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Formation, Characterization, and Segmental Mobilities of Block Copolymers in Their Urea Inclusion Compound Crystals

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ABSTRACT: We report the formation of crystalline inclusion compounds (ICs) between the small-molecule host urea (U) and two block copolymer guests: (i) poly(ϵ-caprolactone)−polybutadiene (PCL−PBD) and (ii) PCL−poly(ethylene oxide)−PCL (PCL−PEO−PCL). Both block copolymer−U-ICs are formed by cocrystallization from saturated solutions of urea, and each block copolymer−U-IC was observed with DSC, X-ray diffraction, and ^{13}C NMR and FTIR spectroscopies. It was found that both blocks of the PCL−PBD diblock copolymer are included in the U-IC channels while only the terminal PCL blocks of the PCL−PEO−PCL triblock copolymer are included. The structure of the PCL−PBD−U-IC appears to be a combination of the traditional hexagonal form with narrow ca. 5.5 Å channels surrounding the PCL blocks, while the PBD blocks are included in an "expanded tetragonal" structure observed previously for PEO(oligomer)−U-IC and polypropylene−U-IC, where the urea matrix channel diameter is believed to be expanded beyond 7 Å. This might explain how the PBD blocks, which contain 12% 1,2 units with bulky $-CH{=}CH_2$ side chains, are accommodated in the U-IC channels. Similarly, in the PCL−PEO−PCL−U-IC, where only the terminal PCL blocks are included, the IC structure appears very similar to the usual narrow channel, hexagonal structure as found, for example, in PCL−U-IC, the IC between the PCL homopolymer and urea. As a consequence, we may observe PCL blocks in two distinct U-IC environments and may compare their behaviors to those of PCL chains in the homopolymer PCL−U-IC and homopolymer and block copolymer bulk crystals. In addition, $T_{1\rho}$ measurements of ^{1}H spin diffusion reveal structural aspects of the block copolymer−U-ICs, and the isolation of U-IC included polymer chains from their neighbors may permit the probing of 1-dimensional ^{1}H spin diffusion by observing the $T_{1\rho}(^1H)$ relaxation in these block copolymer−U-ICs.

Introduction

We have recently begun to form crystalline inclusion compounds (ICs) between guest block copolymers and host urea (U). The impetus for this work is two-fold: (i) creation of a new class of materials characterized by U-IC crystals formed with one of the polymer blocks embedded in a matrix formed by the remaining blocks, which do not form an IC with urea and are thereby excluded from the IC crystals, and (ii) comparing the conformational and dynamic behavior of block copolymers constrained to occupy the narrow IC channels formed by the host urea with the behavior exhibited by the bulk block copolymer which typically has a phase-separated structure with distinct domains containing constituent blocks of a single type. Formation of poly(ϵ-caprolactone) (PCL)−polybutadiene (PBD)−U-IC [1] was carried out in the hope that only the PCL blocks of the diblock copolymer would be included in the U-IC crystals, with the excluded PBD blocks serving as an amorphous matrix for the PCL block−U-IC crystals. We anticipated exclusion of the PBD blocks due to their content (12%) of 1,2-units with bulky $-CH{=}CH_2$ side chains. On the other hand, because PCL and poly(ethylene oxide) (PEO) homopolymers both form U-ICs,[2,3] we expected the PCL−PEO−PCL triblock copolymer to form a U-IC with the entire triblock copolymer included in the channels of the host urea lattice.

In this report we describe the formation of ICs formed between urea and PCL−PBD diblock and PCL−PEO−PCL triblock copolymers. Both block copolymer−U-ICs were characterized by observations with DSC and X-ray diffraction and ^{13}C NMR and FTIR spectroscopies. Much to our surprise we find the entire PCL−PBD diblock included in the U-IC whose structure differs from the usual hexagonal lattice with narrow channels (5.5 Å)[4,5] The PBD blocks seem to be included in an "expanded tetragonal" structure similar to those observed previously for the U-ICs formed with olgomeric PEO (PEG) and with polypropylene, both isotactic and syndiotactic.[6,7] Only the PCL blocks are included in the PCL−PEO−PCL−U-IC crystals which appear to be hexagonal with narrow channels like those including the PCL blocks in PCL−PBD−U-IC. In addition, a motional study of the block copolymer chains in their U-ICs was undertaken by observing ^{13}C NMR relaxations, which are compared to similar observations made on their bulk and constituent homopolymer−U-IC samples. The distinct and sometimes unique morphologies of these two block copolymer−U-ICs provide the impetus for observing the mobilities of the polymer chain segments in their constituent blocks.

Experimental Section

Materials. The PCL−PBD diblock and PCL−PEO−PCL triblock copolymers have been previously described[1,8,9] and are characterized by PCL, PBD block lengths of 47, 112 repeat units and PCL, PEO block lengths of 35, 140 repeat units, respectively. Formation of PCL−PBD−U-IC by cocrystallization from solution has been reported,[1] and a similar preparation was used to obtain the PCL−PEO−PCL−U-IC. A solution of PCL−PEO−PCL in acetone (0.5 g/100 mL) was added dropwise with continuous stirring and warming to 100 mL of methanol saturated with urea. The combined solution was slowly cooled to room temperature with stirring, followed by quiescent precipitation over a 12 h period. The resultant white precipitate was then filtered off and dried.

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DSC and X-ray Diffraction Measurements. Thermal characteristics of the bulk and U-IC block copolymer samples were determined with a Perkin-Elmer Model 7 differential scanning calorimeter (DSC). Samples of 5−10 mg were sealed in aluminum pans designed for volatile materials and scanned from 25 to 150 °C at a heating rate of 10 °C/min. Temperatures at the maximum peak heights were consistently taken as the melting temperatures. X-ray diffraction data were collected from powdered samples on a Scintag 2000 XDS in a wide-angle setup. Samples were mounted on a solid circular sample holder, and the proportional counter detector was set to collect data at a rate of $2\theta = 5°$/min over the range $2\theta = 0-50°$. Cu Kα X-ray radiation with a Ni-filtered wavelength of 1.54 Å was used, with voltage and current set at 45 kV and 40 mA, respectively.

FTIR Spectroscopy. Absorbance spectra were recorded from 400 to 4000 cm^{-1} on a Nicolet 510P FTIR spectrometer. Samples were thoroughly mixed with KBr and pressed into pellet form. Due to the hygroscopic nature of KBr, the sample cell was purged with dry, or desiccated, air. FTIR spectra were recorded under the following conditions: resolution = 2 cm^{-1}, gain = 1, and number of scans = 32.

NMR Spectroscopy. High-resolution ^{13}C NMR spectra were recorded using a Chemagnetics 200S NMR spectrometer at 50.1 MHz, under cross-polarization (CP), magic angle sample spinning (MAS), and high-power ^{1}H dipolar decoupling (DD). The optimum Hartmann−Hahn and magic angle conditions were obtained using the standard sample, *p*-di-*tert*-butylbenzene (PDTBB, 31.0 ppm vs TMS). The sample spinning speed ranged from 4 to 4.3 kHz. ^{1}H DD was applied during acquisition at 47 kHz. The spectral width was 15 kHz in 2K data points, which were zero-filled to 8K before Fourier transformation. The number of scans ranged from 500 to 2000. Spin−lattice relaxation times (T_1) were measured using the CP-T_1 exponential decay function[10] with 10−18 different τ values. Spin−lattice relaxation times in the rotating frame ($T_{1\rho}$) were measured by the conventional method.[11−13] The contact time used was in the range 0.5−2.0 ms depending on the nature of the samples, and a 3 s pulse delay was employed. T_1(^{13}C) measurements allow the study of motion in the mid-megahertz frequency range of fast molecular motions, while $T_{1\rho}$(^{13}C) techniques provide a way to investigate the slow motions in the low to mid-kilohertz range. $T_{1\rho}$(^{13}C) is site specific for each carbon nucleus, and because ^{13}C is a rare nucleus, spin diffusion between carbon nuclei is not important and does not average $T_{1\rho}$(^{13}C). Because of the heterogeneity of the dynamics in a polymer, there can be many different $T_{1\rho}$(^{13}C) in a sample. On the other hand, $T_{1\rho}$(^{1}H) detected through the carbon channel provides information about spatially sensitive proton spin diffusion, which can be utilized to query the phase-separated or homogeneous character of a sample. The T_1 and $T_{1\rho}$ values were obtained from semilogarithmic plots of ^{13}C resonance intensity in a spreadsheet program on a PC. Several single-pulse MAS/DD spectra were recorded to obtain quantitative peak intensities, where the delay between pulses was maintained at $5T_1$ of the slowest relaxing ^{13}C nucleus.[14]

Results and Discussion

Figure 1 presents the DSC scans observed for PCL−PBD−U-IC during the first and second heatings. The endotherm observed on the first heating is complex and is the result of the melting of free tetragonal urea (T_m = 136.5 °C) and the PCL−PBD−U-IC crystals (T_m = 140.5, 142.0 °C). This may be contrasted with the DSC scan reported previously for PCL−U-IC (2), where a clear separation of free urea (T_m = 134 °C) and PCL−U-IC (T_m = 142 °C) melting endotherms are observed. This comparison of PCL−PBD−U-IC and PCL−U-IC melting leads us to suggest that in the diblock copolymer−U-IC sample, three different crystals are present: (1) free urea with a T_m = 136.5 °C, (2) PBD block−U-IC with T_m = 140.5 °C, and (3) PCL block−U-IC with T_m = 142.0 °C.

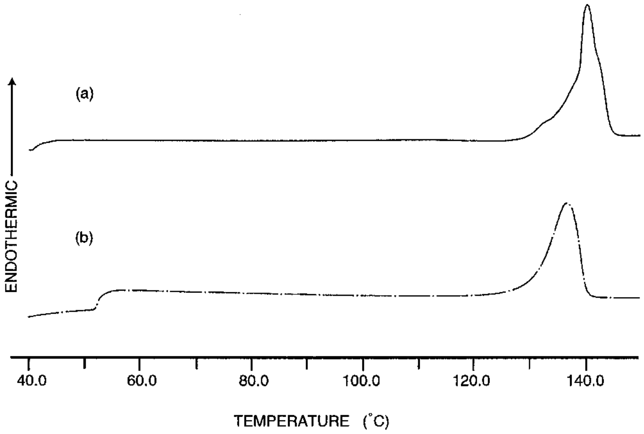


Figure 1. DSC scans observed for PCL−PBD−U-IC during the first (a) and second (b) heating at a rate of 10 °C/min.

During the second heating of the PCL−PBD−U-IC sample (Figure 1b) we only observe the melting of free tetragonal urea at 136.5 °C. From the known melting enthalpy of tetragonal urea (49.4 cal/g),[2] we can determine the total amount of urea in the PCL−PBD−U-IC sample, both IC and free urea. An estimate of the amount of IC urea contained in the PCL−PBD−U-IC can be obtained by subtracting the contribution made by free urea to the complex endotherm seen in the first heating of PCL−PBD−U-IC from the total heat observed in the second heating, which is now all free tetragonal urea originating from free and IC urea in our PCL−PBD−U-IC sample. This analysis leads to an estimate of 25/75 for the ratio of free/IC urea in our PCL−PBD−U-IC sample.

Subtracting the total amount of urea contained in our sample of PCL−PBD−U-IC from the total sample weight gives us a measure of the amount of PCL−PBD diblock in our sample. We are now able to estimate the ratio of urea/PCL−PBD contained in the PCL−PBD−U-IC crystals and find 2.35/1.0 (g/g). This stoichiometry is close to U/PCL = 2.1/1.0 (g/g) obtained previously[2] in a similar manner for PCL−U-IC. Because the molecular weights per backbone bond of PCL (16.3) and PCL−PBD diblock (15.3) are comparable, the similar stoichiometries found for PCL−U-IC and PCL−PBD−U-IC strongly suggest that both blocks of PCL−PBD are included in the urea channels of PCL−PBD−U-IC. When this is coupled to the appearance of two PCL−PBD−U-IC melting peaks observed during the first heat, we are led to conclude that the PCL and PBD blocks may be included in U-IC crystals with distinct structures.

Figure 2 presents the first and second heating scans of PCL−PEO−PCL−U-IC. Note the clear separation of free urea (T_m = 137.0 °C) and triblock−U-IC (T_m = 130.0 °C) melting endotherms. In the second heating scan an endotherm appears at 53.7 °C and is attributed to bulk crystalline PCL, because this is the melting temperature observed, but not shown here, for the second heating scan of the bulk PCL−PEO−PCL triblock sample. As discussed below, X-ray diffraction indicates no bulk crystalline PEO in either the bulk or U-IC triblock copolymer samples, so we tentatively attribute the endotherm at 53.7 °C to the melting of bulk crystalline PCL blocks. Remarkably, the endotherms corresponding to the melting of PCL−PEO−PCL−U-IC (126.5 °C) and free urea (134.1 °C) increase and decrease dramatically during the second heating, which suggests that our initial PCL−PEO−PCL−U-IC sample,

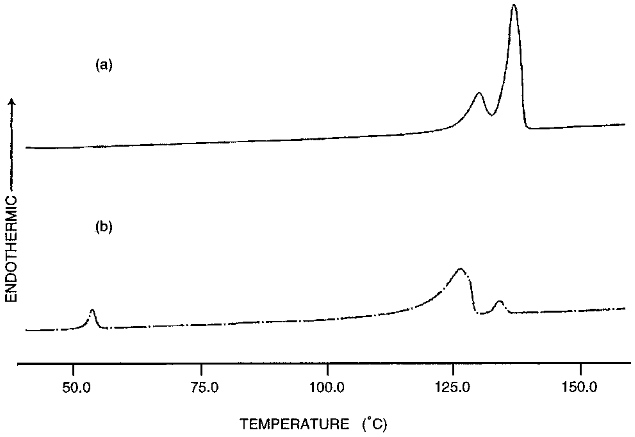


Figure 2. DSC scans observed for PCL−PEO−PCL−U-IC during the first (a) and second (b) heating at a rate of 10 °C/min.

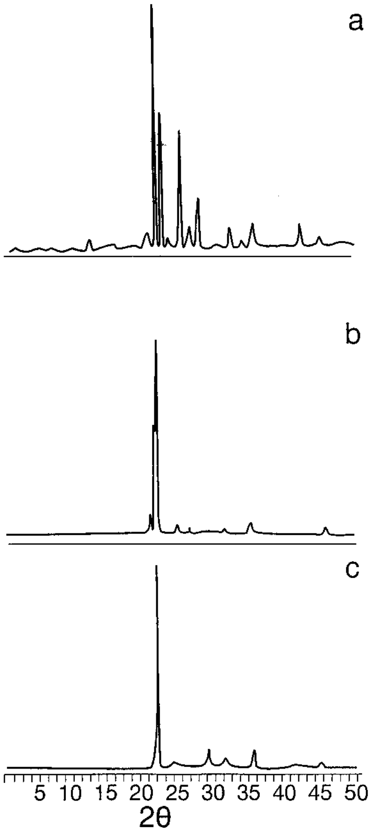


Figure 3. X-ray diffractograms of PCL−PBD−U-IC (a), PCL−PBD (b), and urea (c).

containing an excess of free urea compared with the triblock−U-IC, is converted upon melting and cooling to a sample where most of the urea has been used in the formation of PCL−PEO−PCL−U-IC crystals. In fact the melt crystallization of the triblock copolymer in the presence of molten urea may have led to the formation of a triblock−U-IC where both the PCL and PEO blocks are included in the crystalline IC channels. We are currently pursuing the structure of melt-formed PCL−PEO−PCL−U-IC crystals, but until this is complete we are unable to analyze the DSC scans of our PCL−PEO−PCL−U-IC for the purpose of estimating its stoichiometry.

We can, however, estimate that our PCL−PEO−PCL−U-IC sample (first heating scan) is roughly 80% uncomplexed amorphous, bulk triblock copolymer, 15% free urea, and 5% PCL−PEO−PCL−U-IC. This estimate of sample composition is based on the heats of fusion of PCL−U-IC (54 cal/g) and free urea (49.4 cal/g) obtained previously[2] in our study of the U-IC of PCL homopolymer. Also, the melting temperature of PCL−PEO−PCL−U-IC is ca. 10 deg lower than observed for PCL−U-IC. This is likely a result of the short PCL block lengths (35 repeat units) and the fact that at most two PCL blocks are included in the PCL−PEO−PCL−U-IC crystals, because the PEO blocks are excluded.[5]

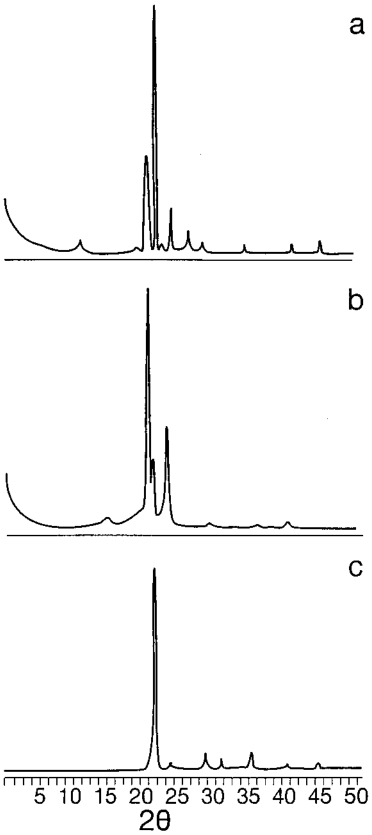


Figure 4. X-ray diffractograms of PCL−PEO−PCL−U-IC (a), PCL−PEO−PCL (b), and urea (c).

The X-ray diffractograms observed for PCL−PBD−U-IC, bulk PCL−PBD, and free tetragonal urea are presented in Figure 3, where their comparison clearly reveals that our sample of PCL−PBD−U-IC is not simply a mixture of free urea and bulk diblock copolymer but that a crystalline IC has been formed between the two. When the PCL−PBD−U-IC diffractogram is compared with those observed for PCL−U-IC[2] and polypropylene (PP)−U-IC,[7] it is evident that at least a portion of the PCL−PBD−U-IC has adopted the familiar hexagonal structure characterized by narrow (5.5 Å) inclusion channels.[4] The X-ray diffractograms of all known hexagonal polymer−U-ICs evidence a peak at $2\theta = 12.6°$, which can also be seen in the diffractogram observed for PCL−PBD−U-IC.

The X-ray diffractograms of PCL−PEO−PCL−U-IC, bulk PCL−PEO−PCL, and pure urea are presented in Figure 4 and provide direct evidence that the PCL−PEO−PCL−U-IC has been formed. Comparison of the diffractograms of PCL−U-IC, PCL−PEO−PCL−U-IC, PCL, and PCL−PEO−PCL also reveal that the triblock-U-IC likely adopts the narrow-channeled, hexagonal structure where only the terminal PCL blocks reside. Only diffraction peaks attributable to crystalline PCL blocks are evident[2] in the bulk triblock copolymer, and there are no PEO diffraction peaks visible in the PCL−PEO−PCL−U-IC diffractogram, so the excluded PEO

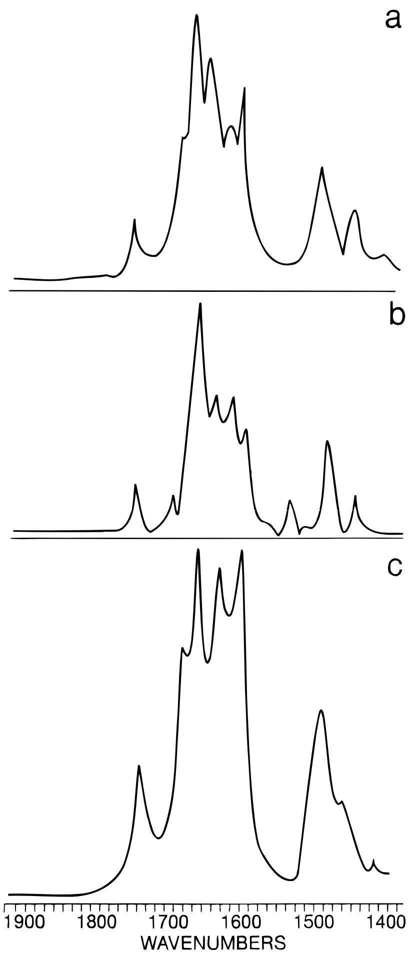


Figure 5. FTIR spectra of PCL−PBD−U-IC (a), PCL−PEO−PCL−U-IC (b), and PCL−U-IC (c).

blocks apparently do not crystallize in either the U-IC or bulk triblock copolymer samples.

The FTIR spectra of PCL−PCB−U-IC, PCL−PEO−PCL−U-IC, and PCL−U-IC are given in Figure 5. We have previously demonstrated that the stoichiometry of PCL−U-IC can be estimated via FTIR[15] by observing the ratio of intensities for the stretching vibrational bands of the carbonyl groups belonging to urea (1660 cm^{-1}) and PCL (1730 cm^{-1}) in the IC crystals. When the intensity ratio of these carbonyl bands are evaluated for PCL−PBD−U-IC and PCL−PEO−PCL−U-IC, we find 8.5/1.0 and 4.6/1.0 (mol/mol), respectively, for the U/PCL ratio, which can be compared to a value of U/PCL = 4.0 obtained for PCL−U-IC. Thus the FTIR spectra of the block copolymer−U-ICs are consistent with inclusion of both blocks of PCL−PBD and only the terminal PCL blocks of PCL−PEO−PCL in their ICs with urea.

We present quantitative, single-pulse MAS/DD ^{13}C NMR spectra for PCL−PBD−U-IC and PCL−PEO−PCL−U-IC in Figure 6. Integration of the carbonyl carbon peaks of U (163 ppm) and PCL (172 ppm) yields molar U/PCL ratios of 4.2/1.0 and 4.0/1.0 for the di- and triblock copolymer−U-ICs, respectively. This is the expected stoichiometry for PCL−PEO−PCL−U-IC, where only the terminal PCL blocks are included in a hexagonal IC with urea. However, because our DSC and FTIR observations are consistent with the incorporation of both PCL−PBD blocks into the U-IC, we expected the ratio of U/PCL carbonyl carbon intensities to be more like 8/1 and not the 4.2/1.0 ratio observed.

A possible explanation for the unexpected PCL−PBD−U-IC stoichiometry obtained by ^{13}C NMR is provided by our previous ^{13}C NMR observations of PEG− and PP−U-ICs.[7,16] Each of these homopolymer−U-ICs was suggested to adopt an "expanded tetragonal" structure with urea channels larger than 7 Å in diameter. We observed that the urea C═O resonance was nearly impossible to detect for both of these homopolymer−U-ICs, much as pure tetragonal urea is also transparent to our spectrometer when operated under the conditions outlined above.[17,18] If the urea forming the IC with the PBD blocks in PCL−PBD is also crystallizing in the "expanded tetragonal" structure, then we might also expect it to be transparent to solid state ^{13}C NMR. Thus roughly half of the urea in the PCL−PBD−U-IC would be transparent in the PBD-block-U-IC and the other half visible in the hexagonal PCL−block-U-IC portion of the PCL−PBD−U-IC sample, and the expected 8/1 U/PCL ratio would be reduced by 50% to 4/1, as is observed here by ^{13}C NMR.

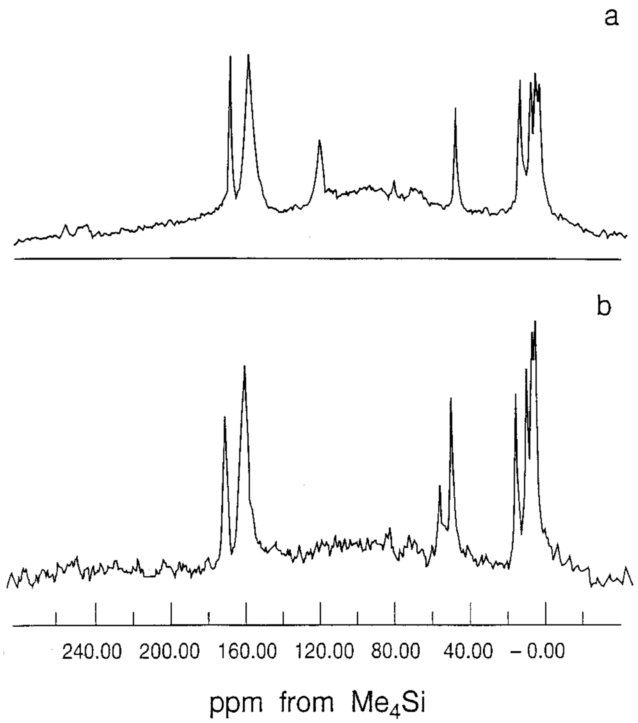


Figure 6. ^{13}C NMR MAS/DD, single pulse spectra for PCL−PBD−U-IC (a) and PCL−PEO−PCL−U-IC (b) measured with a delay time between pulses sufficiently long to give quantitative resonance intensities.[14]

Though our suggestion that the PCL−PBD−U-IC is a dimorphic crystal, with the PCL blocks forming a narrow channel, hexagonal structure and the PBD blocks, containing 12% 1,2-units with $-CH{=}CH_2$ side chains, forming an "expanded tetragonal" structure with wider channels, may seem unusual, a similar crystalline morphology has previously been reported for the IC formed with 1,3-butadiene (BD) and perhydrotriphenylene (PHTP) during its conversion by in situ polymerization to a *trans*-1,4-polybutadiene (TPBD)−PHTP-IC. Colombo and Allegra[19] observed a single crystal of BD−PHTP-IC by X-ray diffraction as BD was polymerized in the PHTP-IC channels to yield a single crystal of TPBD−PHTP-IC. It was clear from their observations that the transformation of BD−PHTP-IC to TPBD−PHTP-IC was a solid−solid, crystal−crystal transition that occurred without melting. The BD− and TPBD−PHTP-ICs are not isomorphous, so during the PHTP-IC polymerization of BD to TPBD, the distinct IC crystalline forms were part of the same single

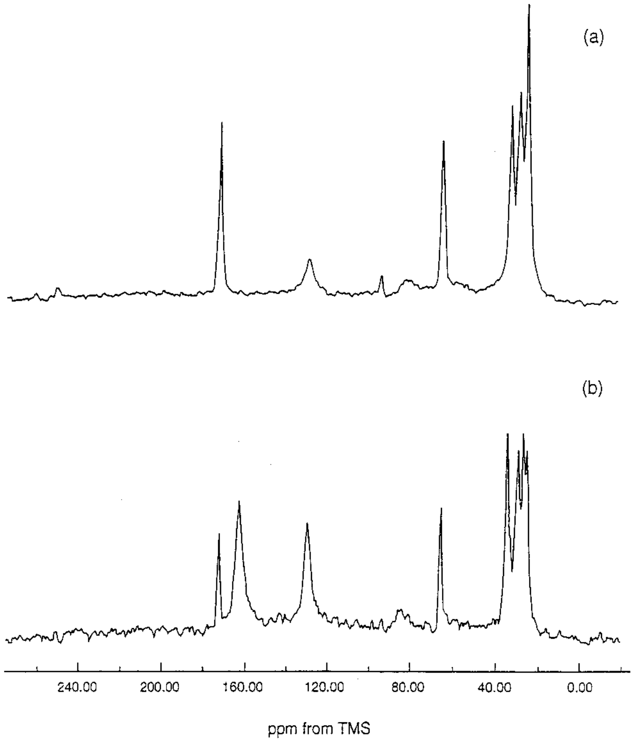


Figure 7. CPMAS/DD ^{13}C NMR spectra of PCL−PBD (a) and PCL−PBD−U-IC (b).

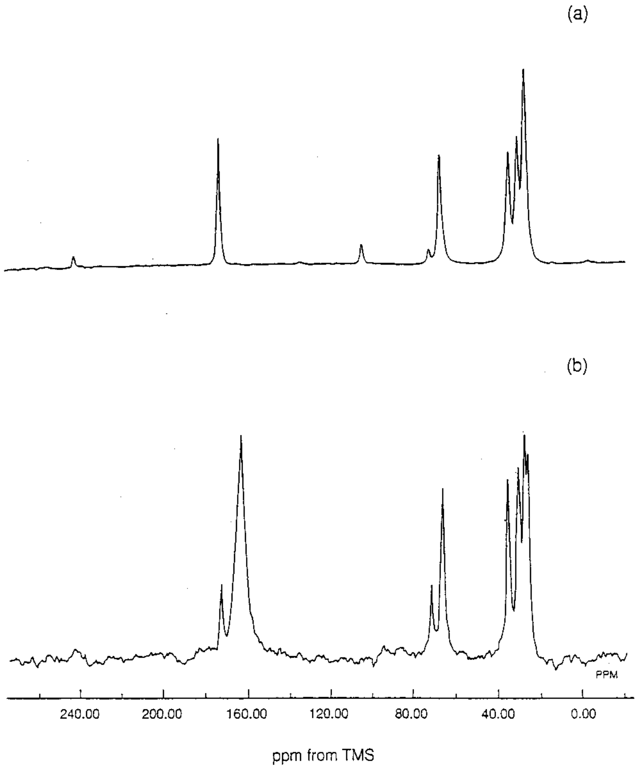


Figure 8. CPMAS/DD ^{13}C NMR spectra of PCL−PEO−PCL (a) and PCL−PEO−PCL−U-IC (b).

crystalline sample. It is not unlikely that a similar integral or connected dimorphism occurs in PCL−PBD−U-IC, because the occupants of the two distinct U-IC structures are chemically linked by the junction of PCL and PBD blocks.

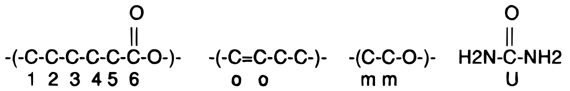
We can think of two ways of testing our suggested finding that both of the blocks in PCL−PBD are included in the U-IC crystals, although with different structures. The most unambiguous method would be to grow a large single crystal of PCL−PBD−U-IC and to employ a single-crystal X-ray diffraction analysis of the complete crystal structure. A second means to at least unambiguously determine whether or not the PBD blocks are included in the U-IC would rely on forming the U-IC with PCL−PBD(perdeutero), where the PBD block is completely deuterated. Observation of this sample by CPMAS/DD ^{13}C NMR would reflect an absence of resonances from the perdeuterated PBD only if the PBD blocks were excluded from the protonated urea channels and resided exclusively in phase-separated PBD domains where the PBD carbon nuclei could not be cross polarized with protons, because of their absence.

The CPMAS/DD ^{13}C NMR spectra of PCL−PBD and PCL−PEO−PCL bulk and U-IC samples are presented in Figures 7 and 8. The resonance frequencies of the carbon nuclei in the PCL, PBD, and PEO blocks are nearly independent of whether or not the block copolymers are included in the U-IC crystals or are phase-separated in their bulk samples. For the PCL blocks this implies that the U-IC included and bulk crystalline chains are adopting a nearly fully extended, all trans conformation in both structural environments, as was observed previously for bulk and U-IC included PCL homopolymer.[2,15] This is not an unexpected result, since the PCL blocks are included in the narrow channel, hexagonal structure in both the block copolymer and homopolymer U-ICs. Because the PEO blocks are not included in the urea channels of the PCL−PEO−PCL−U-IC, we expect the PEO CH_2 carbons to resonate at similar frequencies in both the U-IC and bulk block copolymer samples.

At first it may seem unexpected that the olefin carbons in the PBD blocks should resonate at nearly identical frequencies in both the bulk and U-IC samples. The olefin carbon chemical shifts are determined by the conformations adopted by the nearest, nonbonded $-CH_2-CH_2-$ and $=CH-CH_2-$ bonds, which prefer the trans and gauche(±) and cis and skew(±) conformations, respectively.[20−22] Surely the overall conformations of IC-included and bulk PBD are not the same, but rather the distribution of shielding $-CH_2-CH_2-$ gauche bond and $=CH-CH_2-$ cis bond conformations must be very similar to produce such a close correspondence in PBD olefin carbon resonance frequencies. This has already been observed to occur in PBD−PHTP-IC (PHTP = perhydrotriphenylene), where the CH and CH_2 resonance frequencies are quite close to those observed in bulk amorphous PBD.[23] In fact, when the conformations permitted to *trans*-1,4-PBD fragments confined to occupy cylinders of various diameters are compared to the unconstrained conformations,[24] the following results are noted: (i) for cylinder diameters <9 Å over 90% of the included conformations have trans $-CH_2-CH_2-$ bonds, compared with 47% of the unconstrained conformers, and (ii) for cylinder diameters <9 Å over 30% of the cylinder conformers have cis $=CH-CH_2-$bonds, while just 21% of the unconstrained PBD fragment conformers have cis $=CH-CH_2-$ bonds.

It is clear from the modeling of PBD fragment conformers constrained to occupy cylinders[24] that the channel conformers have more trans $-CH_2-CH_2-$ bonds and more cis $=CH-CH_2-$ bonds than unconstrained PBD. This shift in conformer populations between the unfettered and channel-included PBD chains is not manifested in distinct olefin carbon resonance frequencies, because the reduction in shield-

Table 1. Spin−Lattice Relaxation Times (T_1) Observed for the Carbon Nuclei in Bulk and U-IC Samples of PCL, PEO, PCL−PBD, and PCL−PEO−PCL



$$\underset{1\ 2\ 3\ 4\ 5\ 6}{\text{-(-C-C-C-C-C-}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{-O-)-}}\quad \underset{\text{o}\ \ \text{o}}{\text{-(-C=C-C-C-)-}}\quad \underset{\text{m m}}{\text{-(C-C-O-)-}}\quad \underset{\text{U}}{\text{H2N-}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{-NH2}}$$

$T_1(^{13}C)$, s

C	PCL	PCL−U-IC	PEO	PEO−U-IC	PCL−PBD	PCL−PBD−U-IC	PCL−PEO−PCL	PCL−PEO−PCL−U-IC
1	100	21			13	1.6	49	1.4
2	94	48			11.5	1.2	47	1.0
3	93	34, 16			16.1	1.1, 1.2	46	1.1, 1.3
4	93	16, 34			16.1	1.2, 1.1	46	1.3, 1.1
5	111	48			14	1.3	58	1.1
6	146	44			34	6.7	51	5.7
o					0.84	1.4		
m			8.2	4.2			0.2	1.8
		0.5						
U		16		35		6.1		6.3

ing produced by a 53% to 10% reduction in the shielding gauche conformations about $-CH_2-CH_2-$ bonds is balanced by the increase in shielding due to the 21% to 30% increase in shielding cis conformations about the $=CH-CH_2-$ bonds when PBD chains are taken from their amorphous bulk and included in the channels of their ICs formed either with urea or PHTP.

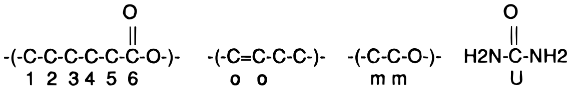
Table 1 presents the ^{13}C T_1, spin−lattice relaxation times, observed for the bulk and U-IC samples of PCL−PBD and PCL−PEO−PCL block copolymers. For comparison we have included the T_1's observed for the bulk and U-IC samples of the constituent PCL and PEO homopolymers, though the molecular weights of the homopolymers (PCL = 350 repeat units, PEO = 2300 repeat units) far exceed those of the copolymer block lengths (PCL = 35 and 47 repeat units, PEO = 140 repeat units). Because the T_1's observed for those carbon nuclei in the crystalline portions of a polymer sample have been shown to be sensitive to the thickness of crystalline lamellae,[25] we will not attempt a comparison of the T_1's observed for the homopolymers with those observed for the corresponding block in the copolymers. This behavior is illustrated by the significant differences between the CP-T_1's observed for the crystalline PCL carbons in the PCL homopolymer and block copolymer samples. Instead, we confine our discussion to a comparison of the T_1's observed on the bulk and U-IC samples of a given homopolymer or block copolymer.

In general the T_1's observed for PCL carbons in the channels of their ICs with urea are substantially reduced compared with their bulk samples irrespective of whether or not the PCL is the homopolymer or is in the phase-separated PCL−PBD and PCL−PEO−PCL block copolymers. The reduction in T_1 observed when removing a PCL chain from its cooperatively interacting, bulk crystalline environment to the isolated channel environment of its U-IC is smallest for PCl homopolymer (factor of 2−6) and largest for the PCL−PEO−PCL triblock copolymer (factor of 10−50). Since the PCL homopolymer and copolymer blocks are believed to form similar narrow channel, hexagonal U-ICs, we cannot attribute the nearly 10-fold greater reduction in the T_1's observed for U-IC versus bulk PCL blocks in PCL−PEO−PCL, compared to the reduction in T_1's observed for PCL−U-IC versus bulk PCL homopolymer, to different environmental constraints.

Instead, it would appear that the high-frequency (ca. 100 MHz) motions of the U-IC included PCL chains are dependent on the length and possibly number of PCL chains included in the U-IC. In the PCL−U-IC many PCL chains lying in an end-to-end fashion occupy each urea channel. However, in each of the block copolymer−U-ICs, at most only 2 PCL blocks arranged end-to-end can reside in each U-IC channel. This is obvious for PCL−PEO−PCL, where the PEO blocks are excluded from the U-IC channels, while for PCL−PBD with incommensurate U-IC structures for each block, the hexagonal U-IC portion of the crystals can also include no more than two PCL blocks. Just as the thickness of crystalline lamellae affects the spin−lattice relaxation times of bulk crystalline polymers, a similar dependence seems to occur for polymer chains confined to occupy the narrow, hexagonal channels of their ICs formed with urea. Taken together, it would appear that T_1 is monitoring nonlocalized motions of the PCL chains, in both the bulk and U-IC crystalline environments, and these megahertz frequency motions are possibly more sensitive to the length of the moving chain than to the immediate solid state environment in which these highly extended chains are moving. This latter suggestion can only be verified after PCL chains are included in a PCL-IC whose structure is different from the narrow channel, hexagonal structure assumed by PCL−U-IC. It is already clear, however, that localized segmental motions are not dominating the spin−lattice relaxation times of the carbon nuclei belonging to PCL chains included in the narrow channels of homopolymer and block copolymer PCL−U-IC crystals.

If we focus our attention on the spin−lattice relaxation times observed for the nonprotonated ester carbonyl carbon of PCL in these varied bulk and U-IC crystalline environments, then it is possible to suggest that the T_1's observed for PCL are not dominated by the motions of nearby, nonbonded protons belonging to either other surrounding PCL chains or urea in the bulk and U-IC samples, respectively. The T_1 observed for the PCL carbonyl carbon in PCL−U-IC is 6−7 times longer than those observed in the PCL block copolymer−U-ICs, despite the strong evidence that the PCL chains in all three U-ICs are included in the narrow channel, hexagonal U-IC matrix structure. In addition, the reduction in PCL carbonyl carbon T_1's observed upon removing the PCL chains from their bulk crystals and including them in their U-IC crystals is very comparable for PCL homopolymer and block copolymer samples. If the PCL carbonyl carbon spin−lattice relaxation times are not strongly influenced by the motions of surrounding, nonbonded protons, from either other PCL chains or the urea lattice, then the methylene carbon T_1's must be less affected by the motion of surrounding protons, because they have two directly bonded protons which are much closer.

Table 2. Spin−Lattice Relaxation Times Measured in the Rotating Frame ($T_{1\rho}$) for the Carbon Nuclei in Bulk and U-IC Samples of PCL, PEO, PCL−PBD, and PCL−PEO−PCL



$$\text{-(}\underset{1}{\text{-C}}\underset{2}{\text{-C}}\underset{3}{\text{-C}}\underset{4}{\text{-C}}\underset{5}{\text{-C}}\underset{6}{\text{-}\overset{\overset{\text{O}}{\|}}{\text{C}}}\text{-O-)-}\quad \text{-(-}\underset{\text{o}}{\text{C}}\text{=}\underset{\text{o}}{\text{C}}\text{-C-C-)-}\quad \text{-(-}\underset{\text{m}}{\text{C}}\text{-}\underset{\text{m}}{\text{C}}\text{-O-)-}\quad \underset{\text{U}}{\text{H2N-}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{-NH2}}$$

$T_{1\rho}$(^{13}C), ms

C	PCL	PCL−U-IC	PEO	PEO−U-IC	PCL−PBD	PCL−PBD−U-IC	PCL−PEO−PCL	PCL−PEO−PCL−U-IC
1	1.1	4.5			5.1	19.4	7.1	9.1
2	3.7	4.3			3.8	13.1	6.1	8.1
3	3.8	3.6, 4.6			3.4	13.1, 14.1	5.3	6.1, 6.5
4	3.8	4.6, 3.6			3.4	14.1, 13.1	5.3	6.5, 6.1
5	1.2	4.5			3.8	15.1	5.5	7.6
6	5.3	18.2			26.7	48.7	39.2	18.7
o					3.2	13.8		
m			2.2	4.0			10.2	10.3
U		4.1		7.8		11.2		8.7

The spin−lattice relaxation time for the olefin carbons of PBD increases from 0.84 to 1.4 s when the PBD chains are removed from their phase-separated morphology in bulk PCL−PBD and placed in the “expanded tetragonal” U-IC channels surrounding the PBD blocks in PCL−PBD−U-IC crystals. It is not surprising that rubbery, bulk PBD chains are experiencing more megahertz frequency motions than the extended PBD chains in the channels of PCL−PBD−U-IC.

It is well-known[26−29] that the spin−lattice relaxation time for the methylene carbons in crystalline PEO is relatively short (ca. 10 s). We observe a value of 8.8 s for the crystalline carbons and 0.5 s for the amorphous carbons in our bulk PEO sample, and in the trigonal PEO−U-IC channels the POE chains exhibit a $T_1 = 4.2$ s. When phase-separated in the bulk PCL−PEO−PCL triblock sample, the PEO chains show a $T_1 = 0.2$ s, which is consistent with the short $T_1 = 0.5$ s seen for the amorphous carbons in PEO homopolymer. As previously suggested, the phase-separated PEO chains must not crystallize in the bulk PCL−PEO−PCL triblock copolymer. Even though the central PEO blocks are excluded from the U-IC channels in PCL−PEO−PCL−U-IC, the observed PEO $T_1 = 1.8$ s is several times longer than $T_1 = 0.2$ s observed for PEO in bulk PCL−PEO−PCL, this despite a lack of PEO crystallinity in both bulk and U-IC samples of the triblock copolymer. Apparently, the constraints against megahertz motion occurring in the amorphous PEO domains are fewer in the bulk triblock copolymer sample than in the PCL−PEO−PCL−U-IC sample. This may be explained by realizing that PEO blocks in the bulk triblock sample may form loops and tie chains to the same and different PCL block crystallites, while in the U-IC sample the PEO blocks serve predominantly as tie chains, because of the manner in which the PCL block−U-IC is formed. Growth of the PCL block−U-IC crystals occurs in the PCL block chain direction, while in the bulk sample the crystallites grow in directions perpendicular to the PCL block chains. Apparently, when amorphous PEO blocks are tethered as tie chains between PCL block−U-IC crystals, their megahertz frequency motions are more effectively restricted than when they loop and are tethered at both ends by the same bulk PCL block crystallites. This suggests that the high-frequency motions experienced by PEO chains in the amorphous regions of their semicrystalline, bulk samples may depend upon the nature of the chains on the crystallite surface, i.e., folded versus tie chains or adjacent versus random reentry of folded chains, for example.

It is interesting to observe that the urea carbonyl carbon shows the same $T_1 = 6.1$, 6.3 s in both block copolymer U-IC crystals, even though roughly half of the urea in PCL−PBD−U-IC is crystallized around the PBD blocks in an “expanded tetragonal” structure, while the remaining urea forms hexagonal, narrow channel PCL block−U-IC crystals. By way of contrast, in the two homopolymer−U-ICs T_1’s = 16 (PCL) and 35 (PEO)s are observed. The PCL− and PEO−U-ICs adopt the hexagonal and trigonal structures, respectively, though both have similar channel diameters. Furthermore, in PEO−U-IC one-third of the urea is hydrogen-bonded directly to the PEO oxygen atoms[3] and therefore actually resides in the channel. A consistent interpretation of these observations can be constructed if it is assumed that the spin−lattice relaxation times of urea carbonyl carbons are influenced not only by the motions of their geminal amide protons but also by the motions of the hydrogen-bonded amide protons and possibly the motions of the protons belonging to the included polymer chains. Consequently, the shorter urea carbonyl T_1’s seen for the block copolymer−U-ICs compared with PCL−U-IC may be caused by the greater megahertz motion of the included blocks compared with the longer, included PCL homopolymer, even though all the PCL− and PCL block−U-ICs have the same structure. The distinctly different structure of PEO−U-IC (included urea, different hydrogen-bonding pattern, etc.) may lead to a $T_1 = 35$ s for its urea carbonyl carbon, which is more than twice that seen for PCL−U-IC, even though both urea lattices exhibit comparable channel diameters.

The C^{13} $T_{1\rho}$, spin−lattice relaxation times in the rotating frame, observed for the bulk and U-IC samples of PCL−PBD and PCL−PEO−PCL block polymers, are presented in Table 2, where we have included the $T_{1\rho}$(^{13}C) observed for the bulk and U-IC samples of the constituent PCL and PEO homopolymers as well. During the contact time between ^{13}C and ^{1}H spins (CP), T_{CH} dominates the buildup of ^{13}C magnetization, because T_{CH} = ca. 100 μs (see Figure 9), while $T_{1\rho}$(^{13}C) = ca. 10 ms, as seen in Table 2. However, after the contact time, with the proton field turned off, the decay of carbon magnetization under spin-locking conditions is determined by spin−lattice relaxation of carbon nuclei in the rotating frame [$T_{1\rho}$(^{13}C)], because the proton spin source dies off rapidly due to the absence of the spin-locking field (spin−spin relaxation usually occurs in the microsecond range).[30,31] Because the dipolar coupling between ^{13}C and ^{1}H nuclei is on the order of 10 kHz, $T_{1\rho}$(^{13}C) relaxation times are sensitive to motions in the same frequency range. Thus we may probe the slower and presumably larger amplitude motions occurring in polymers with $T_{1\rho}$(^{13}C), and these motions are believed[32]

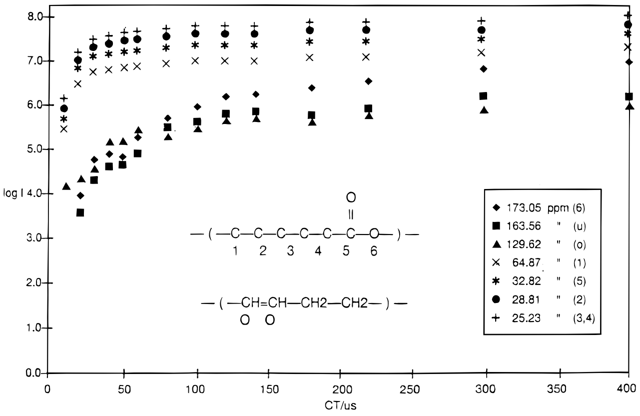


Figure 9. Estimation of T_{CH} from the variation in ^{13}C resonance intensity with contact time (CT) for PCL−PBD−U-IC.

to be more closely coupled with the mechanically active motions of polymers responding to applied strains than are the higher frequency (megahertz) motions probed by $T_1(^{13}C)$ relaxation measurements.

However, there is a well-known[13,33] complication to the use of $T_{1\rho}(^{13}C)$ to characterize the midkilohertz segmental motions of solid polymers. Static ^{1}H−^{13}C spin−spin interactions may shorten the observed $T_{1\rho}(^{13}C)$'s in samples whose carbon nuclei have tightly spin-coupled protons,[33] thereby complicating the interpretation of $T_{1\rho}(^{13}C)$ as a motional parameter. Because we have not performed the elaborate set of experiments necessary[33] to determine the relative contributions made by the static, nonmotional, ^{1}H−^{13}C spin−spin interactions to the observed $T_{1\rho}(^{13}C)$ relaxations, we will limit our discussion to qualitative comparisons of the $T_{1\rho}(^{13}C)$'s observed on the same homopolymers, block copolymers, and U-IC polymers, and refrain from comparing the rotating frame relaxations observed in different polymers.

As an example, if the static spin−spin contribution to $T_{1\rho}(^{13}C)$ was dominating the relaxation of carbon nuclei in the homopolymers and block copolymers in their U-IC crystals, then we would expect closely similar $T_{1\rho}(^{13}C)$ to be observed for the PCL carbons in PCL−U-IC, PCL−PBD−U-IC, and PCL−PEO−PCL−U-IC crystals, because the PCL chains are confined to occupy the narrow, hexagonal U-IC channels in all three samples. It is clear from Table 2 that this is not the case, so segmental motions in the midkilohertz range must be contributing significantly to their $T_{1\rho}(^{13}C)$ relaxations.

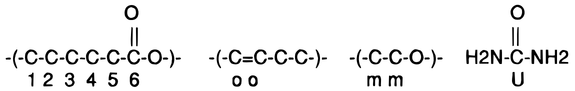
We begin a discussion of observed $T_{1\rho}(^{13}C)$ relaxation times by comparing the $T_{1\rho}(^{13}C)$'s for the PCL carbon nuclei in the homopolymer and block copolymer bulk and U-IC samples. The central methylene carbons (2, 3, and 4) evidence nearly identical $T_{1\rho}(^{13}C)$'s in both the bulk and U-IC samples of PCL, while the terminal methylene (1 and 5) and the carbonyl carbons in the PCL−U-IC sample have $T_{1\rho}(^{13}C)$'s several times longer than observed in the bulk PCL sample. This stands in marked contrast to the behavior of the spin−lattice relaxation times $T_1(^{13}C)$'s for the PCL carbons, which are all reduced by a factor of 2−6 in the U-IC crystals compared with bulk PCL crystals. In addition, very similar $T_1(^{13}C)$'s are observed for all methylene carbons in bulk PCL. The $T_{1\rho}(^{13}C)$'s observed for the PCL carbons in the phase-separated block copolymer samples are quite similar and are characterized by comparable values for all methylene carbons, which in turn are smaller by a factor of 5−6 than the $T_{1\rho}(^{13}C)$'s measured for the nonprotonated carbonyl carbons. In fact the $T_{1\rho}(^{13}C)$'s observed for the PCL carbons in the bulk copolymer samples are more similar to the values seen in PCL−U-IC than those observed in the bulk PCL homopolymer.

Except for the carbonyl carbon, the $T_{1\rho}(^{13}C)$'s observed in the PCL−PEO−PCL−U-IC are slightly longer (less than a factor of 2) than those seen in PCL−U-IC. In PCL−PBD−U-IC, however, $T_{1\rho}(^{13}C)$'s are observed to be uniformly a factor of 3−4 times longer than those of PCL−U-IC or of the phase-separated PCL chains in the bulk PCL−PBD sample. Except for the carbonyl carbons, $T_{1\rho}(^{13}C)$'s observed for the PCL chains in the bulk and U-IC samples of PCL−PEO−PCL are quite similar.

Unlike the longitudinal $T_1(^{13}C)$ relaxation times, which are dramatically shortened for the PCL carbons when the homopolymer or copolymer blocks are removed from their bulk phases and crystallized into U-ICs, the lower frequency motions dominating $T_{1\rho}(^{13}C)$ seem to be slightly to moderately hindered when the PCL chains are included in U-ICs. The largest $T_{1\rho}(^{13}C)$'s are exhibited for the PCL carbons in PCL−PBD−U-IC crystals. In PCL−PBD−U-IC the PCl chains in the narrow hexagonal U-IC channels are constrained by their attachment to PBD blocks, which are also IC-included, but likely in an “expanded tetragonal” structure.[6,7] On the other hand, the PCL chains in bulk and U-IC crystals in all of the other samples are covalently bonded to chains that are amorphous and mobile, whether or not they are the noncrystalline portions of bulk PCL or the phase-separated PBD and PEO blocks in PCL−PBD and PCL−PEO−PCL bulk and U-IC samples. Of course in PCL−U-IC the PCL chains are not covalently bonded on either end. The ca. 100 kHz motions occurring in crystalline bulk and U-IC PCL apparently are sensitive to the mobilities of the polymers to which they are attached. This is supported by the $T_{1\rho}(^{13}C)$'s observed for the olefin and methylene carbons in the PBD and PEO blocks which scale with the $T_{1\rho}(^{13}C)$'s observed for the PCL blocks to which they are attached. $T_{1\rho}(^{13}C)$ of the olefin carbons in PCL−PBD−U-IC (13.8 ms) is more than 4 times longer than that observed in the bulk, phase-separated PCL−PBD diblock copolymer (3.2 ms). This far exceeds the difference in $T_1(^{13}C)$'s observed for the olefin carbons in U-IC (1.4 s) and bulk (0.84 s) samples of PCL−PBD and provides more compelling evidence that the PBD blocks are also included in the U-IC matrix channels of PCL−PBD−U-IC. Apparently, the higher frequency motions (megahertz) reflected in $T_1(^{13}C)$ are not hindered as much by the restrictive environment found in the PCL−PBD−U-IC channels as the lower frequency (10−100 kHz), higher amplitude motions of chain segments which dominate $T_{1\rho}(^{13}C)$. By elimination, the cooperative motions of PBD chains in phase-separated domains well above T_g, as found in the bulk PCL−PBD diblock copolymer, place less of a restriction on the $T_{1\rho}(^{13}C)$, kilohertz motions than does the geometric constraint of the channels created by the U-IC matrix. This may imply that center of mass translational motions of chain segments might contribute significantly to $T_{1\rho}(^{13}C)$ relaxation, because they are possible in the bulk above T_g but are prevented in the U-IC channels, though in both environments rapid conformational interconversions are known to occur.[21−24]

The $T_{1\rho}(^{13}C)$'s observed for the PEO chains in bulk and U-IC samples of PCL−PEO−PCL are identical and serve to confirm the exclusion of PEO blocks from the

Table 3. ^{13}C-Observed $T_{1\rho}(^1H)$ for the Carbon Nuclei in the Bulk and U-IC Samples of PCL, PEO, PCL−PBD, and PCL−PEO−PCL



$$\underset{1\,2\,3\,4\,5\,6}{\text{-(-C-C-C-C-C-}\overset{\overset{\displaystyle O}{||}}{\text{C}}\text{-O-)-}}\quad \underset{o\,o}{\text{-(-C=C-C-C-)-}}\quad \underset{m\,m}{\text{-(-C-C-O-)-}}\quad \underset{U}{\text{H2N-}\overset{\overset{\displaystyle O}{||}}{\text{C}}\text{-NH2}}$$

$T_{1\rho}(^1H)$, ms

C	PCL	PCL−U-IC	PEO	PEO−U-IC	PCL−PBD	PCL−PBD−U-IC	PCL−PEO−PCL	PCL−PEO−PCL−U-IC
1	20	0.6			16.2	0.8	28	0.7
2	18	0.6			12.1	1.0	25	0.7
3	18	0.5			13.6	0.9	24	0.7
4	18	0.5			13.6	0.9	24	0.7
5	18	0.5			12.9	0.9	26	0.7
6	21	0.4			16.3	0.7	28	0.7
o					1.4	1.2		
m			0.5	0.4			11	1.2
u		0.31	4.4	0.35		0.73		0.67

PCL−PEO−PCL−U-IC crystals and the amorphous character of the PEO chains in both triblock copolymer samples. $T_{1\rho}(^{13}C) = 2.2$ and 4.0 ms for bulk PEO homopolymer and trigonal PEO−U-IC crystals, respectively, which are about 20−50% of the values observed in the corresponding PCL−PEO−PCL triblock samples (10.2−10.3 ms). Inclusion of the PEO homopolymer into U-IC crystals increases $T_{1\rho}(^{13}C)$ by a factor of 2, which is smaller than the factor of 4−5 increase observed for the PBD blocks in the PCL−PBD diblock when they are included in the U-IC crystals.

Comparison of the $T_1(^{13}C)$'s and $T_{1\rho}(^{13}C)$'s observed for PCL and PEO chain carbons in their bulk and U-IC crystals reveals opposing dependencies on their solid state environments. $T_1(^{13}C)$'s are dramatically reduced and $T_{1\rho}(^{13}C)$'s increase as we remove each of these polymer chains from their bulk crystals and include them in the narrow channels of their ICs with urea. The high-frequency megahertz motions effective in $T_1(^{13}C)$ relaxation are apparently more facile in the U-IC channels than in the bulk polymer crystallites, while the lower frequency kilohertz motions monitored by $T_{1\rho}(^{13}C)$ are retarded in the U-IC channels compared to the bulk crystalline environment. The high-frequency, low-amplitude, nonlocalized motions characteristic of $T_1(^{13}C)$ relaxation are apparently more sensitive to cooperative polymer−polymer interactions found in bulk polymer crystals, which are somewhat relieved in the U-IC channels where the urea lattice channel walls do not interact strongly with the included polymer chains except to serve as a geometric constraint upon their mobilities. The lower frequency, larger amplitude, more localized motions effective in $T_{1\rho}(^{13}C)$ relaxation apparently benefit from the cooperativity possible in the bulk polymer crystallite, at least on a localized scale, which is absent in the geometrically rigid U-IC channels.

This behavior is consistent with the molecular factors responsible for the stabilities of bulk and U-IC polymer crystals. In polymer crystallites the close packing and specific intermolecular interactions between neighboring polymer chains dominate their stabilities, while in polymer−U-ICs the packing and hydrogen-bonding in the host urea lattice dominate. As a consequence, the melting temperatures of bulk polymer crystals are very dependent on their detailed molecular microstructures, but polymer−U-ICs generally melt a few degrees above the T_m of bulk tetragonal urea[1,2,7,15−18,34,35] independent of the chemical and microstructural nature of the included polymers. Anything that disturbs the U-IC lattice structure, like the more localized, larger amplitude, lower frequency motions characteristic of $T_{1\rho}(^{13}C)$ relaxation, would be more strongly prohibited than similar motions in a bulk polymer crystallite. At the same time, the less localized, lower amplitude, higher frequency $T_1(^{13}C)$ motions might meet a lower resistance in U-IC channels than in bulk polymer crystals, because the degree of motional cooperativity there is extended in the case of $T_1(^{13}C)$ motions but the rigid U-IC channel environment does not place cooperative constraints on these high megahertz frequency motions. The larger amplitude, lower frequency, more localized $T_{1\rho}(^{13}C)$ motions, on the other hand, might benefit from the local cooperativity available in bulk crystals without melting and which is not possible in the rigid channel environment available to polymer chains in their U-IC crystals.

Judging from the $T_{1\rho}(^{13}C)$'s observed for the urea carbonyl carbons in the U-IC's formed with PCL (4.1 ms), PEO (7.8 ms), PCL−PBD (11.2 ms), and PCL−PEO−PCL (8.7 ms), the 10−100 kHz motions of urea are not very sensitive to either the structure of the U-IC crystals (hexagonal, trigonal, or "expanded tetragonal") or the mobilities of the included polymer chains. This contrasts with the $T_1(^{13}C)$'s observed for the urea carbonyl carbons in the homopolymer and block copolymer−U-IC crystals, which show a much greater sensitivity to the IC structure and also a dependence on the mobility of the included polymer chain. The higher frequency (megahertz) motions of the urea carbonyls are evidently sensitive to the structure of the hydrogen-bonded U-IC structures and the motions of the included polymers, while the larger amplitude, lower frequency (kilohertz) motions are almost independent of their microenvironment.

That the $T_{1\rho}(^1H)$'s measured by observing the decay of ^{13}C signal intensities are dominated by facile diffusion of ^1H spins is confirmed by the nearly identical values observed for the protonated methylene and nonprotonated carbons in each bulk and U-IC sample containing PCL chains. The results presented in Table 3 also demonstrate only a moderate dependence of $T_{1\rho}(^1H)$'s for PCL carbons on the morphologies of bulk homopolymer and block copolymer samples. However, ^1H spin diffusion is dramatically enhanced for PCL chains residing inside the channels of the U-IC crystals, as evidenced by a 10−40-fold decrease in the $T_{1\rho}(^1H)$'s observed for PCL carbons in the homopolymer and block copolymer−U-ICs. It is also significant to note that the $T_{1\rho}(^1H)$'s observed for the included PCL carbons and the urea carbonyl carbons of the U-IC matrix are closely similar, suggesting that the diffusion of abundant urea matrix proton spins is dominating the $T_{1\rho}(^1H)$ relaxations observed for the carbons of the PCL chains included in the U-IC crystals. We hope to form PCL−Ud-4-IC using perdeuterated urea (Ud-4) to test this suggestion and to learn what effects removal of urea channel protons might have on the $T_1(^{13}C)$ and $T_{1\rho}(^{13}C)$ relaxation times for the carbon nuclei of the included PCL chains.

The $T_{1\rho}(^1H)$'s observed for bulk and U-IC crystalline PEO carbons are similar, though both are reduced from the $T_{1\rho}(^1H)$ observed for bulk, amorphous PEO. PEO blocks in the phase-separated PCL−PEO−PCL triblock show $T_{1\rho}(^1H)$ ca. 10 times longer than the PEO blocks that are excluded from the PCL−PEO−PCL−U-IC crystals. The distinct $T_{1\rho}(^1H)$'s observed for the PCL and PEO chains in both the bulk and U-IC samples of the PCL−PEO−PCL triblock confirm the phase-separated morphologies for both.

The fact that similar $T_{1\rho}(^{13}C)$'s are observed for the PEO carbons in both bulk and U-IC triblock samples, despite having very dissimilar $T_{1\rho}(^1H)$'s, indicates that their morphological differences are not affecting PEO motions in the 10−100 kHz range but do influence the diffusion of PEO proton spins. Thus, the similar $T_{1\rho}(^{13}C)$'s observed for the phase-separated PEO chains in the bulk and U-IC triblock samples are not a result of averaging by proton spin diffusion but rather may be attributed to similar mobilities of the PEO chains in the 10−100 kHz frequency range. On the other hand, the disparate $T_{1\rho}(^1H)$'s observed for PEO carbons in the bulk and U-IC triblock copolymer samples is a consequence of different ^1H spin diffusion in phase-separated, PEO domains of the two PCL−PEO−PCL triblock samples.

If we assume the usual dependence of domain size L on $T_{1\rho}(^1H)$,[36−38] $L^2 = 6DT_{1\rho}(^1H)$, where D is the spin diffusion coefficient $= 10^4$ Å^2/s, then the ratio of $T_{1\rho}(^1H)$'s observed for PEO in the bulk and U-IC samples, 11/1.2, leads to an estimate of relative domain sizes of $(11/1.2)^{1/2} = 3$. The PEO domains in the bulk triblock sample are $L = [6(10^4\ \text{Å}^2/\text{s})(0.011\ \text{s})]^{1/2} = 26$ Å, while those in the PCL−PEO−PCL−U-IC sample are estimated as $L = [6(10^4\ \text{Å}^2/\text{s})(0.0012\ \text{s})]^{1/2} = 8.5$ Å, so the average volume of a PEO domain in the bulk sample is ca. 30 times that in the U-IC sample of the PCL−PEO−PCL triblock copolymer. If $T_{1\rho}(^1H) = 0.7$ ms, the relaxation time observed for the diffusion of PCL proton spins in PCL−PEO−PCL−U-IC is used to estimate the PCL domain size in the triblock−U-IC, then $L = 6.5$ Å is obtained. Each PCL block included in the channels of PCL−PEO−PCL−U-IC extends ca. (35 repeat units) × (7 bonds/repeat unit) × (1.22 Å/bond) = 300 Å (1). Thus, the diffusion of urea matrix proton spins perpendicular to the IC channel must dominate the $T_{1\rho}(^1H)$'s observed for PCL carbons in PCL−PEO−PCL−U-IC. Diffusion of urea proton spins across the U-IC channels must also dominate the $T_{1\rho}(^1H)$'s observed for PCL−U-IC and PCL−PBD−U-IC, because in all three U-ICs the PCL carbons exhibit $T_{1\rho}(^1H)$'s = 0.4−1.0 ms, which lead to $L = 4.9$−7.7 Å and approximate the U-IC channel diameter = 5.5 Å.[4]

The $T_{1\rho}(^1H)$'s observed for the phase-separated PCL domains in the bulk di- and triblock copolymer samples (12.1−16.3 and 24−28 ms, respectively) bracket the values observed in the PCL homopolymer (18−21 ms), implying that the PCL domains in the phase-separated block copolymer samples are slightly smaller (diblock) and slightly larger (triblock) than the crystalline regions in the bulk PCL homopolymer sample. In PCL−PBD domain sizes $L = 10$ and 30 Å are estimated for the phase-separated PBD and PCL domains, respectively, while for the bulk PCL−PEO−PCL triblock sample $L = 26$ and 40 Å are obtained for the PEO and PCL domain sizes. The $T_{1\rho}(^1H)$'s observed for the PBD olefin carbons in the bulk (1.4 ms) and U-IC (1.2 ms) samples of PCL−PBD are very comparable, unlike the large difference between $T_{1\rho}(^1H)$'s observed for the PCL carbon nuclei in bulk and U-IC samples. $T_{1\rho}(^1H) = 1.2$ ms corresponds to a domain size $L = 8.2$ Å for PBD chains included in PCL−PBD−U-IC, which is close to the 9.2 Å found for the PBD domains in the bulk PCL−PBD. For the PBD blocks we cannot conclude that $T_{1\rho}(^1H)$ observed in the PCL−PBD−U-IC channels is dominated by diffusion of the urea channel proton spins, as we did for the included PCL chains, because of the small size (9.2 Å) found for the PBD domains in bulk PCL−PBD.

Formation of PCL−PBD−Ud-4-IC would surround both included PCL and PBD blocks with a ca. 7 Å proton-free barrier[4] separating them from the protons belonging to the PCL and PBD blocks in nearest neighbor Ud-4-IC channels. As a consequence, proton spin diffusion would be forced to occur within each IC channel among the proton spins belonging to the included polymer block. This should correspond closely to 1-dimensional spin diffusion, where the domain size is given by[38] $L^2 = 2DT_{1\rho}(H)$. Since the PCL blocks are 47 repeat units in length and the PBD blocks 112 repeat units long, they would be expected to extend ca. 400 and 500 Å, respectively, down the Ud-4-IC channels. These 1-dimensional domain sizes correspond to $T_{1\rho}(^1H)$'s = 8 and 12.5 s for the PCL and PBD blocks. This means that the $T_{1\rho}(H)$'s measured by observing the decays of ^{13}C resonance intensities would not be averaged by proton spin diffusion in 1-dimension between included polymer blocks. We would therefore be able to compare these 1-D $T_{1\rho}(^1H)$'s with the 3-D $T_{1\rho}(1H)$'s observed for the U-ICs formed with fully protonated urea, as presented in Table 3.

In addition, the $T_{1\rho}(^1H)$'s observed for the urea carbonyl carbons in PCL− or PCL−PBD−Ud-4-ICs should be dominated by the diffusion of PCL or PBD proton spins across the IC channel. Since the distances between urea carbonyl carbons and the protons of the polymers in the IC channel are very short (ca. 1−2 Å), $T_{1\rho}(^1H) = [(1-2\ \text{Å}^2)/(2 \times 10^4\ \text{Å}^2/\text{s})] = 0.05-0.2$ ms should be observed for the carbonyl carbons of Ud-4, and this may permit a verification of the spin diffusion coefficient D, which is usually assumed to be 10^4 Å^2/s.[35]

We close our discussion concerning the effects of various solid state environments on the mobilities of polymer chains, as monitored by several ^{13}C NMR relaxation times, by summarizing the principal conclusions reached through comparison of the relaxation behavior observed in bulk and U-IC homopolymer and block copolymer samples. The spin−lattice relaxation times $T_1(^{13}C)$, which monitor the high-frequency (megahertz) motion of carbon nuclei, seem to depend on nonlocalized polymer chain motions in both bulk and U-IC crystalline environments. These motions seem to be more sensitive to the lengths of the moving chains than to the immediate solid state environment in which they move. $T_1(^{13}C)$'s are not therefore monitoring the localized segmental motions of polymers in their bulk or U-IC crystals. Motions of nearby, nonbonded protons belonging to surrounding polymer chains or to urea in bulk and U-IC crystals are not contributing significantly to the spin−lattice relaxation of carbon nuclear magnetization. Though the PEO blocks in both bulk and U-IC samples of PCL−PEO−PCL are phase-separated and amorphous, their spin−lattice relaxation times differ by 1 order of magnitude, with the bulk sample having the shorter $T_1(^{13}C)$. This observation may be a result of the different modes of PEO chain tethering in these two samples. In bulk PCL−PEO−PCL the PEO blocks are tethered on both ends to PCL blocks which may be part of the same or different PCL crystallites. In the former case this would lead to PEO loops and in the latter case PEO tie chains. In PCL−PEO−PCL−U-IC the PEO blocks are much less likely to form loops during the formation of the PCL block−U-IC crystals. Because the $T_1(^{13}C)$ observed for PEO in the bulk sample is much shorter than seen in the U-IC sample, high-frequency (megahertz) motion of amorphous PEO chains is apparently sensitive to their mode of tethering to the PCL block crystals, with PEO loops being more mobile than PEO tie chains.

The lower frequency (kilohertz) motions effective in $T_{1\rho}(^{13}C)$ relaxation of PCL carbon nuclei in bulk and U-IC crystals are sensitive to the mobilities of the polymers to which they are attached. Cooperative motions of PBD chains in phase-separated domains well above T_g, as found in the PCL−PBD diblock copolymer, place less of a restriction on $T_{1\rho}(^{13}C)$, kilohertz motion than does the geometric constraint of the channels created by the U-IC matrix. This may indicate that center of mass translations of chain segments might contribute to $T_{1\rho}(^{13}C)$ relaxation, because they are possible in the bulk above T_g, but are prevented in the U-IC channels.

Unlike the high-frequency (megahertz) motions probed by $T_1(^{13}C)$, the low-frequency (kilohertz) motions effective in $T_{1\rho}(^{13}C)$ relaxation of urea carbon magnetization are not very sensitive to either the structure of the U-IC crystals (hexagonal, trigonal, or “expanded teragonal”) or to the mobilities of the included polymer chains.

$T_{1\rho}(^1H)$'s observed for U-IC included polymer chains are dominated by the diffusion of abundant urea matrix proton spins. Formation of polymer−Ud-4-ICs will remove the effect of urea proton spins and will also enable an assessment of their importance to $T_1(^{13}C)$ and $T_{1\rho}(^{13}C)$ relaxations of carbon nuclei belonging to polymer chains residing in the narrow channels of their U-ICs. The diffusion of proton spins in amorphous PEO phases is influenced by the morphology of the sample. Just as the $T_1(^{13}C)$'s observed for amorphous PEO carbons in bulk and U-IC samples differ, so do the $T_{1\rho}(^1H)$'s. While the high-frequency (megahertz) motions and the diffusion of proton spins in amorphous PEO phases are affected by their morphology, the lower frequency (kilohertz) motions are not, because identical $T_{1\rho}(^{13}C)$'s are observed for bulk and U-IC samples of the PCL−PEO−PCL triblock, and their coincidence is not the result of averaging by proton spin diffusion. The disparate $T_{1\rho}(^1H)$'s observed for PEO carbons in the bulk and U-IC triblock samples are attributed to different rates of ^1H spin diffusion in their phase-separated domains of ca. 26 and 8.5 Å in size, respectively.

PCL domain sizes of 30 and 40 Å are estimated from the $T_{1\rho}(^1H)$'s observed in the bulk PCL−PBD diblock and PCL−PEO−PCL triblock samples, respectively. At the same time the $T_{1\rho}(^1H)$ observed for PBD in the bulk diblock copolymer yields a PBD domain size estimate of 10 Å.

The $T_{1\rho}(^1H)$'s observed for the urea carbonyl carbons all fall in the range 0.31−0.73 ms, independent of U-IC structure or the nature of the included polymer. Clearly diffusion of urea proton spins is dominating the $T_{1\rho}(^1H)$ of the urea carbonyl carbons, and it is likely that the four geminally bonded protons are making the major contribution to $T_{1\rho}(^1H)$ relaxation.

Formation of PCL−PBD−Ud-4-IC would produce a nonprotonated U-IC channel for each of the PCL and PBD included blocks. The Ud-4 matrix would separate the PCL−PBD chains residing in nearest neighbor channels by a ca. 7 Å proton-free barrier, thereby assuring a 1-dimensional diffusion of proton spins along each included diblock copolymer. Because the lengths of the included and extended PCL and PBD blocks are in the range 400−500 Å, the $T_{1\rho}(^1H)$'s observed for the carbon nuclei in each block would be distinct and not averaged by ^1H spin diffusion, because $T_{1\rho}(H)$'s > 10 s would be required for averaging by ^1H spin diffusion. Comparison of the 1-dimensional $T_{1\rho}(^1H)$'s measured for the diblock copolymer−Ud-4-IC with the 3-dimensional $T_{1\rho}(^1H)$'s observed in the U-IC samples of Table 3, would permit a separation of the effects of “across the channel” diffusion of urea proton spins and “down the channel” diffusion of proton spins along the included polymer blocks. This separation of proton spin diffusion might even permit an estimate of the spin diffusion coefficient D (usually taken as 10^4 Å^2/s) to be derived independently from the 1- and 3-dimensional $T_{1\rho}(^1H)$'s, based on the distances between protons on included polymers and between urea and included polymer protons, which can be estimated from the U-IC structure.[4]

Finally, it was observed that each of the ^{13}C NMR relaxation measurements, $T_1(^{13}C)$, $T_{1\rho}(^{13}C)$, and $T_{1\rho}(^1H)$, yielded results which confirmed the structures of both block copolymer−U-ICs. Both PCL and PBD blocks are included in the PCL−PBD−U-IC, but the structures of PCL block−U-IC and PBD block−U-IC are distinct. For PCL−PEO−PCL−U-IC, only the PCL blocks are included, and the excluded central PEO blocks do not form bulk crystals. We hope that this paper serves to illustrate the utility of the formation and the observation of polymer−U-ICs to learn more about the detailed connections between a polymer's solid state environment and its behavior.

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