Structure, Conformation, and Motions of Poly(ethylene oxide) and Poly(ethylene glycol) in Their Urea Inclusion Compounds

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ABSTRACT: X-ray diffraction and FTIR and ^{13}C NMR spectroscopies have been utilized to observe the inclusion compounds (ICs) formed by poly(ethylene oxide) (PEO) and low molecular weight poly(ethylene glycol) (PEG) oligomer with urea (U). We have confirmed that PEO-U-IC formed from solution has a trigonal crystal structure, while recrystallization from the melt produces a hexagonal PEO-U-IC. PEG-U-IC apparently adopts a crystal structure different from the trigonal and hexagonal forms of PEO-U-IC, and single crystals of PEG-U-IC are currently under investigation by X-ray diffraction. The conformations of PEO and PEG chains in their U-ICs appear similar to the TGT bulk crystalline conformation, while the all-trans conformer does not appear to be consistent with either the FTIR or the ^{13}C NMR observations. For solution-formed PEO-U-IC in the trigonal crystal structure, where one-third of the urea molecules are hydrogen-bonded to the PEO chains and reside in the channels, the mobility of the included PEO chains is similar to that of the bulk crystalline PEO. This is quite different from the usual observations made on hexagonal polymer-U-ICs, where spin-lattice relaxation times observed for the carbon atoms of the included polymers are much reduced (often more than 1 order of magnitude) from those observed for the same polymer in their bulk crystals. It is proposed that the direct involvement of the urea molecules in the trigonal channels of PEO-U-IC with the included PEO chains is the source of their reduced mobility.

Introduction

It has been known for many years that certain small molecules such as urea, thiourea, perhydrotriphenylene (PHTP), and cyclodextrin form crystalline inclusion compounds with semicrystalline polymers via a cocrystallization process.[1] Among the polymers examined are poly(L-lactic acid) (PLLA),[2] poly(ϵ-caprolactone) (PEC),[3] *n*-hexadecane (H), and poly(tetrahydrofuran) (PTHF).[4] Principal among the experimental techniques utilized to investigate these polymer inclusion compounds (ICs) are FTIR and solid state ^{13}C NMR spectroscopies. Some polymers may be prepared directly in the channels of their inclusion compounds by irradiation of the inclusion compounds formed by their monomers.[5] Inclusion compounds have many uses, such as separating isomers, preparing highly stereoregular polymers, and obtaining monodispersed fractions from unfractionated polymer samples.[6]

Polymers in dilute solution at the θ temperature,[7] where the chains are free from excluded volume and cooperative chain interactions, are often used to understand the properties of bulk amorphous polymers. However we do not have a dilute solution analog to help understand the properties of bulk-ordered polymer phases. We believe that polymer ICs, formed with urea clathrate, can usefully serve as model systems, or touch tones, for observing the behavior of extended polymer chains in the solid state, which are free from cooperative interchain interactions, often found to be dominant in bulk crystalline or liquid crystalline polymers.[1] Molecular modeling techniques, including complete conformational searches[8] and molecular dynamic simulations[9] of a polymer chain confined in the narrow IC channel, have been coupled with spectroscopic observations[10] of polymer-ICs to determine the conformational and motional behavior of the included polymers.

Inclusion compounds formed between urea and polyethers ($[-\mathrm{O(CH_2)}_m-]-\mathrm{n}-$, $m = 2-4, 6, 8-10$) were characterized by Suehiro et al.[11] Low molecular weight poly(ethylene oxide) (PEO) of number-average molecular weight 400−2000 was found to crystallize in two urea (U)-IC modifications. These two different crystalline modifications have different melting temperatures and IR spectra. X-ray diffraction observations indicated that PEO in the channel is considerably more extended than the most stable TGT conformation adopted in the bulk PEO crystal.[12] Modeling of a PEO chain in the channel also suggested that PEO chains in the clathrate adopt more extended conformations than the conformation found in the bulk crystal.[13] Conformational differences occurring in the urea channel were previously attributed to polar interaction between urea and the PEO chain. Infrared spectroscopic investigation showed that there is strong interaction between the urea carbonyl and PEO chain. On the other hand the inclusion compound formed between polyethers ($m > 3$) and urea is similar to inclusion compounds formed between hexadecane and urea. In the work presented herein, PEO-U-IC is prepared via a solution method. Wide angle X-ray diffraction and FTIR and solid state NMR spectroscopies are used to examine the conformations and mobility of isolated PEO chains in the narrow U-IC channel.

Experimental Section

Samples. PEO and poly(ethylene glycol) (PEG) samples with weight-average molecular weight 100 000 and 600, respectively, were obtained from Aldrich Chemical Co. The solution-grown PEO crystals were obtained from dilute (0.1%) xylene solution at room temperature, filtered, and air-dried. PEO and PEG-U-ICs were prepared via a cocrystallization method. One gram of PEO or PEG was dissolved in 100 mL of methanol saturated with urea while the solution was continuously warmed and stirred. The solution was then cooled down to room temperature, and a white precipitate was observed to form over several hours.

X-ray Diffraction. Wide angle X-ray diffraction of powder samples was obtained at ambient conditions on a Scintag 2000

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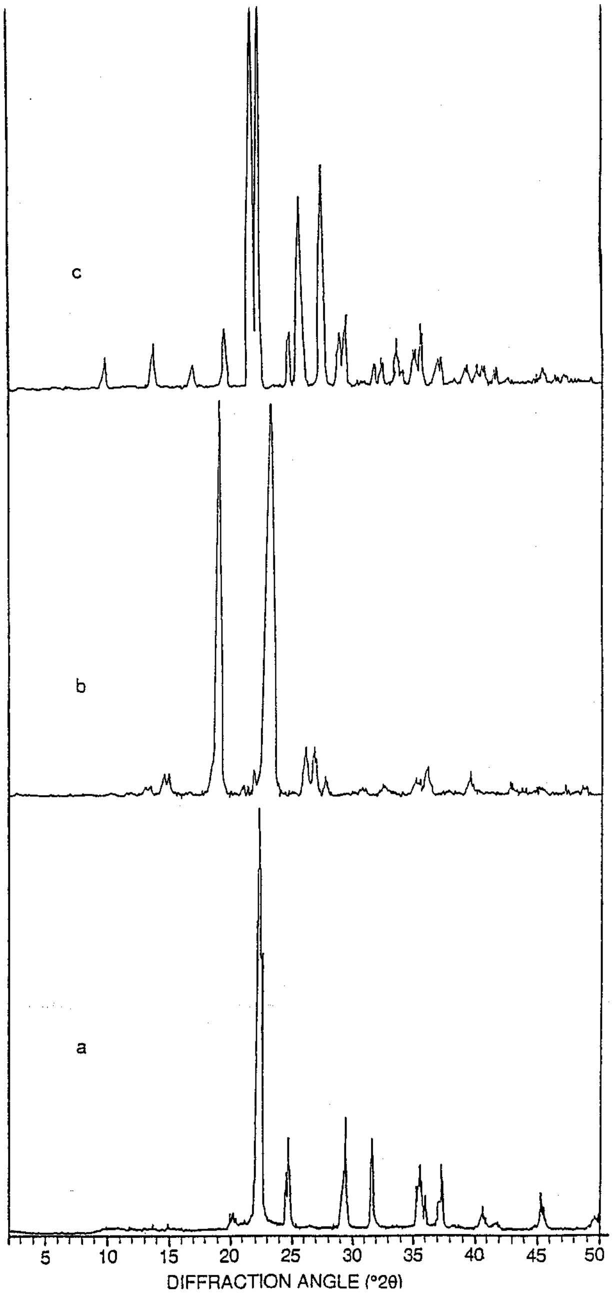

Figure 1. Wide angle X-ray diffraction patterns observed for (a) urea, (b) PEO, and (c) PEO-U-IC.

XDS instrument using Ni-filtered Cu Kα radiation. The supplied voltage and current were set to 45 kV and 40 mA, respectively. Samples were mounted on a glass slide with double-sided tape and exposed at a scan rate of $2\theta = 5°$/min between $2\theta = 0°$ and 50°.

Infrared Spectroscopy. Fourier transform infrared spectra were recorded on a Nicolet 510p FTIR spectrometer at frequencies from 500 to 4000 cm^{-1} with a resolution of 2 cm^{-1}.

NMR Measurements. High-resolution solid state NMR spectroscopy was carried out at 50.14 MHz on a Chemagnetics CMC 200S NMR spectrometer. The cross-polarized (CP), magic angle spinning (MAS), and one-pulse spectra were observed with probes using Zirconia rotors at spinning rates of 3−4 kHz. High-power dipolar decoupling (DD) was applied at about 47 kHz during acquisition. The spectral width was 15 kHz stored in a memory that was zero-filled to 8k before fourier transformation. The spin lattice relaxation (T_1) times were measured using a CP−T_1 pulse sequence.[14] Chemical shifts were referred to *p*-di-*tert*-butylbenzene (PDTBB, 31.0 ppm vs TMS).

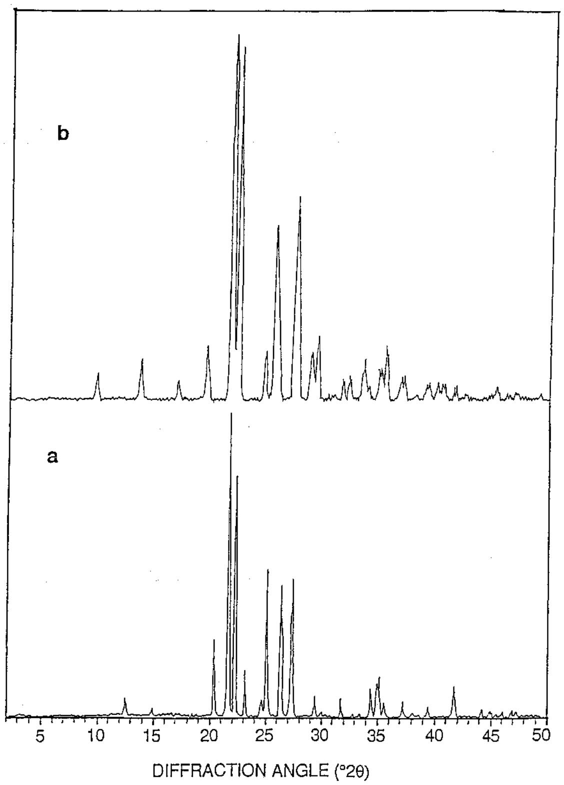

Figure 2. Comparison of X-ray diffractograms recorded at room temperature for (a) PTHF-U-IC and (b) PEO-U-IC.

Results and Discussion

X-ray Diffraction. Figure 1 shows the wide angle X-ray diffraction pattern recorded for PEO-U-IC, PEO, and tetragonal urea at room temperature from $2\theta = 0°$ to 50°. Major peaks at $2\theta = 22.5°$, 35.5°, and 29.5° are observed for pure urea. The corresponding *d*-spacings are assigned to the tetragonal crystal structure. PEO shows two strong reflections at $2\theta = 19.3°$ and 23.5°. The diffractogram of PEO-U-IC shows several new reflections which are not present in the diffractograms of PEO and urea and constitutes primary evidence that an inclusion compound is formed. X-ray diffraction patterns of the H-U-IC, PEC-U-IC, and PTHF-U-IC[4] were investigated previously using X-ray diffraction. These diffraction patterns were indexed with a hexagonal unit cell with a cell dimension of $a = b = 8.19$ Å and $c = 11.03$ Å. Figure 2 shows the wide angle X-ray diffraction patterns of PEO-U-IC and PTHF-U-IC. A unique peak at 12.6° is normally used to identify the hexagonal crystal structure. The peak at 12.6° is not apparent in the PEO-U-IC diffractogram, indicating that the crystal structure of PEO-U-IC is different from the hexagonal crystal structure observed for PTHF-U-IC and PEC-U-IC.

All the reflections from the PEO-U-IC diffractogram were indexed with a trigonal unit cell. In fact, a PEO-U-IC single crystal was prepared, and the three-dimensional structure analysis was established by Brisse et al.[15] It was found that the complex takes a trigonal crystal structure and has the stoichiometry of four PEO repeat units per nine urea molecules. It was also indicated that there are two types of urea molecules in the complex. Two-thirds contribute to the formation of the trigonal matrix, while the remaining one-third is located inside the channel together with the PEO chains. The effect of temperature on the diffraction pattern of PEO-U-IC was investigated. It has been

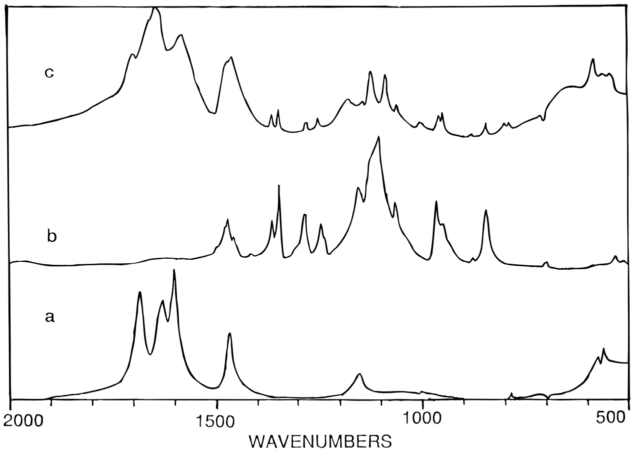

Figure 3. Fourier transform infrared spectra in the region between 500 and 2000 cm^{-1}: (a) urea, (b) PEO, and (c) PEO-U-IC.

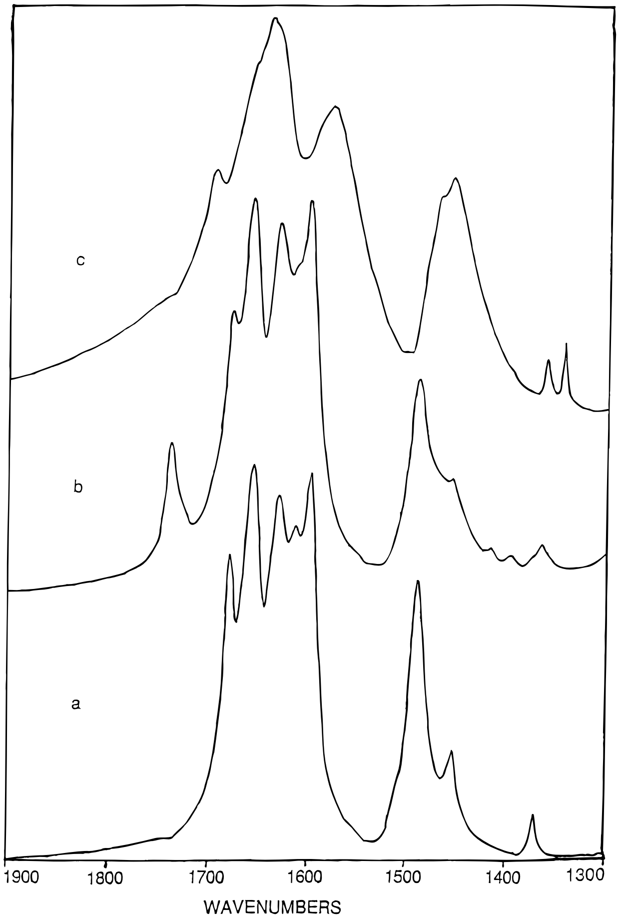

Figure 4. Comparison of infrared spectra in the region between 1300 and 1900 cm^{-1} for urea-based inclusion compounds: (a) PTHF-U-IC, (b) PEC-U-IC, and (c) PEO-U-IC.

shown that heating the trigonal crystal form to 150 °C and then quenching to 0 °C yields a crystal form different from the usual trigonal or hexagonal crystal structure. However, when the quenched samples are heated to 90 °C, the usual trigonal crystal modification, stable at room temperature, reappeared.[16]

PEG-U-IC was investigated using X-ray diffraction previously by Suehiro et al. It was suggested that all the reflections in the PEG-U-IC diffractogram can be indexed with a large tetragonal unit cell with unit cell dimension of $a = b = 9.3$ Å and $c = 19.51$ Å. However, to date there is no report on the structural determination of PEG-U-IC single crystals. We have recently obtained single crystals of this PEG-U-IC. Structural determination of these single crystals is underway and will be published later.[17]

FTIR Spectroscopy. Figure 3 shows the FTIR spectra in the region from 500 to 2000 cm^{-1} obtained for urea, PEO, and PEO-U-IC. The urea spectrum shows bands at 1682 cm^{-1} due to C=O stretching, at 1628 and 1599 cm^{-1} due to N−H bending vibrations, and at 1467 cm^{-1} due to the N−C−N antisymmetric stretching vibration. The bands due to tetragonal urea are greatly affected by the formation of inclusion compound. The bands due to PEO are not much affected by the formation of the complex. The bands at 1682, 1628, 1599, and 1467 cm^{-1} due to tetragonal urea are shifted to 1694, 1659 1639, 1577, and 1457 cm^{-1}, respectively, in PEO-U-IC.

PEC-U-IC, PTHF-U-IC, and H-U-IC were investigated previously using X-ray diffraction and FTIR spectroscopy.[4] This study demonstrated that these inclusion compounds are isostructural. Vibrational bands due to hexagonal urea were assigned. The bands at 1658 and 1491 cm^{-1} were attributed to C=O stretching and N−C−N stretching in the hexagonal urea. Also it was indicated that the infrared spectra of the channel-forming urea is independent of the polymer included in the narrow (5.5 Å) urea channel. FTIR spectra of PEO-U-IC, PTHF-U-IC, and PEC-U-IC in the region between 1300 and 1900 cm^{-1} are presented in Figure 4. It is clear that the vibrational bands observed for PEO-U-IC are different from the vibrations observed for PTHF-U-IC or PEC-U-IC. This suggests that the crystal structure of PEO-U-IC is different from the hexagonal crystal structure.

Single-crystal structural determination of this PEO-U-IC suggested that the crystal structure of PEO-U-IC is a trigonal form.[15] Therefore we can tentatively assign the bands at 1694 and 1658 cm^{-1} for C=O stretching vibrations, the bands at 1639 and 1577 cm^{-1} for N−H bending vibrations, and the band at 1457 cm^{-1} for the N−C−N stretching vibration to the trigonal form of urea. As we see two different vibrations for C=O stretching, we can conclude that urea molecules are found in two different environments in the complex. In fact single-crystal diffraction studies suggested that two-thirds of the urea molecules form the matrix which are strongly hydrogen-bonded to each other and one-third of the urea molecules reside in the channel. The urea molecules residing in the channels are also hdyrogen-bonded to the oxygen atoms of the PEO chain as well as to the channel-forming urea. However the strength of this hydrogen bonding is probably weaker than the strength of hydrogen bonding within the matrix. This is consistent with our infrared studies which show two vibrations for carbonyl stretching. The PEO-U-IC was heated to 150 °C and crystallized from the melt at room temperature. The FTIR spectrum observed for the melt-crystallized sample is quite different from the infrared spectrum observed for the original sample in the following regions: the band at 1694 cm^{-1} dissappears, the band at 1638 cm^{-1} shifts to 1630 cm^{-1}, and the band at 1577 cm^{-1} shifts to 1595 cm^{-1}. This spectrum closely resembles hexagonal urea. The temperature dependence of IR spectra of PEO-U-IC was studied, and similar observations were made previously.[18]

The inclusion compound was also formed between PEG oligomer with MW = 600 and urea. The infrared spectrum of this PEG-U-IC is shown in Figure 5 along with that of PEO-U-IC. The vibrational bands due to

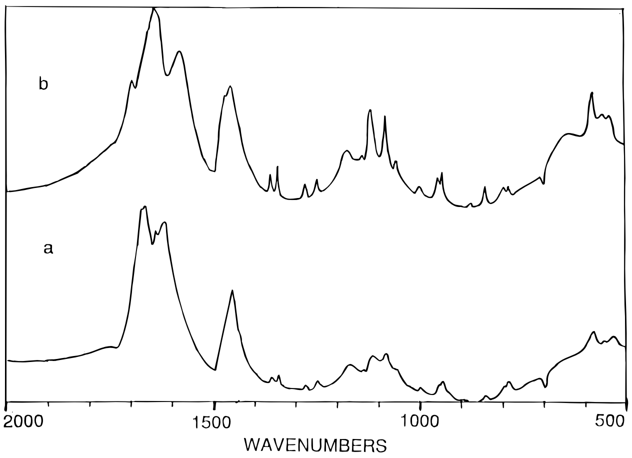

Figure 5. Fourier transform infrared spectra in the region between 500 and 2000 cm^{-1}: (a) PEG-U-IC and (b) PEO-U-IC.

urea in the PEG-U-IC are apparently different from usual hexagonal or trigonal urea vibrations, indicating that the crystal structure of PEG-U-IC might be different from these two crystal structures. In the PEG-U-IC spectrum, the band due to C=O stretching vibration is shifted to 1665 cm^{-1}, the bands due to N−H bending vibrations are shifted to 1631 and 1617 cm^{-1}, and the band due to N−C−N stretching vibration is shifted to 1454 cm^{-1}. In fact, wide angle X-ray diffraction studies of the inclusion compound formed between PEG oligomers with MW = 400 and urea were reported in the literature.[11] All reflections were indexed with a large tetragonal unit cell of dimensions $a = b = 9.30$ Å and $c = 19.51$ Å. Therefore the above-mentioned vibrations can be attributed to large tetragonal urea vibrations. The bands due to PEG in the PEG-U-IC do not show any differences from those due to PEO in PEO-U-IC. Similar infrared spectra were also observed for the inclusion compounds formed between poly(vinylidene fluoride),[19] poly(propylene),[20] and *trans*-1,4-poly(isoprene)[21] with urea, suggesting that the crystal structure of these ICs might be similar to that of PEG-U-IC.

In the present study, vibrational spectroscopy is also used to obtain information about the conformation of the PEO and PEG chains in the urea channels. Before we determine the conformations of PEO and PEG in the channels, it is necessary to examine the infrared spectra of pure PEO and PEG. The infrared spectrum of PEO shows characteristics of both crystalline and amorphous components. In the crystalline state, the PEO chains adopt trans (COCC)−gauche (OCCO)−trans (CCOC) (TGT) for its repeating unit, $-CH_2-CH_2-O-$, forming a helical structure with a period of seven units in two turns. On the basis of previous normal coordinate calculations, the infrared spectra of crystalline PEO is well understood. Vibrational bands are broader in the bulk spectrum compared to the IC spectrum, indicating greater conformational heterogeneity in the bulk PEO due to the presence of crystalline and amorphous components. A number of vibrational bands sensitive to conformational changes in PEO were identified.[22] The bands at 1360 and 1342 cm^{-1} are assigned to CH_2 wagging modes; the bands at 1282, 1242, and 1234 cm^{-1} are associated with CH_2 twisting modes; the bands at 1150, 1100, 962, and 945 cm^{-1} are associated with combinations of CH_2 rocking, C−O stretching, and COC deformation modes. It can clearly be seen that the vibrations due to C−O stretching are shifted to lower wavenumbers in the U-IC. These shifts may be partially interpreted in terms of bond weakening due to the hydrogen bond formation between the urea N−H and the oxygen atom in the PEO chain, as well as the difference between the structural environments of the PEO chain in bulk and U-IC samples.

It is well known that PEO adopts different conformations when it forms complexes with inorganic salts or is mechanically deformed. Vibrational spectroscopy was often used to obtain the conformation of PEO chains. The complex formed between $HgCl_2$ and PEO showed new vibrational bands at 1326 cm^{-1} due to CH_2 wagging, at 1486 cm^{-1} due to CH_2 scissor, and at 862 cm^{-1} due to CH_2 rocking. This suggested that PEO-$HgCl_2$ complex adopts the T_5GT_5G conformation, which contains a high trans content compared to the bulk TGT conformation.[23] PEO can take up the all-trans conformation when it is mechanically deformed.[24] Recently, the complex formed between PEO and $MgCl_2$ was studied using infrared spectroscopy and indicated that PEO adopts the TGT-TGT-GTT-TTG conformation in the complex.[25] These spectroscopic observations served as a basis of the conformational analysis of PEO-U-IC in this paper.

It has been demonstrated previously by several groups that the bulk crystalline conformation cannot be accommodated in the urea channel. From the differences in the vibrational spectra, we can also conclude that the conformation in the channel is different from the bulk crystalline conformation. Our modeling indicates that the all-trans, kink, or jog conformations are able to fit in the channel.[13] If we assume PEO takes the all-trans conformation in the channel, we would expect to see a simpler spectrum with fewer bands compared to the spectrum observed for bulk PEO. However, we have not seen any differences in the number of bands in the IC spectrum. Therefore we tenatively rule out the possibility of the all-trans conformation in the channel. On the other hand, our solid state NMR indicates that there is no possibility of having gauche C−O bonds in the channel. Therefore it is reasonable to assume that the PEO chains in the channels adopt a conformation which is similar to the bulk conformation, which has trans C−O bonds and gauche C−C bonds, but in the U-IC channels the C−C bonds may be displaced somewhat from the perfect gauche states toward the more extended trans conformation.

NMR Spectroscopy. The CP/MAS/DD ^{13}C NMR spectra of PEO and PEO-U-IC are shown in Figure 6. It is well known that the bulk PEO spectrum shows a resonance containing narrow and broad components due to the presence of both amorphous and crystalline PEO. Figure 6b shows the NMR spectra of PEO-U-IC. It can clearly be seen that the peak width in the PEO-U-IC spectrum is reduced extensively compared to that in the PEO spectrum. The resonance frequencies are very similar for bulk PEO and PEO-U-IC, consistent with a single-crystal X-ray diffraction study of PEO-U-IC,[12] which showed the included PEO chains in a conformation similar to but more extended than that adopted in its bulk crystals. The spin-lattice relaxation times for bulk PEO and PEO-U-IC were observed using the CP−T_1 exponential decay method at room temperature. The T_1s measured for the crystalline component of bulk PEO and PEO-U-IC are 8.2 and 4.2 s, respectively, and $T_1 = 0.5$ s was observed for the amorphous carbon. The inclusion compound between PTHF and urea was investigated using solid state NMR spectroscopy.[4] In

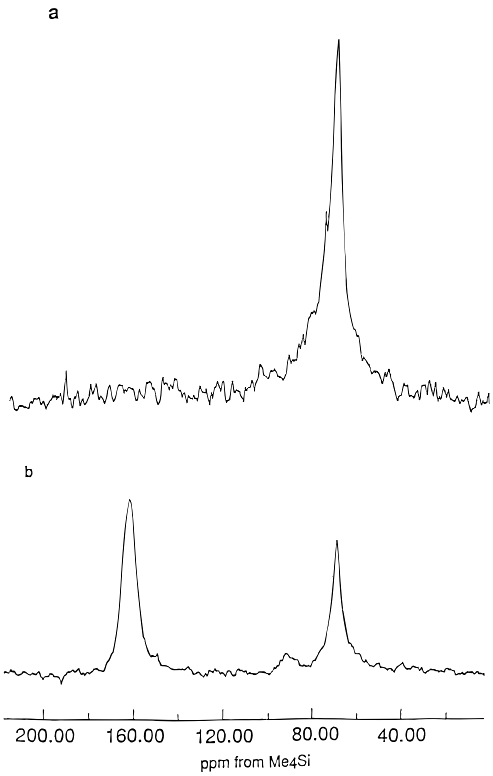

Figure 6. Magic and angle spinning dipolar-decoupled ^{13}C NMR spectra with cross-polarization: (a) PEO and (b) PEO-U-IC.

this study, we found that T_1s observed for the included PTHF chain are reduced by a factor of 50 from bulk PTHF values. A similar observation was also made for PE chains in the PHTP channel.[26] The fact that the PEO chain contains a main chain oxygen, and is hydrogen-bonded to urea, may produce a significant retardation of PEO chain motion in the channel compared to PTHF chains included in the hexagonal urea channels not containing urea.

The stoichiometry between PEO and urea was observed using solid state NMR spectroscopy. We recorded the one-pulse spectrum without cross-polarization with a long delay time between the signal accumulations. A molar stoichiometry of 2:3:1 urea: PEO repeat unit was observed. This is in very close agreement with the stoichiometry obtained from single-crystal X-ray diffraction.

Single-crystal X-ray diffraction of PEO-U-IC revealed two unusual features about its structure. First, the channel cross sections are trigonal rather than hexagonal. Second, one-third of the urea molecules are directly complexed to PEO chains and actually reside in the IC channels formed by the remaining two-thirds of the urea molecules. It would therefore appear that two distinct types of urea exist in the PEO-U-IC. An expansion of the urea carbonyl portion of the CPMAS/DD spectrum of PEO-U-IC shows an asymmetric line shape. It seems likely that two distinct types of urea found in PEO-U-IC contribute to the line shape asymetry. The CP$-T_1$ for the urea carbonyl resonance in the PEO-U-IC was measured to be 35 s, which is about 2 times longer than the T_1 of the urea carbonyl in the hexagonal U-ICs. Differences in the mobility of the urea carbonyl carbon may be attributed to differences in the crystal form and the types of host−guest interactions.

In summary, we have confirmed that PEO-U-IC formed from solution has a trigonal crystal structure and PEG-U-IC has a different, possibly tetragonal, crystal structure. It has also been shown that crystallizing PEO-U-IC from the melt does not yield a trigonal or tetragonal crystal structure but instead a hexagonal structure. The PEO chains in the channel adopt a conformation, similar to bulk PEO conformation, as evidenced by FTIR and solid state NMR spectroscopies.

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