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NMR Observation of the Conformations and Motions of Polymers Confined to the Narrow Channels of Their Inclusion Compounds

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Abstract

When polymers are guests in crystalline inclusion compounds (ICs) formed with small-molecule hosts, they occupy a unique environment. In a cocrystallization process the small-molecule host forms a crystalline lattice containing long narrow channels where the guest polymer chains are included. Because of the narrow channel diameter and because neighboring channels are separated by walls formed exclusively from the small-molecule host lattice, the included polymer chains are highly extended and separated from polymer chains in other IC channels. As a consequence, polymer-IC crystals provide a unique solid state environment for the included polymer chains and serve as models useful for assessing the contributions made by the inherent behavior of individual polymer chains to the properties of ordered, bulk polymers, which can be obscured by pervasive interactions between their tightly packed polymer chains. In this paper we describe the conformations and motions of polymer chains confined to the narrow channels of the following polymer-ICs: i. polyethylene and trans-1, 4-polybutadiene in their ICs with perhydrotriphenylene, ii. poly-epsilon caprolactone and its diblock and triblock copolymers with polybutadiene and poly (ethylene oxide) in their ICs with urea, and iii. nylon-6 in its ICs with alpha-, beta-, and gamma-cyclodextrins. High resolution, solid state NMR serves as both the conformational (C-13 chemical shifts) and motional (relaxation times and line shapes) probe. Comparison with identical NMR measurements performed on the bulk homo- and copolymer samples permits us to draw several conclusions regarding the relationships between the conformations and motions of polymers and their dependence on their ordered solid state environments.

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Introduction

The long-chain nature of polymers, coupled with their ability to adopt an almost inexhaustable variety of different conformations, permits them to adjust their sizes and shapes in response to both external stresses and internal (intrachain) interactions. It is this additional internal degree of freedom that confers upon polymers many of their unique physical properties. In disordered bulk polymers (melts and glasses) each polymer chain is in contact with or influences many (ca. 100) neighboring polymer chains, solely because of their large sizes and pervasive, randomly coiling shapes. By comparison, the number of neighboring polymer chains influenced by any given polymer chain in bulk ordered samples (semi- and liquid- crystalline) is much reduced as a consequence of the highly extended polymer chain conformations adopted there. Although fewer in number, the interactions between polymer chains in bulk, ordered samples are stronger, more intimate and extend over longer portions of their chain contours.

Understanding the physical properties of bulk polymer systems requires two distinct types of information: first, the inherent or intrinsic characteristics (conformations and mobilities) of individual polymer chains, which depend solely on intramolecular or intrachain interactions, and second, the effects of cooperative interactions between polymer chains. Observation of isolated polymer chains in dilute solutions at the θ temperature[1], where the chains are free from both excluded volume self-intersections and cooperative interchain interactions, provides the means to secure a useful description[2] of the inherent intramolecular behavior of disordered polymer chains. Comparison with the behavior of molten polymers, for example, can provide some measure of the nature of cooperative, interchain interactions occurring in disordered, bulk polymers.

We have no dilute solution analog for the conformationally, orientationally, and/or positionally ordered polymer chains found in liquid-crystalline and crystalline polymer samples. How, then, might we attempt to understand the properties of ordered, bulk polymers? We believe that certain inclusion compounds (ICs) formed between small-molecule hosts and guest polymers can serve as solid state analogs/model systems/touchstones useful for separating the inherent, single-chain behavior from the cooperative interchain interactions occurring in ordered, bulk polymer phases.

Certain small molecules, such as urea (U), perhydrotriphenylene (PHTP), and the cyclodextrins (CD), are able to form crystalline ICs with polymers[3–8] via a cocrystallization process. The guest polymer chains in these ICs are included in and confined to occupy narrow channels provided by the crystalline matrix formed by the small-molecule host. Three such polymer-ICs are illustrated in Figures 1 and 2 and are based on x-ray diffraction analyses[9–11] performed on single crystals of n- hexadecane-U-IC, trans-1, 4-polybutadiene-PHTP-IC, and oligomeric poly (ethylene oxide)-alpha-CD-IC.

The channels occupied by the included polymer chains are nearly cylindrical and fairly narrow with channel diameters D in the range 4.8 – 5.5Å. In addition, each included polymer chain is separated, and therefore decoupled, from all neighboring chains by the walls of the IC channels, which are constructed exclusively of the host matrix molecules. Polymer chains included in the narrow channels of their ICs with U, PHTP, and CD are clearly both highly extended[12] and isolated from neighboring polymer chains. It is precisely these two features of polymer-ICs which serve to recommend them as model

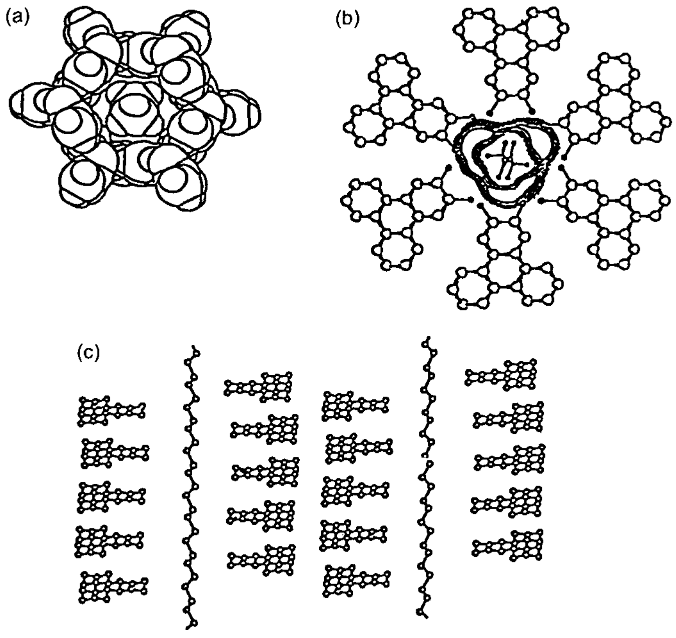


Figure 1. View down the channel of the (a) n-hexadecane-U-IC crystal, (b) polybutadiene-PHTP-IC crystal, (c) view perpendicular to the channel of the polybutadiene-PHTP-IC crystal

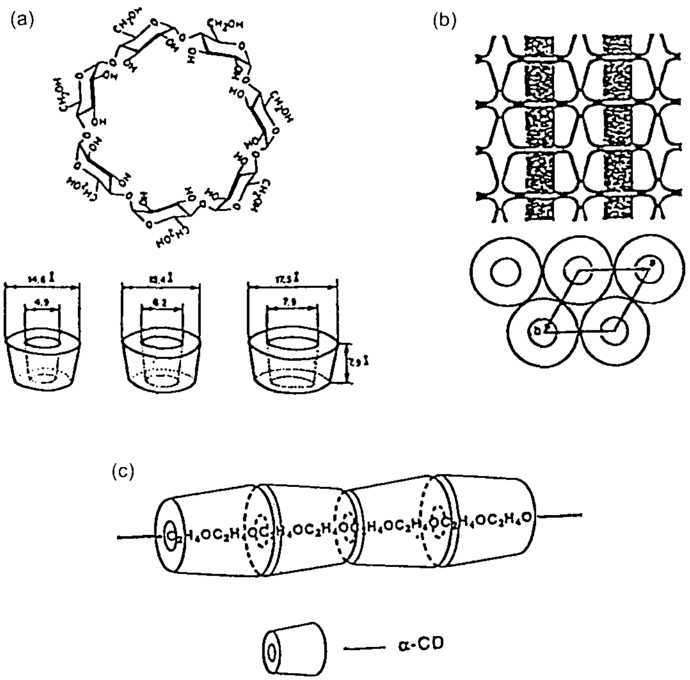


Figure 2. Structure of (a) β-cyclodextrin, and molecular dimensions of α-, β-, γ-cyclodextrins, (b) channel type crystal structures formed by crystalline cyclodextrin inclusion complexes, (c) the α-CD-PEG inclusion compound

systems whose study can lead to an assessment of the inherent, single-chain behavior of ordered, bulk polymer solids.

Principal among the experimental probes used to study polymer-ICs is solid state NMR spectroscopy. C-13 (CP/MAS/DD) NMR techniques report individual resonances for each structurally and environmentally unique nucleus in the IC sample and can provide both conformational and motional information. By contrast, the pattern of broad line shapes observed by H-2 NMR can be analyzed for motional behavior. Interpretation of the NMR observations is facilitated by molecular modeling, which attempts to define those conformations which are accessible to a polymer chain confined to occupy its narrow IC channel and the feasibility of interconverting between channel conformers. In addition, NMR observations and modeling analyses performed on polymer-ICs are compared with identical NMR observations recorded for ordered, bulk samples of the same polymers. In this way we attempt to gauge the relative contributions made to the properties of ordered, bulk polymer samples by the inherent behavior of single, isolated and stretched polymer chains and by the cooperative, interchain interactions. Here we illustrate this approach by way of application to several polymer-U-, -PHTP-, and –CD-ICs.

NMR Observations

High resolution C-13 NMR spectra of polymer-ICs were recorded under cross-polarization (CP), magic angle spinning (MAS), high-power H-1 dipolar decoupling (DD), and sometimes without CP in the single-pulse mode at 50.3 and 100.5 MHz. Spin-lattice relaxation times (T_1) were measured using the 180 - τ - 90 inversion-recovery pulse sequence[13] employing a 5T_1 delay between pulse repetitions. For the more slowly moving, rigid carbon nuclei the CP-T_1 pulse sequence[14] was employed, and spin-lattice relaxation times in the rotating frame ($T_{1\rho}$) were measured by the conventional method [15-17]. Solid state H-2 NMR were recorded at 55.3 and 61.4 MHz[18-20] using the standard quadrupolar echo pulse sequence. The reader is referred to the original papers and the Figure captions of the NMR spectra presented below for further details.

Modeling Polymer Chains in IC Channels

Two approaches have been taken when modeling polymers confined to the channels of their ICs. Mattice and coworkers[21-25] employed molecular dynamics simulation techniques. They place a polymer chain fragment inside a single IC channel formed by the host clathrate crystalline lattice, whose molecules are positioned according to their x-ray determined structures[10]. For example[21], a 10-repeat unit fragment of trans-1, 4-polybutadiene (TPBD) was placed in the clathrate channel which is formed by 6 stacks containing 15 PHTP molecules each [See Figure 1 (b, c)], which results in a channel that is 60% longer than the fully extended TPBD fragment. Each of the 4422 atoms of the TPBD fragment and PHTP lattice channel was explicitly considered, and the CHARMm potential was employed to calculate the energy of the system. Their dynamic simulation was carried out for a 70 ps trajectory using the Verlet algorithm with 0.5 ns integration steps.

We have adopted another approach to modeling the behaviors of polymer in their Ics[12, 26-32], which utilizes a complete search of rotational isomeric states (RIS)[2] conformations of polymer chain fragments confined to occupy structureless, impenetrable cylinders whose diameters, D, mimic the narrow U-, PHTP-, and CD-IC channels. Once a population of channel conformers has been identified, a test is performed to determine if interconversion between channel conformers is possible within the confines of the cylindrical channel.

Both modeling methods have particular advantages and shortcomings. The complete RIS conformational search generates all possible channel conformers, but aside from indicating the potential for interconversion of channel conformers, does not provide detailed information concerning the dynamics of the included polymer motions. The molecular dynamics simulation, on the other hand, must assume a starting channel conformation to begin the trajectory. In a sense, one must know ahead of time the channel conformers. Even if one "guesses" a potential channel conformer, the molecular dynamics approach will never reveal alternative channel conformers unless they are readily obtained by interconversions of the starting conformer during the course of the dynamics trajectory. A practical way out of this dilemma would seem to be afforded by beginning a separate molecular dynamics trajectory from each of the channel conformers found in a preliminary, yet complete, RIS conformational search performed on the included polymer fragment. The polymer-IC modeling references may be consulted for further details, and here we will only mention their results when relevant to the interpretation of NMR observations of the conformations and mobilities of polymer chains in their ICs.

Results and Discussion

PE- and TPBD-PHTP-ICs

We will begin by discussing the NMR observations made on polyethylene (PE)- and TPBD-ICs formed with PHTP. Figure 3 presents the CP/MASS/DD (a) and MAS/DD (b) C-13 spectra observed for PE- PHTP-IC[33]. Note the clean separation of PE and PHTP peaks afforded by comparing the spectra with and without CP, which favor, respectively, observation of rigid (PHTP) and mobile (PE) carbon resonances. The PE carbons resonate at 33.6-33.7 ppm in the PHTP-IC, and though not shown here, the crystalline carbons in bulk PE were observed[33] to also resonate at 33.6 ppm. Because PE crystalizes in the all trans, planar zigzag conformation and the PE chains in PE-PHTP-IC resonate at

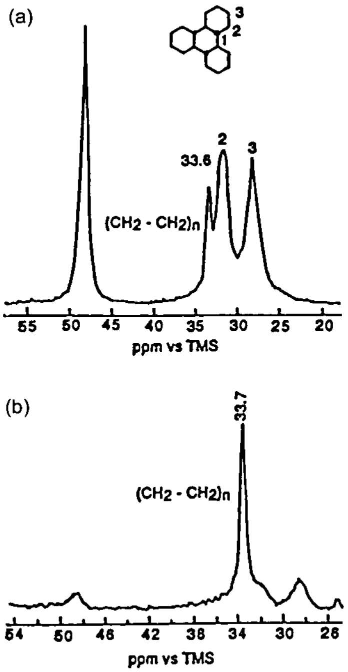


Figure 3. (a) CP/MAS/DD ^{13}C NMR spectrum at 100.5 Mhz for PE-PHTP-IC at 22 °C.[35] The projection of PHTP with the axial hydrogens represented as black dots. (b) MAS/DD ^{13}C NMR spectrum at 100.5 Mhz for PE-PHTP-IC at 22 °C, with a delay time of 5 s

the same frequency as bulk crystalline PE[34], the PE chains in the narrow PE-PHTP-IC channels are also adopting the all trans conformation. Unlike their conformations, the mobilities of PE chains in bulk crystalline and PHTP-IC samples differ markedly, ie., spin-lattice relaxation times (T_1) of 320 and 6.4 s were observed, respectively. The three PHTP carbons in PE-PHTP-IC exhibited T_1s = 150, 120, and 70 s, all many times longer than the spin-lattice relaxation time observed (6.4 s) for the included PE chains. In summary, the PE chains in PE-PHTP-IC, though adopting the same all trans conformation as PE chains in the bulk crystals, are experiencing a much greater degree of local segmental motion in the MHz frequency regime than bulk, crystalline PE chains or the carbon nuclei of the PHTP lattice in the IC. It should also be mentioned that modeling PE chain fragments in narrow channels (D = 5.0 – 5.5Å)[27] indicated that PE chains adopting the all trans conformation are unable to interconvert into other extended conformers with narrow cross sections like kink and jog conformers.

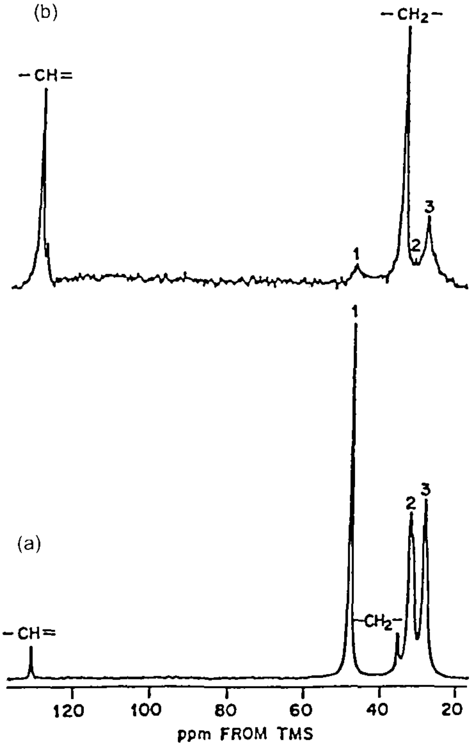


Figure 4. (a) 50.3-MHz ^{13}C NMR spectrum of the inclusion compound PHTP/1,4-*trans*-polybutadiene; CP/MAS/DD; delay time, 5 s; contact time, 2 ms. (b) 50.3-MHz MAS/DD ^{13}C NMR spectrum of the inclusion compound PHTP/1,4-*trans*-polybutadiene; delay time, 1 s

In Figure 4 the CP/MAS/DD and MAS/DD C-13 NMR spectra observed[35] for TPBD-PHTP- IC are presented. Again note that observation with and without CP favors observation of the PHTP and included TPBD carbons, respectively. Included TPBD chains exhibit T_1s = 6 - 10 s, while the PHTP carbons have T_1s = 180, 160, and 110 s, which explains why they and not the included TPBD carbon nuclei cross-polarize efficiently. Sozzani et al.[35] also reported the chemical shifts and T_1s for bulk crystalline TPBD. TPBD exhibits two crystalline polymorphs[36-39]. In form I, which is stable below 75°C, the TPBD chains are in an extended, trans, skew±, trans, skew- conformation, where the CH=CH and CH2-CH2 bonds are trans and the CH-CH2 bonds are skew. Above 75° C form II TPBD is stable and here the TPBD chains are thought to be conformationally disordered with CH-CH2 bonds able to adopt and interconvert between skew and cis conformations. T_1s of 50 – 130 s were observed for the form I TPBD carbons, while T_1s of 8 – 10 s were measured for the form II carbon nuclei. Also the chemical shifts observed for form II TPBD were very similar to those exhibited by the TPBD chains in TPBD-PHTP-IC, both being distinct from the chemical shifts of form I TPBD.

Molecular modeling[26] indicated that TPBD chains included in the PHTP channels are able to sample and interconvert between conformers with skew± and cis CH-CH2 bonds, while the CH=CH and CH2-CH2 bonds remain trans. Based on both the C-13 NMR observations and the modeling, it appears that TPBD chains in both the bulk, form II and PHTP-IC crystals are mobile and able to adopt and interconvert between several different extended conformations. When compared to the behavior of PE chains in PHTP-IC, which adopt a single all trans conformation and yet show a small T_1 like the included TPBD chains, it must be concluded that the low amplitude high frequency (MHz) motions effective in spin lattice relaxation of magnetization are not necessarily dependent upon the ability of polymer chains to undergo conformational interconversions.[40]

In Figure 5 the H-2 NMR spectra of PE- and TPBD-PHTP-ICs are presented[20] over a broad range of temperatures. The strong similarity in the spectra of both polymers in their PHTP-ICs suggests that the C-D bonds in both polymers are undergoing the same type of anisotropic reorientation. Because the PE chains remain in the all trans conformation while the TPBD chains are interconverting between skew ± and cis CH-CH2 bond conformers, clearly different local chain motions are responsible for similar C-D bond reorientations in the included PE and TPBD chains. This is supported by the offset of the PE data by ca. 150° C to higher temperatures, and indicates that the PE channel motions are being resisted by interactions of higher energy than those encountered by the conformationally interconverting TPBD chains. As noted by Hirschinger and English[41], analysis of fully relaxed H-2 spectra alone may not always provide unambiguous identification of chain motion. Schilling et al.[20] conclude that high-frequency librations about the CH2-CH2 bonds are the principal motions in the PE chains. Librations at a number of consecutive bonds produce large amplitude reorientations of the C-D bond vectors similar to those experienced by the conformationally interconverting TPBD chains. Thus we can see why PHTP-IC included

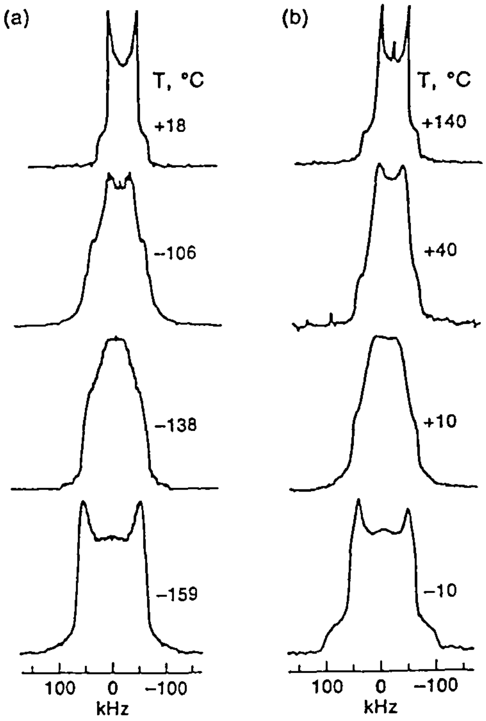


Figure 5. Comparison of the solid-state ^{2}H NMR spectra for the (a) TPBD-d_4/PHTP-IC and (b) PE-d_4/PHTP-IC at the indicated temperatures

PE and TPBD chains show similar C-D bond dynamics even though the local segmental motions of their chains are quite distinct.

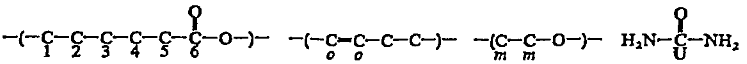
Comparison of the H-2 NMR spectra of bulk crystalline PE and TPBD (not shown) with those presented in Figure 5 reveals[18,20] that the PE chains in the bulk sample are not experiencing the low amplitude high frequency CH2-CH2 bond librations observed for the PE chains in the PHTP-IC.

On the other hand, above 75°C the TPBD chains in the bulk form II crystals are conformationally interconverting like those in TPBD-PHTP-IC. For PE chains the constraints to chain motions in its bulk crystals are more severe than those of the confining PHTP channels, while the PHTP channels and the packing arrangement in form II bulk crystals provide quite similar motional constraints for the TPBD chains.

PCL Homo- and Block Copolymer-U-Ics

Di- and triblock copolymers of poly (epsilon caprolactone) (PCL) with polybutadiene (PBD) and poly (ethylene oxide) (PEO) have been complexed with urea to form PCL-PBD-U- and PCL-PEO-PCL-U-ICs[42]. Through a combination of x-ray diffraction, FTIR, DSC, and NMR observations the following conclusions concerning their structures were reached: i. both blocks of the PCL-PBD diblock copolymer are included in the U-channels; ii. PCL-PBD-U-IC is a dimorphic crystal with the PCL blocks forming a narrow channel, hexagonal structure [see Figure 1 (a)] and the PBD blocks forming an expanded tetragonal structure[43,44] with wider U-channels to accommodate the 12% 1,2-BD units contained in the PBD blocks; iii. only the terminal PCl blocks in PCL-PEO-PCL are included in the narrow hexagonal channels of the PCL-PEO-PCL-U-IC and iv. the excluded central PEO blocks remain amorphous in PCL-PEO-PCL-U-IC and bulk triblock copolymer samples. Starting from this structural information, we undertook a C-13 NMR study of the segmental mobilities of PCL and PEO homopolymers, PCL-PBD di- and PCL-PEO-PCL triblocks, and the U-ICs of these homo-and di- and tri-block copolymers. Spin-lattice relaxation times of the carbon nuclei (T_1 and $T_{1\rho}$) and $T_{1\rho}$ (H-1) for the protons were measured, and the results are presented in Table 1. Without providing the details of the discussion presented in reference 42, here we simply summarize the conclusions drawn there concerning the segmental mobilities of the bulk and U-IC samples of these homo-and block copolymers. The spin-lattice relaxation times [T_1 (C-13)], which monitor high-frequency (10-100 MHz) low amplitude motions of carbon nuclei, seem to depend on the nonlocalized polymer chain motions in both the bulk and U-IC crystalline environments. T_1 (C-13) s are not therefore monitoring the localized segmental motions of polymers in their bulk or U-IC crystals. Motions of nearby yet nonbonded protons belonging to surrounding polymer chains or to urea in their 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 (C-13). 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. The former case

Table 1. Spin-lattice relaxation times (T_1), spin-lattice relaxation times measured in the rotating frame ($T_{1\rho}$) and ^{13}C-observed $T_{1\rho}$ (^{1}H) for the carbon nuclei in the bulk and U-IC samples of PCL, PEO, PCL-PBD and PCL-PEO-PCL



$-(-\underset{1}{C}-\underset{2}{C}-\underset{3}{C}-\underset{4}{C}-\underset{5}{C}-\overset{O}{\underset{6}{C}}-O-)-$ $-(-\underset{o}{C}=\underset{o}{C}-C-C-)-$ $-(\underset{m}{C}-\underset{m}{C}-O-)-$ $H_2N-\overset{O}{\underset{U}{C}}-NH_2$

				$T_1(^{13}C)$ (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 0·5	4·2			0·2	1·8
U		16		35		6·1		6·3
				$T_{1\rho}(^{13}C)$ (ms)				
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
				$T_{1\rho}(^1H)$ (ms)				
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

leads to PEO loops and the latter to PEO tie chains. In PCL-PEO-PCL-U-IC the PEO blocks are much less likely to form loops during the formation of PCL block-U-IC crystals. Because the T_1 (C-13) observed for PEO in the bulk sample is much shorter than seen in the U-IC sample, high-frequency (MHz) 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 (10 – 100 kHz) larger amplitude motions effective in $T_{1\rho}$ (C-13) relaxation of PCL carbon nuclei in bulk and U-IC crystals are sensitive to the mobilities of the polymers that are attached to the PCL blocks. Cooperative motions of PBD chains in phase-separated domains well above their Tg, as found in PCL-PBD diblock copolymer, place less of a restriction on $T_{1\rho}$ (C-13), 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 $T_{1\rho}$ (C-13) relaxation, because they are possible in the bulk sample above Tg, but are prevented in the U-IC channels.

From Table 1 it can be generally concluded that T_1s are reduced and $T_{1\rho}$s show an increase as polymer chains are removed from their bulk, crystalline samples and separated and confined to occupy the narrow U-IC channels. The high-frequency megahertz motions effective in T_1 (C-13) relaxation are apparently more facile in the U-IC channels than in the bulk polymer crystallites, while the lower-frequency kilohertz motions monitored by $T_{1\rho}$ (C-13) are retarded in the U-IC channels compared to the bulk crystalline environment. The high-frequency, low-amplitude, non-localized motions characteristic of T_1 (C-13) 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 $T_{1\rho}$ (C-13) relaxation apparently benefit from the cooperitivity possible in the bulk polymer crystallites, at least on a localized scale, but which is absent in the geometrically rigid U-IC channels.

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

$T_{1\rho}$ (H-1) s observed for the U-IC included polymer chains are dominated by the diffusion of abundant urea matrix proton spins. Formation of polymer-Ud-4-ICs, which are devoid of urea protons, will remove the effect of urea proton spins and will also enable an assessment of their importance to T_1 (C-13) and $T_{1\rho}$ (C-13) 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 (C-13) s observed for amorphous PEO carbons in bulk and

U-IC samples differ, so do the $T_{1\rho}$ (H-1) s. While the high-frequency (MHz) motions and the diffusion of proton spins in amorphous PEO phases are effected my their morphology, the lower-frequency (kHz) motions are not, because identical $T_{1\rho}$ (C-13) s are observed for the 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 $T_{1\rho}$ (H-1) s observed for PEO carbons in the bulk and U-IC triblock samples are attributed to different rates of H-1 spin diffusion in their phase-separated domains of ca. 26 and 8.5Å, respectively.

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

The $T_{1\rho}$ (H-1) 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 $T_{1\rho}$ (H-1) s of the urea carbonyl carbons, and it is likely that the four geminally bonded protons are making the major contribution to $T_{1\rho}$ (H-1) relaxation.

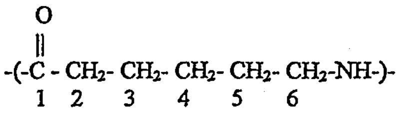
Formation of PCL-PBD-Ud-4-IC would produce a nonprotonated U-IC channel for each of the PCL and PBD included blocks. The Ud-4 matrix would separate the PCL-PBD chains residing in neighboring channels by an ca. 7 Å proton-free barrier, thereby assuring a 1-dimensional diffusion of proton spins along each included diblock copolymer. Because the lengths of the included and extended PCL and PBD blocks are in the range 400 – 500 Å, the $T_{1\rho}$ (H-1) s observed for the carbon nuclei in each block would be distinct and not averaged by H-1 spin diffusion. Averaging by spin diffusion would require $T_{1\rho}$ (H-1) s > 10s. Comparison of the 1-dimensional $T_{1\rho}$ (H-1) s measured for the diblockcopolymer-Ud-4-IC with the 3-dimensional $T_{1\rho}$ (H-1)s observed in the U-IC samples of Table 1, 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)[45] to be derived independently from the 1- and 3-dimensional $T_{1\rho}$ (H-1)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[9].

It should also be mentioned that each of the C-13 relaxation measurements, T_1 (C-13), $T_{1\rho}$ (C-13), and $T_{1\rho}$ (H-1), yielded results which confirmed the structures that were previously derived for both block copolymer-U-ICs. Both PCL and PBD blocks are included in the PCL-PBD-U-IC, but the structures of the 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 PEO blocks do not form bulk crystals.

Nylon-6-CD-ICs

Recently we were able to form ICs with alpha-, beta-, and gamma-CD and nylon-6[46,47], and we have made some preliminary observations of the conformation and mobilities of the nylon-6 chains included in the CD-ICs and in an annealed bulk sample. In Tables 2,3, and 4 we present the C-13 chemical shifts, spin-lattice relaxation times T_1 (C-13), and in the rotating reference frame $T_{1\rho}$ (C-13), respectively, observed for the annealed bulk and CD-IC samples of nylon-6. Note in Table 2 the close correspondence between the resonance frequencies observed for all 6-carbon nuclei of nylon-6 in the bulk and CD-IC samples. This provides evidence that the nylon-6 chains in all 4 solid samples are assuming very similar conformations. Nylon-6 is known to crystallize into two polymorphs the alpha and gama forms.[48,49] In the alpha-form crystals the nylon-6 chains are fully extended in the all trans conformation, while the nylon-6 chains in the gamma-form crystals exhibited a somewhat shortened fiber repeat distance consistent with some very minor deviations from the all trans conformation. Because of the close similarity of

Table 2. Comparison of chemical shifts (in ppm) for nylon-6 in bulk and CD-IC samples



$$-(-\underset{1}{\overset{\overset{O}{\|}}{C}}-\underset{2}{CH_2}-\underset{3}{CH_2}-\underset{4}{CH_2}-\underset{5}{CH_2}-\underset{6}{CH_2}-NH-)-$$

C	1	2	3	4	5	6
Bulk Nylon 6	167.9	31.0	20.9	24.2	24.2	36.2
Nylon 6-α-CD-IC	167.6	31.0	20.6	24.4	24.4	37.0
Nylon 6-β-CD-IC	168.0	30.9	20.5	24.3	24.3	37.5
Nylon 6-γ-CD-IC	168.1	30.8	20.8	24.4	24.4	36.8

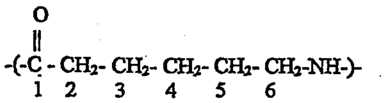
the C-13 chemical shifts observed for nylon-6 carbon nuclei in the bulk and CD-IC samples, it seems likely that a nearly fully extended, all trans conformation is adopted by the nylon-6 chains whether or not they reside in bulk crystals or in the channels of their CD-ICs (see Figure 2).

The conformations and mobilities of nylon-6 chains confined to occupy rigid cylinders with a range of diameters have been previously examined.[28] There it was observed that for D ca. 5.0 Å, which corresponds closely to the channel cross section in alpha-CD (see Figure 2), only the all trans and the kink conformers tg±tg∓tt and tt g±tg∓t of nylon-6 can be accomodated. However, at this channel diameter the nylon-6 chains are not able to interconvert between the all trans and the kink channel conformers. Expansion of the channel diameter to ca. 6 Å, which is appropriate for beta-CD (see Figure 2), allows other gauche-bond-containing conformers to fit, in addition to the kink conformers, such as those containing adjacent gauche bonds. Once again, however, there is insufficient room in the D = 6 Å channel for interconversion between any of the channel conformers. Expansion of the cylinder diameter beyond 7 Å up to and including the 8 Å diameter found in gamma-CD (see Figure 2) was observed to provide enough room for interconversion between channel conformers, but these were limited to interconversions between the kink channel conformers. Because the all trans conformation is the lowest energy conformation for single, isolated nylon-6 chains[2] , and because nylon-6 chains in cylinders with $D \leq 8$ Å are not able to interconvert between all of their channel conformers, we would expect, as is observed (see Table 2), that the nylon-6 chains in all 3 CD-ICs would be restricted to the all trans conformation.

Without the ability to interconvert, we would not expect a mixture of low energy all trans and higher energy gauche-containing conformers to be present in the CD-ICs, because the absence of interconversion removes the possibility of gaining conformational entropy sufficient to offset the higher energies of the gauche-containing conformers. Without sufficient room for conformer interconversion, we would generally expect polymer chains confined in their IC channels to exclusively assume their lowest energy conformations.

The spin-lattice relaxation times T_1 (C-13) observed for the nylon-6 carbon nuclei in bulk and CD-IC samples are summarized in Table 3. Comparison with the T_1 (C-13) s observed for PCL bulk and U-IC homo- and block copolymer samples in Table 1 reveals

Table 3. Spin-lattice relaxation times (T_1) observed for the carbon nuclei in bulk nylon-6 and nylon-6-α-, β-, γ-CD-IC samples



$-(\underset{1}{\overset{\overset{O}{\|}}{C}}-\underset{2}{CH_2}-\underset{3}{CH_2}-\underset{4}{CH_2}-\underset{5}{CH_2}-\underset{6}{CH_2}-NH-)-$

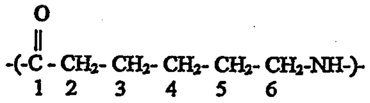
$T_1\,(^{13}C)$, s

C	1	2	3	4	5	6
Nylon 6	9.5	1.2 11.1	0.51 9.4	1.1 12.0	1.1 12.0	1.41 9.0
Nylon 6-α-CD-IC	16.7	3.0 14.1	1.0 22.6	3.1 22.3	3.1 22.3	3.2 17.2
Nylon 6-β-CD-IC	12.3	17.7	16.2	12.5	12.5	12.1
Nylon 6-γ-CD-IC	14.5	1.8 16.3	0.8 17.5	1.5 17.7	1.5 17.7	4.8 18.8

a striking difference in behavior. While the T_1 (C-13) s observed for PCL carbon nuclei depend sensitively on the bulk or U-IC nature of the samples, the nylon-6 T (C-13) s are observed to vary little between the bulk and CD-IC samples, even though the channel sizes of the CD-ICs range from 5 – 8 Å. Though not presented here, the T_1 (C-13)s measured for the host CD lattice carbons are also comparable or a bit shorter than the nylon-6 carbon spin-lattice relaxation times. Unlike PCL, high-frequency (MHz), low amplitude nylon-6 chain motions appear to be relatively unaffected by their ordered, solid state environments. The suggestion that in the bulk and CD-IC crystals nylon-6 chains are restricted to the nearly fully extended, all trans conformation, which was offered by modeling, may play a role in the uniformity of T_1 (C-13) s observed for the nylon-6 carbon nuclei in these distinct ordered, solid state samples.

The $T_{1\rho}$(C13) relaxation times presented in Table 4 are similarly striking for their homogeniety. Like the T_1 (C-13) s, nylon-6 $T_{1\rho}$ (C-13) s are almost independent of their ordered, solid state, structural environments. $T_{1\rho}$ (C-13) s for the CD carbons are a bit

Table 4. Spin-lattice relaxation times $T_{1\rho}$ (^{13}C) observed for the carbon nuclei in bulk nylon-6 and nylon-6-α-, β-, γ-CD-IC samples



$$-(\overset{\overset{O}{\|}}{C}-CH_2-CH_2-CH_2-CH_2-CH_2-NH-)-$$

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

C	1	2	3	4	5	6
Nylon 6	7.2	0.8 1.2	0.8 1.4	0.8 2.2	0.8 2.2	0.7 2.4
Nylon 6-α-CD-IC	6.1	0.7		0.7	0.7	0.8
Nylon 6-β-CD-IC	5.4	0.7	1.1	1.3	1.3	
Nylon 6-γ-CD-IC	6.7	0.6 1.4		0.6 1.0	0.6 1.0	0.6 1.1

longer/shorter than those of the CH2/C=O nylon-6 carbon nuclei. Again this behavior contrasts with that observed for bulk and U-IC samples of PCL homo- and block copolymer samples. It should be noted that the $T_{1\rho}$ (C-13)s observed for all CH2 carbon nuclei fall in the range 0.6 – 2.4 ms.

This suggests that static spin-spin interactions[17,50], and not high amplitude, mid-kilo-hertz (100 khz) motions of nylon-6 chains, may be dominating the $T_{1\rho}$(C-13) relaxations.

We hope by way of illustration with these several polymer-IC samples and their observation by NMR spectroscopy, that you might begin to see the value of polymer-ICs as models for ordered, bulk polymer phases, which permit the decoupling of inherent, isolated chain contributions from those made by cooperative interchain interactions to their properties.

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