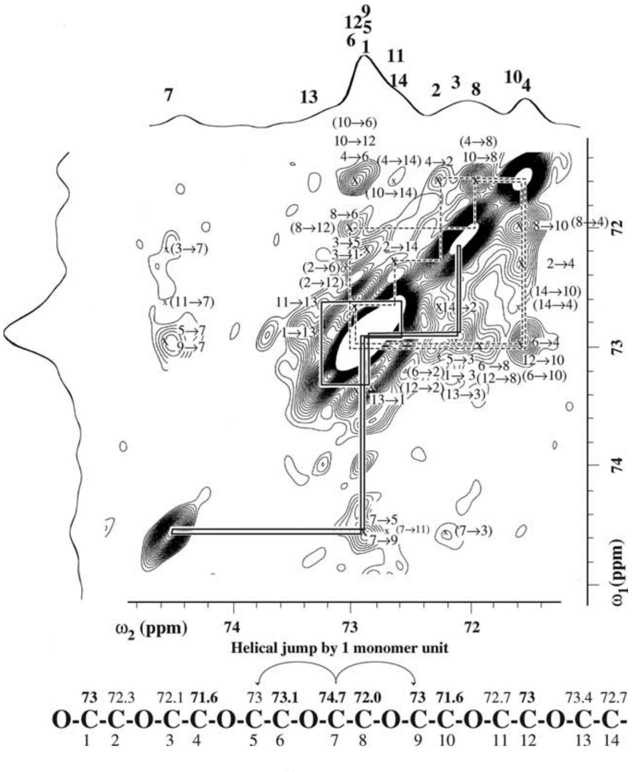


Fig. 5. Two-dimensional exchange ^{13}C spectrum of unlabeled crystalline PEO. The spectrum was obtained at 225 K with a spinning frequency of 4 kHz and a mixing time of 0.6 s. The contours are plotted from 1.8 to 23.2% in increments of 0.63%. The off-diagonal intensity arises from helical jumps during the mixing time where the helix rotates and shifts by one monomer unit per jump. One possible assignment of chemical shifts is shown below the spectrum, and the expected exchange peaks are marked with the symbol *x*.

Two pairs of low-level two-step exchange peaks are resolved (**3**→**7**), (**7**→**3**) and (**10**→**14**), (**14**→**10**), labeled by small crosses, while the others overlap with the one-step cross peaks. The assignment of chemical shifts to the seven carbon pairs in the helical repeat unit is consistent with the INADEQUATE-CMR7 spectrum.

The sequential assignment of chemical shifts to the helix began with the well-resolved carbon **7** at 74.7 ppm and its neighbor, **8**, identified in the INADEQUATE spectrum, at 72.0 ppm. The exchange peaks at (74.7, 73.0 ppm) results from helical jumps of carbon **7** to positions **5** and **9**. The low-intensity peak at (74.7, 72.1 ppm) must be assigned to a two-step process. The absolute numbers in this assignment are arbitrary because neither the direction of the jump, nor the torsion angles of the OC–CO and CO–CC bonds can be determined in this experiment on unlabeled PEO. The chemical shifts of carbons **6** and **10** can be identified as 73.1 and 71.6 ppm, respectively, on the basis of their cross peaks at (72.0, 73.1 ppm) and (72.0, 71.6 ppm) with carbon **8**. These pairs are also expected from the INADEQUATE-CMR7 spectrum. Thus, the six carbons **5–10** can be assigned quite reliably. The other eight assignments of chemical shifts to specific repeat units were made on the basis of the limitations provided by the observed 22 off-diagonal intensities in the exchange spectrum and the pairings determined by the INADEQUATE-CMR7 spectrum. The correct identification of the chemical shifts in the INADEQUATE-CMR7 and the number of individual peaks at various chemical shifts obtained from deconvolution of the CP-MAS spectra were critical for this interpretation. While the sequential assignment of the six carbons **5**–**10** is clear, the assignments of carbons **1**–**4** and **11**–**14** presented in this paper are less definitive, due to the significant peak overlap near 73.0 ppm.

3.5. Effects of packing on the chemical shift

The isotropic chemical shifts of carbons in crystalline PEO vary by 3.1 ppm. Given the DOQSY spectra show that the 7_2 helix of PEO is actually more ordered than the disordered proposed X-ray structure, the chemical-shift dispersion must be attributed to packing effects. Previously reported packing effects in crystalline polymers have been on the order of 1.5 ppm. Larger shifts on the order of 4 ppm have been attributed to conformational differences, such as *trans*/*gauche* of the γ-carbon site (γ-*gauche* effect). However, if one of the CO–CC torsion angles in crystalline PEO deviated significantly from 180°, the resulting γ-*gauche* shift should be upfield rather than the observed down-field. In addition, two carbons, on either side of the *gauche* defect, rather than the observed one out of 14 should be strongly shifted. Since the 3.1-ppm dispersion of crystalline-PEO resonances cannot be attributed to *trans*/*gauche* differences, we must conclude that effects of packing or small conformational distortions on the chemical shift can be significantly larger than previously believed.

4. Conclusions

Several two-dimensional solid-state NMR techniques were used to study the OC–CO torsion angles and to assign the ^{13}C chemical shifts for crystalline PEO. Simulations of both ^{13}C–^{13}C undecoupled and decoupled static DOQSY-NMR spectra determined that the average torsion angle of the OC–CO bonds is 74±4°, larger than the 68° average angle of the previously suggested structure [3]. The Gaussian half-width of the torsion angle distribution is less than 8°, which is smaller than the previously suggested value of 14° [3].

The CP-MAS, MAS-INADEQUATE-CMR7, and 2D exchange ^{13}C NMR spectra yielded the different isotropic chemical shifts of the 14 carbon sites in each helical repeat unit. Deconvolution of the CP-MAS spectra based on observed peaks in the 2D spectra indicates that the carbon nuclei in each helical repeat unit have chemical shifts of 74.7, 73.4, 73.1, 73.0, 73.0, 73.0, 72.9, 72.7, 72.7, 72.3, 72.1, 72.0, 71.6, and 71.6 ppm. The connectivity between the carbons was studied by INADEQUATE-CMR7 and 2D exchange spectroscopy. The 2D spectra prove that the peaks are not due to different modifications of PEO and confirm that PEO takes a well-defined conformation that is replicated throughout its crystallites. A possible assignment of chemical shifts was presented that is consistent with the observed cross-peak positions. With the chemical-shift values of CH_2 pairs, in ppm, written in parentheses, the proposed sequential assignment is (73, 72.3) (72.1, 71.6) (73, 73.1) (74.7, 72.0) (73, 71.6) (72.7, 73) (73.4, 72.7).

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References

[1] Yoshihara T, Murahashi S, Tadokoro H. J Chem Phys 1964;41(9): 2902–11.
[2] Tadokoro H, Chatani Y, Yoshihara T, Tahara S, Murahashi S. Makromol Chem 1964;73:109–27.
[3] Takahashi Y, Tadokoro H. Macromolecules 1973;6(5):672–5.
[4] Schmidt-Rohr K, Spiess HW. Multidimensional solid-state NMR and polymers. San Diego: Academic Press; 1994.
[5] Hu W-G, Schmidt-Rohr K. Acta Polym 1999;50(8):271–85.
[6] Schilling FC, Tonelli AE, Cholli AL. J Polym Sci, Part B: Polym Phys 1992;30(1):91–6.
[7] Spevácek J, Straka. J Makromol Chem, Macromol Symp 1993;72: 201–13.
[8] Schmidt-Rohr K. Macromolecules 1996;29(11):3975–81.
[9] Schmidt-Rohr K. J Magn Reson 1998;131(2):209–17.
[10] Harris DJ, Bonagamba TJ, Schmidt-Rohr K. Macromolecules 1999; 32(20):6718–24.
[11] Harris DJ, Bonagamba TJ, Hong M, Schmidt-Rohr K. Macromolecules 2000;33(9):3375–81.

[12] Bennett AE, Rienstra CM, Auger M, Lakshmi KV, Griffin RG. J Chem Phys 1995;103(16):6951–8.
[13] Hong M. J Magn Reson 1999;136(1):86–91.
[14] Rienstra CM, Hatcher ME, Mueller LJ, Sun BQ, Fesik SW, Griffin RG. J Am Chem Soc 1998;120(41):10602–12.
[15] Lee YK, Kurur ND, Helmle M, Johannessen OG, Nielsen NC, Levitt MH. Chem Phys Lett 1995;242(3):304–9.
[16] Hagemeyer A, Schmidt-Rohr K, Spiess HW. Adv Magn Reson 1989;13: 85–129.
[17] Torchia DA. J Magn Reson 1978;30(3):613–6.
[18] Kaji H, Schmidt-Rohr K. Macromolecules 2001;34(21):7368–81.
[19] Schmidt-Rohr K. J Am Chem Soc 1996;118:7601–3.
[20] Nakai T, McDowell CA. Mol Phys 1993;79(5):965–83.
[21] Dunbar MG, Novak BM, Schmidt-Rohr K. Solid State Nuclear Magn Reson 1998;12(23):119–37.
[22] VanderHart DL, Earl WL, Garroway AN. J Magn Reson 1981;44(2-3): 361–401.
[23] Maricq MM, Waugh JS. J Chem Phys 1979;70(7):3300–16.