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Conformational and Motional Characterization of Isolated Poly(ϵ-caprolactone) Chains in Their Inclusion Compound Formed with Urea

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ABSTRACT: The behavior of isolated poly(ϵ-caprolactone) (PEC) chains confined to the narrow channels of their crystalline inclusion compound (IC) with urea is contrasted with the behavior of PEC chains observed in bulk, semicrystalline samples. DSC observations of bulk and IC-recovered PEC samples revealed that PEC recovered from PEC–U–IC via extraction with a nonsolvent for PEC produces crystals that melt 6 °C higher than PEC samples recrystallized from solution or the melt. Presumably an extended chain morphology results when PEC crystals are obtained from the collapse of PEC–U–IC. FTIR and CPMAS/DD ^{13}C NMR observations both point to similar extended, nearly all-trans conformations for PEC chains in PEC–U–IC and in the bulk. Quantitative observations by both techniques yield a molar stoichiometry of U/PEC = 4/1. Solid-state ^{13}C NMR observations show channel-bound PEC chains in PEC–U–IC have spin–lattice relaxation times (T_1) only 20–50% as long as those observed for bulk PEC samples. On the other hand, the T_1's observed for the urea carbonyl carbons in PEC–U–IC and *n*-hexadecane–U–IC are nearly identical, though the included *n*-hexadecane chains are known to be considerably more mobile than the included PEC chains.

Introduction

The biodegradability and nontoxicity of poly(ϵ-caprolactone) (PEC) make it of interest for the controlled release of drugs from polymer devices.[1] Two X-ray diffraction studies of PEC have been previously reported,[2,3] both with space group $P2_12_12_1$ and identical unit cell parameters but with different chain conformations and packing. Recent electron diffraction studies[4] showed that the chains pack in the slightly nonplanar structure in space group $P2_12_12_1$, rather than the alternative planar chain conformation which was proposed by Bittiger et al.[3]

The formation of inclusion compounds (ICs) between polymers and small-molecule clathrates like perhydrotriphenylene (PHTP) has been reported previously.[5,6] It also has been shown that linear polymers such as polyethylene, poly(ethylene oxide), and polyesters form inclusion compounds with urea.[7] Some polymer–urea inclusion complexes have been obtained by polymerization of the monomer already present in the urea channel.[8] One of these polymer–urea inclusion compounds is shown in Figure 1. Polymer chains are isolated from their neighbors when they are included in the narrow IC channels (5.5 Å). Formation of a polymer IC provides an opportunity to study the conformations and mobilities of isolated polymer chains. This has been carried out using ^{1}H NMR, ^{13}C NMR, DSC, and ESR spectroscopies.[5,6,9] Differences in chain mobility and conformations between isolated polymer chains in their ICs and bulk polymers have been discussed.[10]

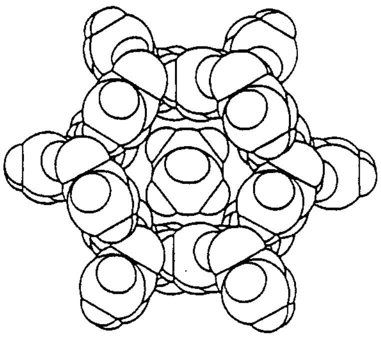

Figure 1. Schematic representation of urea–*n*-hexadecane clathrate as determined by X-ray diffraction.[20]

These studies have led to the observation of unusual conformations for some polymers that are included in the narrow IC channel (5.5 Å). The conformations and mobility of the isolated chains are mainly dependent on the relative cross-sectional dimensions of the polymer chains and the host matrix channel diameter. Though this specific environment places constraints on the degrees of freedom available to the included polymer, an increase in the mobility of included polymer chains relative to bulk, solid polymer samples may result.

Recently, molecular modeling of aliphatic polyesters and polyamides has been carried out.[11] There it was suggested that aliphatic polyesters may be capable of forming inclusion compounds with urea. It was also suggested that the PEC chains in either all-trans or kink conformations are slim enough to fit in the narrow (5.5 Å) IC channel. Subsequently, the urea inclusion complex of PEC was made and studied using X-ray diffraction and DSC.[12] A stoichiometry of 4.4 (U/PEC mole ratio) was obtained from X-ray diffraction, in reasonable agreement with a stoichiometry of 4 obtained by DSC measurement. Comparisons of PEC–U–IC with polyethylene–urea IC (PE–U–IC) were made using X-ray diffraction, and it was concluded that both complex structures are quite similar.

In the present study, PEC–U–IC was prepared via either solution or film techniques. DSC, FTIR, and high-resolution solid-state CP/DD/MAS and DD/MAS ^{13}C NMR spectroscopies were used to study the conformations and mobilities of the isolated IC chains and the chains in the bulk polymer. Differences in the conformations and mobilities are discussed in terms of interchain interactions and packing environments.

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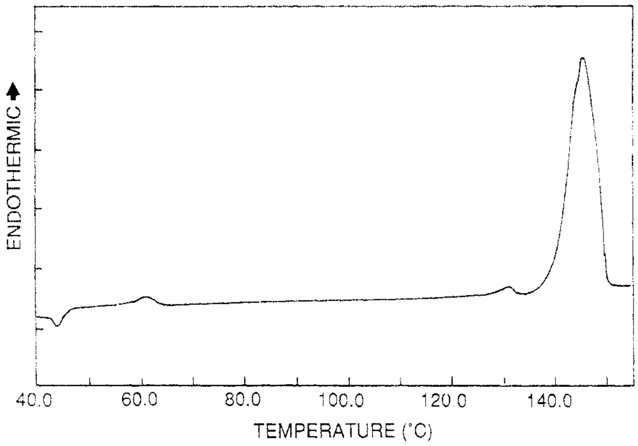


Figure 2. DSC thermogram of the inclusion compound formed between urea and poly(ϵ-caprolactone).

Experimental Section

Samples. PEC–U–IC was prepared by solution or film techniques. In the solution method 0.40 g of PEC (MW = 40 000) was dissolved in 100 mL of acetone at 40 °C. The PEC–acetone solution was slowly added to 100 mL of saturated urea/methanol solution while continuously warming and stirring. Then the solution was cooled to room temperature, and a white precipitate was obtained over 12 h and filtered. In another method the PEC film cast from 1% acetone solution was dipped into a saturated urea/methanol solution. A thick urea–PEC complex was obtained over 3 days.

DSC Measurements. To obtain melting temperatures and heats of fusion, differential scanning calorimetry observations were made on 3–10 mg samples with a Perkin-Elmer DSC 7 thermal analyzer. A heating rate of 10 °C/min was employed. An indium standard was used for calibration.

FTIR Spectroscopy. FTIR spectra were recorded on a Nicolet 510P FTIR spectrometer at frequencies from 500 to 4000 cm^{-1} with a resolution of 2 cm^{-1}. Subtraction of vibrational absorptions due to excess urea present in the IC was carried out using the spectrum of tetragonal urea taken at room temperature.

NMR Measurements. High-resolution solid-state ^{13}C NMR experiments were performed at 50.1 MHz on a Chemagnetics CMC200S spectrometer. The cross-polarization magic-angle spinning (CP/MAS/DD) probe with a small-volume spinner using a zirconia rotor was employed. The spinning speed ranged from 3 to 4 kHz. High-power dipolar decoupling (DD) was applied at about 47 kHz during acquisition. The spectral width was 15 kHz in 2K data points, which were zero-filled to 8K before Fourier transformation. The optimum Hartmann–Hahn and magic-angle conditions were obtained using *p*-di-*tert*-butylbenzene (PDTBB, 31.0 ppm vs TMS). Spin-lattice relaxation times (T_1) were obtained using the CP-T_1 exponential decay[13] function with 10–18 different τ values. The contact time used was either 0.2 ms (for ICs) or 2 ms (for bulk), depending on the nature of the samples, and the pulse delay was 3 s. The T_1 values were obtained from the slope of the semilogarithmic plot in a spreadsheet program on a personal computer.

Results and Discussion

DSC Measurements. The PEC–U–IC was prepared via solution or film techniques. The formation of IC was confirmed from the melting behavior. The thermogram of the PEC–U–IC is shown in Figure 2. The thermogram of PEC–U–IC shows one major endotherm at 143 °C, corresponding to PEC–U–IC, and two very small endotherms at 59 and 133 °C, associated with very little uncomplexed PEC and urea.[12] The thermogram of PEC crystallized from acetone solution is given in Figure 3a and shows a melting temperature at 58 °C and an enthalpy of 25.2 cal/g. Native polymer was recovered from the PEC–U–IC by extracting the urea matrix using methanol at room temperature. The thermogram obtained for native polymer is given in Figure 3b along with the thermogram of PEC recrystallized from the melt (Figure 3c). Melting temperatures of 64 and 58 °C are obtained for polymer extracted from IC and recrystallized from solution or melt, respectively. On the basis of the reported enthalpy of melting for 100% crystalline PEC, which is 32.4 cal/g, the crystallinity of each sample was calculated. These data are given in Table 1, where an average of at least three values was taken for each sample. The melting temperature of extracted PEC is 6 °C higher than the melting temperature of solution- or melt-recrystallized PEC samples, pointing to an enhanced stability of the coalesced PEC chain crystals extracted from the PEC–U–IC. In earlier studies similar behavior was observed when polybutadiene was extracted from its PHTP-IC[9] clathrate. The authors suggested that extended crystals without chain folding are produced during the extraction. The results of this investigation on PEC–U–IC are consistent with that previous work. It is reasonable to assume that the extended chain morphology is recovered during the collapse of the urea matrix from PEC–U–IC when extracting the urea matrix with a nonsolvent for PEC.

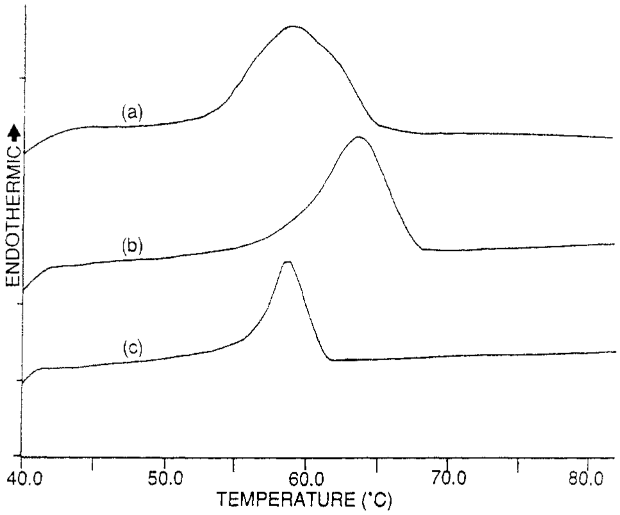


Figure 3. DSC thermogram of poly(ϵ-caprolactone): (a) crystallized from solution; (b) native polymer extracted from PEC–U–IC using methanol; (c) recrystallized from melt.

Table 1. Calorimetric Data of Poly(ϵ-caprolactone)

sample	T_m (°C)	ΔH_m (cal/g)	crystallinity (%)
solution-crystallized PEC	58	25.2	77
melt-recrystallized PEC	58	15.0	46
extracted PEC from its U-IC	64	19.0	59

FTIR Spectroscopy. The Fourier transform infrared spectra obtained for urea, semicrystalline PEC, and PEC–U–IC are given in Figure 4a–c, respectively. The assignments for tetragonal urea are well established.[14] Tetragonal urea has strong absorption bands at 1682 cm^{-1} due to the C=O stretching vibration, 1628 and 1599 cm^{-1} due to NH bending vibrations, and 1467 cm^{-1} due to the N–C–N stretching vibrations. In the spectrum of PEC, we can assume contributions from both crystalline and amorphous regions. It has been demonstrated previously that the crystalline vibrations can be isolated by digital subtraction of amorphous contributions from the semicrystalline samples.[15] Normal coordinate calculations have not been carried out to date to assign the complete spectrum. However, Coleman et al.[16] have assigned some bands using a group frequency approach. The bands at 1724 and 1737 cm^{-1} were previously assigned to C=O stretching for crystalline and amorphous phases, respec-

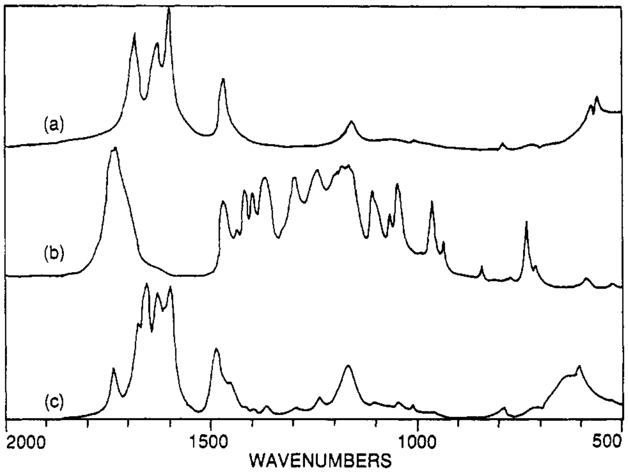


Figure 4. Fourier transform infrared spectra in the region between 500 and 2000 cm^{-1}: (a) urea; (b) PEC; (c) PEC-U-IC.

tively. Our semicrystalline spectrum shows the band at 1724 cm^{-1} with a shoulder at 1738 cm^{-1}, indicating the contribution of both crystalline and amorphous regions. Bands at 1192, 1178, and 1161 cm^{-1} were observed in the 1000–1300 cm^{-1} region. These bands were previously assigned to coupled modes variously associated with C–C–H and O–C–H bending and C–C and C–O stretching vibrations. The band at 1161 cm^{-1} was identified as an amorphous band, and the other two bands are associated with the crystalline conformation. Also these two bands appeared to be sensitive to orientation. To confirm the band assignments made for amorphous contributions, spectra were recorded at a temperature well above the melting temperature (58 °C). The PEC-U-IC spectrum shows bands characteristic of uncomplexed urea, PEC in the channel, and channel-forming hexagonal urea. In fact, the new bands at 1658 and 1491 cm^{-1} are observed and assigned to channel-forming urea. The bands due to PEC in the channel do not show appreciable differences from those of crystalline PEC in the bulk, except for the following: the band at 1724 cm due to the C=O stretching vibration shifts to 1738 cm^{-1}, and a single band at 1178 cm^{-1} is observed for the C–O–C stretching vibration. From X-ray diffraction it is known that crystalline PEC adopts a nearly all-trans conformation. Similarities in both spectra indicate that PEC in the channel takes a conformation similar to bulk crystalline PEC. The PEC carbonyl group in its urea–IC vibrates 14 wavenumbers higher than in the bulk. This is opposite to the behavior expected if the PEC carbonyl group were hydrogen bonded to the urea amide hydrogen in the inclusion compound. Consequently, we conclude that the host–guest interactions are mainly of the van der Waals type.

The inclusion compounds of *n*-hexadecane (H-U-IC)[17] and poly(L-lactic acid) (PLLA-U-IC)[18] with urea were formed and characterized using X-ray diffraction, DSC, FTIR, and solid-state NMR spectroscopy. The infrared spectra of H-U-IC and PLLA-U-IC are given in Figure 5 along with PEC-U-IC for comparison. The bands at 1658 and 1491 cm^{-1} are observed in all these inclusion compounds, indicating that the overall crystal structures of these ICs are similar. The crystal structures of H-U-IC and PLLA-U-IC were studied using X-ray diffraction and showed that urea forms a hexagonal crystal lattice in the presence of *n*-hexadecane and PLLA in the channel. Also in our recent X-ray diffraction studies of PEC-U-IC a very similar X-ray diffraction pattern was obtained. Therefore it is reasonable to assign the bands at 1658 and 1491 cm^{-1} to C=O and N–C–N stretching vibrations in the hexagonal urea.

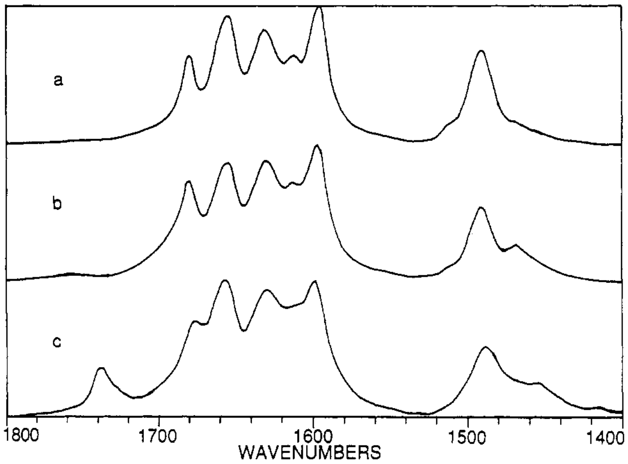


Figure 5. Comparison of infrared spectra in the region between 1400 and 1800 cm^{-1} for urea-based inclusion compounds: (a) H-U-IC; (b) PLLA-U-IC; (c) PEC-U-IC.

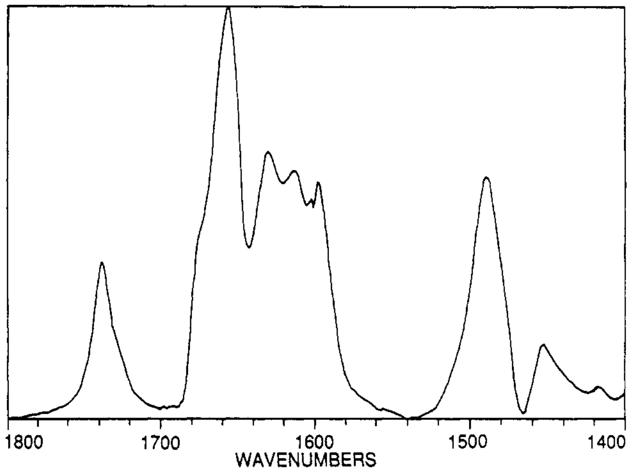


Figure 6. Fourier transform infrared spectrum of 100% PEC-U-IC obtained from the subtraction of uncomplexed urea.

The analysis of the IR spectrum of a polymer IC may provide information about the types and strengths of interactions between urea host matrix and PEC guest molecule. To do any quantiative work, a clean sample should be obtained without any uncomplexed urea or PEC. Our thermogram shows that our particular PEC-U-IC sample contained very little uncomplexed urea and PEC. FTIR spectra obtained for PEC-U-IC show small bands at 1682 and 1467 cm^{-1}, also indicating the presence of a small amount of uncomplexed tetragonal urea (estimated as 5%). Therefore, the uncomplexed tetragonal urea present in the spectrum is removed by subtraction to obtain the pure IC spectrum. The subtraction is carried out by monitoring the disappearance of the 1682 and 1467 cm^{-1} bands due to tetragonal urea. The spectrum of 100% crystalline IC obtained by subtraction is given in Figure 6. This shows bands characteristic of hexagonal urea and PEC in the channel.

The stoichiometry of the IC (moles of urea vs moles of PEC) is calculated by taking the ratio of urea carbonyl (1658 cm^{-1}) versus PEC carbonyl (1738 cm^{-1}) intensities. Knowledge of relative absorption coefficients is necessary to obtain the stoichiometry. Unfortunately, the absorption coefficient is not easily obtained. However, it can be obtained in this case when the integrated carbonyl absorbance is normalized with respect to a PEC-U-IC internal standard band (1491 cm^{-1}). A ratio of 1 is obtained, indicating that the absorption coefficients are approximately equal. On this basis, stoichiometry is obtained by simply taking the area ratio of both carbonyls.

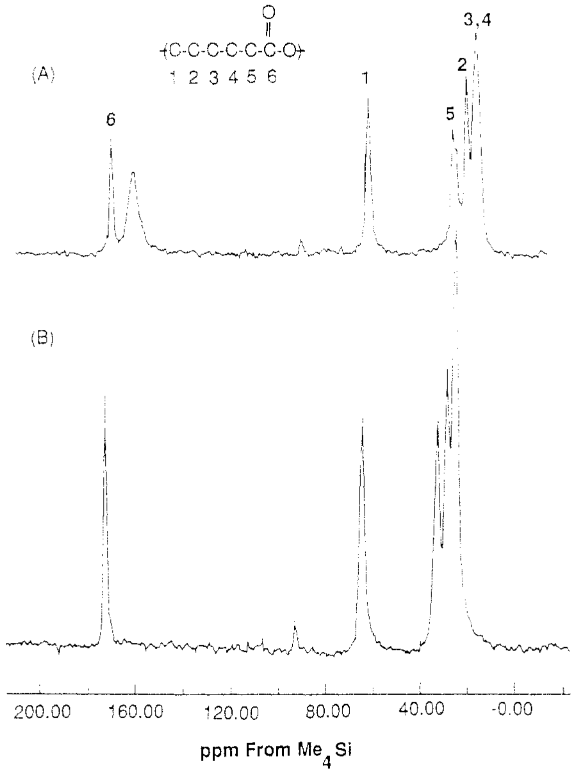


Figure 7. Magic-angle spinning dipolar-decoupled ^{13}C spectra with cross polarization: (A) PEC-U-IC; (B) PEC.

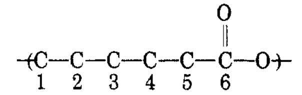
A stoichiometry of 4 is obtained. The comparison of stoichiometry from the infrared method developed in this work with that from prior[12] DSC measurement shows close agreement.

The successful use of infrared spectroscopy, as developed in this work, to determine the stoichiometry is believed to be a consequence of using the C=O bands for these measurements. The bands at 1738 and 1491 cm^{-1} are well separated. The areas of these bands can be obtained without deconvolution. However, the band at 1658 cm^{-1} is not completely separated. Therefore this band was deconvoluted using a manual curve fitting procedure.

NMR Spectroscopy. The CP/MAS/DD spectrum of PEC crystallized from solution is given in Figure 7b. The spectrum shows five resonances at 172.9, 64.8, 32.6, 28.5, and 25.1 ppm. A single resonance is obtained for each carbon though two carbons resonate at identical frequencies. Since the spectrum is recorded with cross polarization, the crystalline carbons, which cross polarize efficiently, are enhanced relative to the mobile carbons in the amorphous phase, which do not cross polarize efficiently at temperatures well above the glass transition temperature. Therefore these resonances are assigned to crystalline carbons. The crystalline structure of PEC was studied by Chatani et al.[2] It was proposed that the chain conformation of bulk PEC is almost all-trans, planar zigzag. This is consistent with single resonances observed for methylene carbons in our NMR studies. To obtain amorphous resonances we recorded the DD/MAS spectrum without cross polarization. This also shows five resonances at 172.0, 63.7, 33.3, 28.2, and 25.0 ppm. The chemical shifts belonging to carbons in the crystalline and amorphous phases are listed in Table 2.

The CP/MAS/DD spectrum observed for PEC-U-IC is shown in Figure 7a. The principal resonances due to the PEC in the channels can be identified by comparison to the spectrum of bulk PEC. Three of its methylene carbons (carbons 3, 4, and 5) show multiple resonances. A similar spectrum is also observed under the DD/MAS condition, reflecting the substantial motion of PEC in the narrow IC channels. Multiple resonances can be attributed to more than a single conformational or packing environment. Our molecular modeling[11] of polyesters suggested that the all-trans conformers account for at least 40% of all channel conformers found for PEC. The remaining conformers found to fit in the channel were identified as the kink g$^{\pm}$tg$^{\mp}$ conformers. The bulk PEC chains crystallize in a nearly all-trans conformation, which is the most stable conformation. However, the conformations around CH$_2$-O bonds in PEC crystals deviate somewhat from 0°. It was also shown that there was no conformational interconversion possible in the channel. Therefore the higher energy kink conformations are not expected to be present in the channel, because the increased entropy attendant with the presence of rapidly interconverting channel conformers is not realized. Furthermore, the splitting observed for the methylene carbon resonances is not consistent with either the pattern or the magnitude of splitting expected for a relative population of rigid trans and kink conformers in the channel. From these observations, it is assumed that only the all-trans conformation resides in the narrow channel. Therefore we attribute the multiple resonances observed for carbons 3, 4, and 5 of PEC in the channel to distinct crystalline packing environments.

Table 2. Chemical Shift Values for Poly(ε-caprolactone) in Bulk and in the IC Channel



$$\text{-(C—C—C—C—C—}\overset{\overset{\displaystyle O}{\|}}{C}\text{—O)-}$$

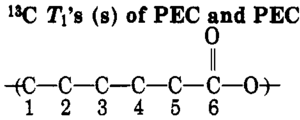
1 2 3 4 5 6

carbon	crystalline chem shift (ppm)	amorphous chem shift (ppm)	PEC-U-IC
1	64.8	63.3	64.7
2	28.5	28.0	28.8
3	25.1	25.0	24.9 26.2
4	25.1	25.0	24.9 26.2
5	32.6	33.3	32.9 34.0
6	172.9	172.0	172.6

Recently, a CRAMPS high-resolution solid-state ^{1}H NMR study was carried out for poly(ethylene adipate) (PEA) and PEA-U-IC by Zumbalyadis et al.[19] They observed two proton resonances for the glycol protons in bulk PEA. This is consistent with rotation of the ethylene group by 80° around the O-CH$_2$ bond, making the two protons inequivalent. However, PEA-U-IC shows single resonances for all protons, which would be expected from our modeling, indicating a uniform symmetric environment for protons in the glycol portion. It is interesting that these two aliphatic polyesters show NMR behaviors for their IC-included and bulk chains which are distinct. PEC evidences heterogeneous environments in its U-IC, while PEA shows a homogeneous environment. Bulk PEA displays a more nearly all-trans conformation in its IC compared to its bulk crystals, while a nearly all-trans conformation is adopted by PEC chains in both of its crystalline environments.

Molecular Motion. Spin-lattice relaxation time (T_1) measurements were performed on bulk PEC and PEC-U-IC using the exponential decay method (see Experimental Section). The T_1 values for the carbon nuclei of the PEC and PEC-U-IC are given in Table 3 and serve to indicate the motional characteristics of PEC chains in the IC channel. This can provide some measure of the nature of cooperative, interchain interactions occurring in an ordered bulk polymer.

Table 3. ^{13}C T_1's (s) of PEC and PEC-U-IC



$$-\!(\underset{1}{C}-\underset{2}{C}-\underset{3}{C}-\underset{4}{C}-\underset{5}{C}-\underset{6}{\overset{\overset{O}{\|}}{C}}-O)\!-$$

carbon	PEC	PEC-U-IC
1	100	21
2	94	48
3, 4	93	34, 16
5	111	51, 45
6	146	44
urea C=O		16

Comparison of T_1's observed for PEC in the bulk and its urea-IC reveals large differences. It should be noted that the T_1's of the included PEC in the channel are reduced by factors of 2-5 compared with the bulk polymer. The T_1's of PEC in the urea channel can be compared with the T_1's of *n*-hexadecane (H) in the urea channel and polyethylene in the PHTP channel. The T_1's of CH_2 carbons in PEC-U-IC are 4-10 times longer than the T_1 observed for PE CH_2 carbons in PHTP-IC. We have observed the central CH_2 carbons of the included, all-trans-bond, alkane to have $T_1 = 15$ s, which is intermediate between the T_1 observed for PE in its PHTP-IC (6 s) and PEC in its urea-IC (20-50 s). Previous[6] variable-temperature spin-lattice relaxation measurements demonstrated that PE in its PHTP-IC is on the fast motion side of its T_1 minimum. If we assume that *n*-hexadecane is also on the fast motion side of the T_1 minimum, then *n*-hexadecane is moving faster than PE in its PHTP-IC. On the other hand, it is most likely that PEC in its U-IC is on the slow motion side of the T_1 minimum. Therefore the motion of PEC is slower compared to that of *n*-hexadecane or PE. T_1's 2-3 times larger are observed for PEC compared with *n*-hexadecane in the urea channel, reflecting the differences in the interactions between guest polymer and urea. PEC contains the bulky and rigid carbonyl group, which may interact with urea amide groups forming the channel, and this may be the reason for the longer T_1's observed for PEC compard with *n*-hexadecane, where there is no possible interaction in the channel. T_1 measurements of the urea C=O's were also carried out for H-U-IC and PEC-U-IC. Approximately the same T_1 (16 s) is observed for both ICs. Differences in the mobilities of the included *n*-hexadecane and PEC chains apparently do not affect the mobilities of urea molecules forming the IC channels.

Recently,[6] an inclusion compound was formed between polyethylene and PHTP. The conformational and motional behaviors of PE and PE-PHTP-IC were studied using solid-state NMR spectroscopy. This indicated that isolated PE chains in the IC adopt the all-trans, planar zigzag conformation similar to bulk PE. The spin-lattice relaxation times for methylene carbons were 320 s in the bulk and only 6.4 s in the inclusion compound. This dramatic drop in T_1 in the IC was explained by the absence of cooperative, interchain interactions and is consistent with our findings in PEC-U-IC.

To determine quantitatively the stoichiometry between urea and PEC, we recorded the MAS/DD spectrum without CP but with a sufficiently long delay time between signal accumulations. We have obtained the stoichiometry using the C=O chemical shifts from both urea and PEC. The longer T_1 of these two chemical shifts is 45 s, so the delay time (200 s) was chosen to be longer than 5 times the longest T_1 associated with the PEC carbonyl (45 s). The areas of these two chemical shifts were determined. A 4:1 mole ratio is observed for the urea carbonyl versus the PEC carbonyl resonance. This is in close agreement with the stoichiometry expected for PEC-U-IC based on the all-trans conformation for included PEC chains and 1.83 Å channel length per urea molecule determined from single-crystal X-ray diffraction performed on H-U-IC[20] and the stoichiometry determined previously by DSC[12] and here by FTIR spectroscopy.

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