Dynamics of Isolated Polycaprolactone Chains in Their Inclusion Complexes with Cyclodextrins

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ABSTRACT: Solid-state carbon NMR with magic-angle spinning has been used to study the structure and dynamics of semicrystalline polycaprolactone (PCL) and its inclusion complexes formed with α- and γ-cyclodextrins (α- and γ-CDs), which are shown to have channel structures occupied by single and two parallel, side-by-side chains, respectively. Guest−host magnetization exchange has been observed, but the results differ substantially from those observed in semicrystalline polymers and blends. The conventional relaxation experiments and 2D wide-line separation NMR with windowless isotropic mixing have been used to measure the chain dynamics. The results suggest that the intermolecular interactions restrict the dynamics of some atoms more than others, but that the chains in the complex are more mobile than in semicrystalline PCL. These results are compared with the inclusion compound formed between the model compound valeric acid and α-CD that is also a channel complex structure.

Introduction

Cyclodextrin (CD) inclusion compounds are of interest for a wide variety of applications ranging from drug delivery to the templating of porous solids.[1] The extensive use of CD's is due to their low cost and availability as well as their ability to form inclusion compounds with a large number of small molecules and polymers. Cyclodextrins are available with pore sizes ranging from 4.9 to 7.9 Å and can be easily modified for specific applications.[2,3]

Polymer inclusion compounds can also be prepared from cyclodextrins, and complexes have been reported for poly(ethylene oxide),[4] polycaprolactone,[5] and nylon-6,[6] for example. These complexes are of interest in the fabrication of high-strength materials and novel composites, because coalescence of polymer-ICs has been shown to lead to a chain-extended crystalline morphology.[7] The CD complexes with low molecular weight guests can either have channel or cage structures (see Figure 1). In the channel structure, the CD rings are stacked on top of each other to produce cylindrical central cavities; in cage structures, the cavity of one CD molecule is closed on both sides by adjacent molecules. Because of the long chain nature of polymers, the crystal structure of polymer−CD complexes is expected to be channel type. The formation of polymer−CD complexes also present a unique opportunity for the study of single polymer chains isolated from their neighboring chains.[8−11] Such studies may eventually provide valuable insights into the single-chain electrical and optical properties of polymers in the solid state.

In the present study we have used solid-state carbon NMR to measure the structure and dynamics of polycaprolactone (PCL) chains in the inclusion complexes as formed with α-CD and γ-CD. α-CD is a pore-forming cyclic molecule that consists of six glucose units arranged around a 4.9 Å pore,[1−3] while γ-CD is composed of eight glucose units around a 7.9 Å cavity. The formation of the complexes has been previously reported.[5,12] We have used conventional NMR relaxation time methods to measure the dynamics of the complexes in both mid-megahertz and mid-kilohertz frequency ranges. We have also employed some recently developed 2D NMR methods to study the chain dynamics of the individual atoms along the polymer backbone. The recently developed 2D wide-line correlation NMR with windowless isotropic mixing[13] allow us to monitor the chain dynamics through the indirectly detected proton line shapes. This has the important advantage that we do not require isotopically labeled polymer to measure the chain dynamics. We also report on the rate of magnetization exchange between the polymer and the rigid host matrix employing the proton $T_{1\rho}$ and 2D heteronuclear correlation experiments. We find that the magnetization exchange does not occur as in other well-studied materials such as semicrystalline polymers and blends.[14,15] There is efficient spin diffusion between the guest PCL and the host γ-CD but incomplete spin diffusion between PCL and the host α-CD. The results for the PCL complexes are compared with those for the complex of valeric acid (VA) with α-CD, which has been characterized by single-crystal X-ray diffraction.[16]

Materials and Methods

PCL was obtained from Scientific Polymer Products, and α-CD, γ-CD, and VA were obtained from Aldrich Chemical Co. The α-CD/PCL inclusion complex was prepared by a sonication method.[5] Both PCL (0.2 g in 50 mL acetone) and saturated α-CD solutions (7.25 g in 50 mL water) were heated to 70 °C, and the PCL solution was slowly added to the α-CD with sonication. The mixture was kept at 70 °C for 17 min with sonication. A white precipitate was formed after 10 h of quiescent storage. The γ-CD/PCL inclusion complex was prepared by a heating method.[12] Both PCL (0.2 g in 50 mL of acetone) and saturated γ-CD solutions (11.6 g in 50 mL of water) were heated to 70 °C, and the PCL solution was slowly added to the γ-CD with stirring and heating. A white precipitate was formed overnight. After filtration and washing with distilled water, the α-CD/PCL and γ-CD/PCL samples were dried in a vacuum oven and collected.

Solid-state carbon NMR measurements were performed on a Varian Unity spectrometer at 100 MHz using a 7.5 mm magic-angle spinning probe at ambient temperature. The

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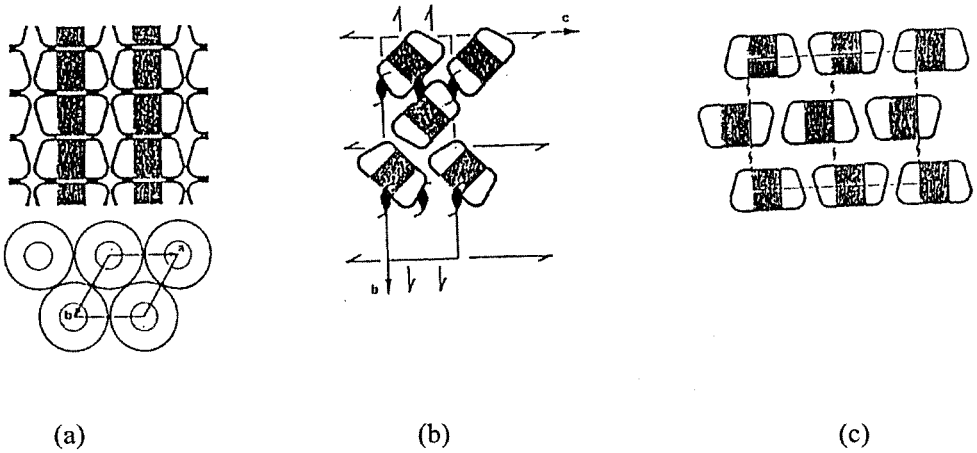

Figure 1. Schematic description of (a) channel-type, (b) cage herringbone-type, and (c) cage brick-type crystal structures formed by cyclodextrin inclusion complexes.

spinning speed was regulated at 3500 or 4500 Hz, and the carbon and proton pulse widths were set to 4.2 μs. The proton $T_{1\rho}$ relaxation times were measured using the cross-polarization pulse sequence preceded by a variable proton spin-lock period.[14] The two-dimensional $^{13}C-^{1}H$ HETCOR spectra were collected using the pulse sequence described previously.[17,18] BLEW-12 /BB-12 decoupling was applied during the evolution period to suppress homonuclear proton and carbon−proton dipolar interactions, and the spectra were acquired with one WIM-24 mixing cycle.[19] Spin−lattice relaxation times (T_1) were measured by two pulse sequences: CP−T_1 and saturation−recovery T_1. The 2D wide-line separation[20] spectra with windowless isotropic mixing[19,21] were measured using a 300 kHz sweep width in the proton dimension and a 30 kHz sweep width in the carbon dimension. Rapid signal decay was observed in the proton dimension, and the maximum evolution time was 106 μs.

Results

The structure and dynamics of PCL inclusion complexes have been studied with solid-state NMR using cross-polarization and magic-angle sample spinning. The inclusion complexes formed by α-CD and γ-CD with PCL have been previously characterized by DSC, FTIR, and X-ray diffraction.[5,12] These studies showed that a complex is formed, and no free crystalline PCL remains in the sample. The X-ray diffraction patterns for these two complexes differ from those observed for semicrystalline CDs and PCL but resemble that observed for the small molecule complexes α-CD/VA and γ-CD/1-propanol, which are known to form channel-type crystal structures by single-crystal X-ray analyses.[16,22]

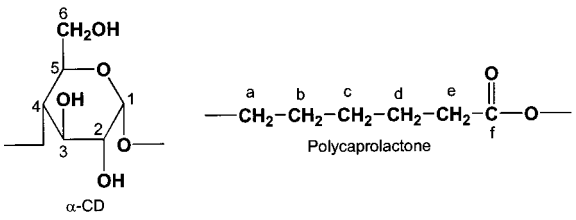

Figure 2 shows the 100 MHz solid-state carbon NMR spectra for α-CD, PCL, and the α-CD/PCL inclusion complex. The signals from PCL are easily identified and are well resolved from the α-CD signals in the complex. The chemical shifts for PCL in the inclusion complex are similar to those observed in the semicrystalline sample, suggesting that the PCL in α-CD channels adopts an extended all-trans conformation.[5] We can

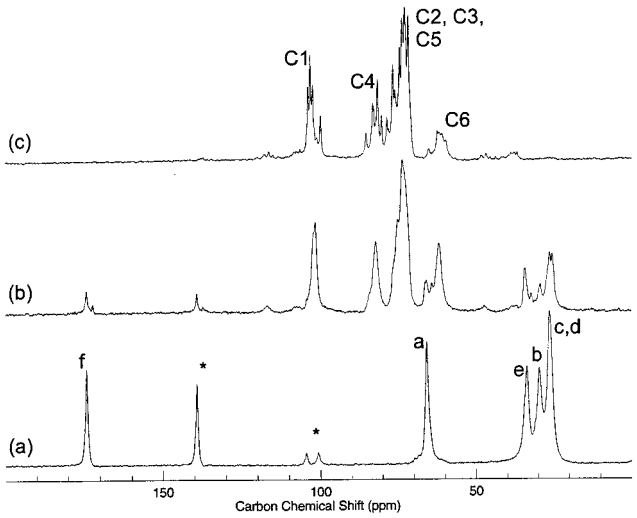

Figure 2. CPMAS spectra of (a) polycaprolactone, (b) the α-CD/polycaprolactone inclusion complex, and (c) α-CD. The spinning sidebands are marked with an asterisk.

observe similar characteristics in the complex between PCL and γ-CD. However, the cross-polarization dynamics indicates that the maximum intensity for the PCL peaks was observed with a 4 ms cross-polarization time, rather than the shorter 1 ms contact time for the α-CD complex.

We observed large changes in the carbon spectrum of α-CD upon inclusion complex formation. Figure 2c shows that very high-resolution spectra are observed for the α-CD, which actually is a cage crystalline structure (see Figure 1) with water as guest. Several lines are observed for each carbon resonance resulting from nonequivalent glucose units in α-CD in the unit cell of the crystal structure. The lines for α-CD are considerably broader in the inclusion complex, which is a channel crystal structure (see Figure 1), reflecting a more symmetric but more disordered structure. Similar results are observed for the γ-CD/PCL inclusion complex and have been reported for other inclusion complexes.[5]

Solid-state NMR is often used to study the length scale of phase separation in semicrystalline polymers and blends. These studies are possible because the rate of magnetization transfer via proton spin diffusion is on the right time scale to measure phase separation over the length scale of 5−200 Å.[14,15,23] The length scale of

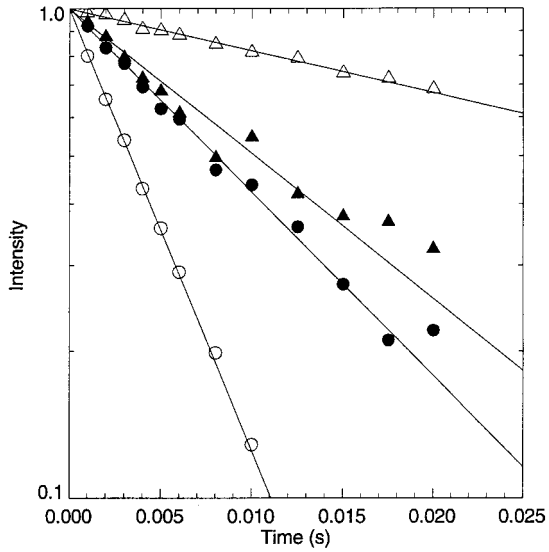

Figure 3. Proton $T_{1\rho}$ relaxation of α-CD in (○) bulk and (●) the inclusion complex with polycaprolactone and the polycaprolactone relaxation in (△) bulk and the (▲) inclusion complex.

Table 1. Proton $T_{1\rho}$ Relaxation Times for α-CD, Semicrystalline Polycaprolactone, and Their Inclusion Complex

	$T_{1\rho}$ (ms)	
sample	α-CD	polycaprolactone
α-CD	4.9	
α-CD/PCL	11.9	15.4
polycaprolactone		54.0

phase separation is of interest in many polymeric systems, and several methods have been developed to measure domain sizes using proton spin diffusion. In the present study we have used the proton $T_{1\rho}$ relaxation rates to measure magnetization exchange between the guest polymer and the CDs.[23] If there is efficient magnetization exchange on a length scale of 20 Å or less, then an averaged relaxation time will be observed between the polymer and the host matrix.

Figure 3 and Table 1 show the results for the proton $T_{1\rho}$ relaxation measurements for α-CD, PCL, and the α-CD/PCL complex. Semicrystalline PCL has a long relaxation time (54 ms) while the relaxation time for the pure α-CD is much shorter (4.9 ms). The values for α-CD and PCL in the complex are intermediate between these two values, showing that there is some spin diffusion between the host and the included polymer. However, the proton $T_{1\rho}$ relaxation times for PCL and α-CD are not identical, demonstrating that spin diffusion is not complete. Such behavior is not expected, since the polymer in the α-CD channel is expected to be within the length scale of spin diffusion probed by proton $T_{1\rho}$ relaxation (20 Å). In contrast to the relaxation in the α-CD/PCL inclusion complex, we observe that both the γ-CD and PCL carbons have the same relaxation times in the complex, showing that there is efficient spin diffusion between the crystal frame γ-CD and included PCL chains (see Table 2). This may indicate that there are two side-by-side, parallel chains incorporated inside the larger γ-CD channels, instead of single PCL chains inside the α-CD channels (see Figure 4 [27]).

Spin diffusion can be more accurately measured using the solid-state heteronuclear correlation experiment (see Figure 5). This experiment is one of the most powerful

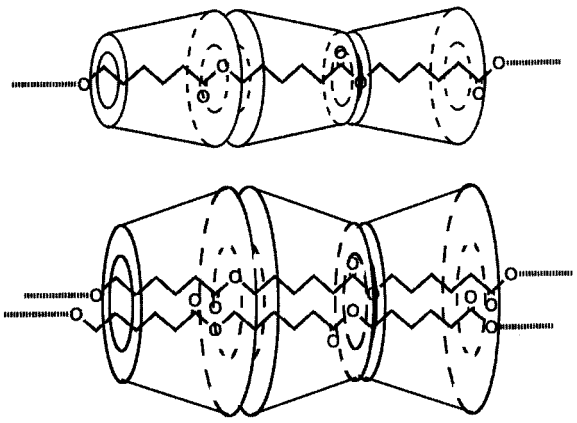

Figure 4. Proposed structures of the PCL-α-CD-IC and PCL-γ-CD-IC.

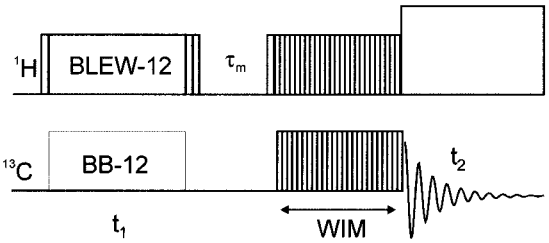

Figure 5. Pulse sequence diagram for solid-state heteronuclear 2D correlation spectroscopy.

Table 2. Proton $T_{1\rho}$ Relaxation Times for γ-CD, Semicrystalline Polycaprolactone, and Their Inclusion Complex

	$T_{1\rho}$ (ms)	
sample	γ-CD	polycaprolactone
γ-CD	2.7	
γ-CD/PCL	9.3	9.1
polycaprolactone		54.0

2D methods available to measure spin diffusion rates and to probe miscibility in a polymer blend.[18,24] With a short mixing time this experiment can give a correlation of the solid-state carbon and proton spectrum. If there is efficient spin diffusion during the mixing time, the average proton chemical shifts for each resolved carbon resonance can be observed due to spin diffusion.

Figure 6 shows the heteronuclear correlation spectrum of α-CD/PCL inclusion complex with two different mixing times: (1) 50 μs and (2) 10 ms. A mixing time of 50 μs is too short for significant spin diffusion, and a normal heteronuclear correlation spectrum is observed. The proton chemical shift difference between the α-CD and the PCL is clearly observed. When the mixing time is increased to 10 ms, which is a relatively short spin diffusion delay, the proton chemical shifts of α-CD and the PCL are shifted toward each other due to spin diffusion; however, the spin diffusion is not complete considering the remaining proton chemical shift difference between the guest and the host. Comparing with the heteronuclear correlation spectrum of γ-CD/PCL complex (see Figure 7), we observed identical proton chemical shifts of the guest PCL and host γ-CD in the complex, indicating that there is strong spin diffusion between them. They must be in closer contact than PCL is with α-CD in its complex. This observation is consistent with the results of proton $T_{1\rho}$ relaxation experiments.

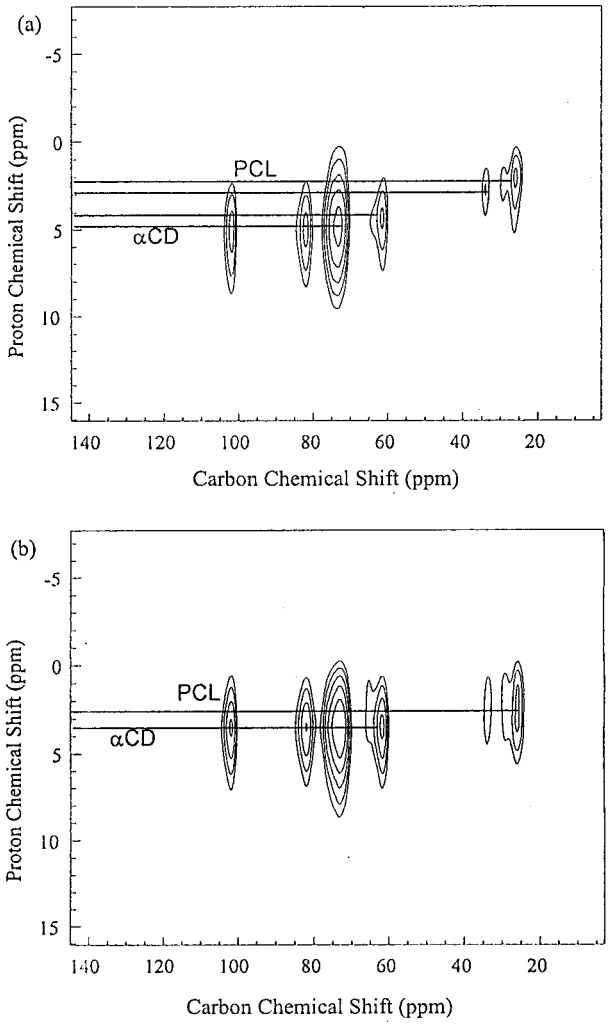

Figure 6. Heteronuclear correlation spectrum for the α-CD/polycaprolactone complex obtained with two different mixing times: (a) 50 μs and (b) 10 ms.

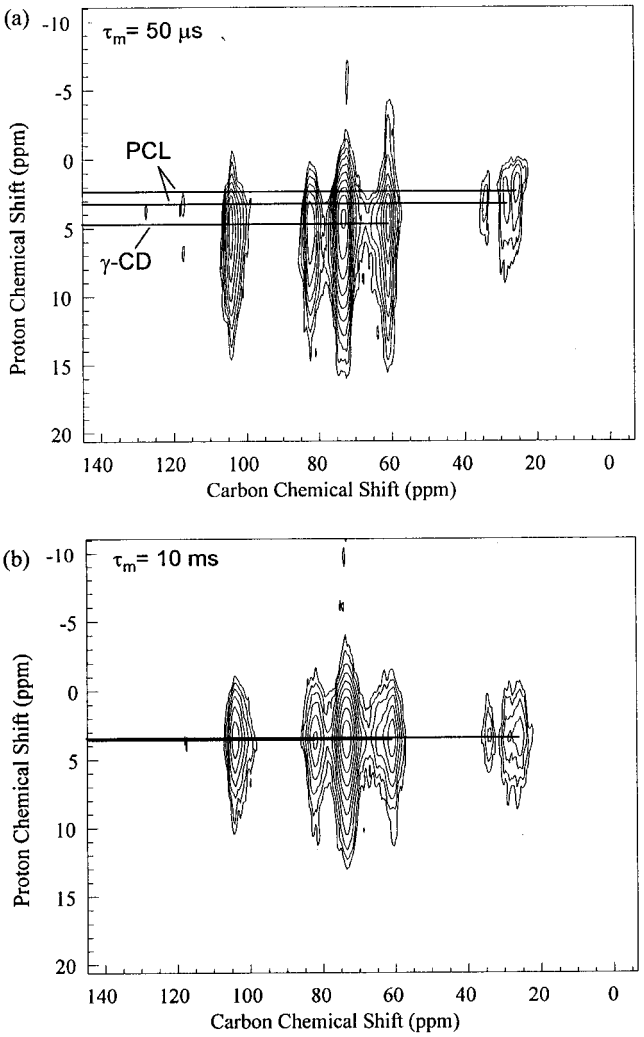

Figure 7. Heteronuclear correlation spectrum for the γ-CD/polycaprolactone complex obtained with two different mixing times: (a) 50 μs and (b) 10 ms.

The dynamic behavior of the inclusion complexes can also be studied by the measurement of the ^{13}C T_1 relaxation times and the application of specific pulse sequences.[25,26] Spin−lattice processes are sensitive to motions at or near the nuclear Larmor frequencies, which are typically 5−500 MHz.[26] In this study, we employed two pulse sequences to measure the ^{13}C T_1 relaxation rates: saturation−recovery T_1 and CP−T_1. We observe similar results by these two methods. However, since the included PCL chains do not cross-polarize efficiently, we can only observe weak signals for the PCL chains. In addition, the methylene carbon *a* of PCL is overlapped by the C6 carbon signal of CDs. Therefore, it is hard to obtain complete information about dynamics of PCL chains by the CP−T_1 method. However, by applying the saturation recovery T_1 pulse sequence, we can achieve information regarding PCL chains with high mobility by using a series of short delay times and the relaxation times of CDs with low mobility by employing a series of longer delay times.

The T_1 values for the carbon nuclei of the PCL, α-CD/PCL, α-CD, γ-CD/PCL, and γ-CD are given in Table 3. Double-exponential relaxation times are observed for the bulk PCL and the α-CD. The long T_1(C)'s for bulk PCL and α-CD are consistent with a semicrystalline phase. Large changes in the T_1(C)'s are observed upon complex formation, and single-exponential recovery is observed for both the polymer and α-CD in the complex. The relaxation times of the PCL chains included inside the α-CD channels are fast: 0.24−0.31s for methylene carbons, which is only 0.1−0.2% of the relaxation times observed for bulk PCL. By comparison with the relaxation times of included PCL chains, the T_1(C)'s of α-CD carbons are much longer. This supports the view that α-CD forms the crystalline frame with isolated PCL chains included inside its narrow channels. We also note that the T_1(C)'s for α-CD are also shorter in the complex than in pure α-CD, indicating that the α-CD is more mobile when the guest polymer is incorporated inside its narrow channels. The relaxation may be facilitated by a fast guest-driven dynamic process.

Comparing the T_1(C)'s of γ-CD/PCL with those of α-CD/PCL inclusion complex, we do not observe much difference between these two complexes. Although the α-CD channel can only accommodate single PCL chains and the γ-CD channel is large enough to accommodate two side-by-side, parallel chains,[12,27] the PCL chains show similar mobility in the megahertz regime in these two different host environments. This would indicate that cooperative motions of side-by-side parallel PCL chains in the γ-CD/PCL inclusion complex, if they occur, are not influencing megahertz $T_1(^{13}C)$ relaxation, because these are not possible for the single isolated PCL chains in the α-CD/PCL inclusion complex. Both α-CD

Table 3. T_1(^{13}C) Values for the Carbon Nuclei of the α-Cd, γ-CD, Polycaprolactone, and Their Inclusion Complexes

	polycaprolactone					α- and γ-CD			
samples	a	b	c, d	e	f	C1	C4	C2, C3, C5	C6
PCL	169.8	160.6	161.5	223.6					
	3.28	1.23	1.22	1.68					
α-CD/PCL	0.24	0.26	0.31	0.29		31.7	24.3	18.3	0.84
α-CD						147.4	169.4	161.5	110.5
						1.32	8.64	3.34	6.65
γ-CD/PCL	0.22	0.19	0.28	0.17		31.3	22.2	18.0	0.85
γ-CD						78.1	35.9	36.4	16.2
									1.04

Table 4. $T_{1\rho}$(^{13}C) Values for the Carbon Nuclei of α-Cd, γ-CD, Polycaprolactone, and Their Inclusion Complexes

	polycaprolactone					α− and γ-CD			
samples	a	b	c, d	e	f	C1	C4	C2, C3, C5	C6
PCL	23.1	17.4	14.8	18.1	169.0				
α-CD/PCL	17.3	14.9	15.3	12.9	24.7	124.5	52.5	46.8	8.5
α-CD						50.5	38.8	34.8	10.5
γ-CD/PCL		3.83	3.82	1.38		40.1	40.8	27.0	10.0
γ-CD						38.2	23.4	33.0	10.4

and γ-CD frames also show similar relaxation rates, although γ-CD is in closer contact with PCL chains than α-CD as evidenced by the heteronuclear correlation and $T_{1\rho}$(H) experiments.

^{13}C spin−lattice relaxation times in the rotating frame ($T_{1\rho}$(^{13}C)) have been shown to be sensitive to molecular motions in polymers with frequencies in the range of tens of kilohertz.[28−30] However, not only can the frequency, the amplitude, and anisotropy of the molecular motion affect the relaxation rate of the ^{13}C nuclei, but also the fluctuations of the dipolar field due to mutual ^{1}H−^{1}H spin flips may cause relaxation of the ^{13}C nuclei, which complicates the interpretation of $T_{1\rho}$(^{13}C) as a motional probe.[31] Table 4 presents the $T_{1\rho}$(^{13}C) relaxation times of semicrystalline PCL, α-CD/PCL, α-CD, γ-CD/PCL, and γ-CD. The results show significant changes in $T_{1\rho}$(^{13}C) with complex formation for both the polymer and the CDs. And we also note that there is a difference for PCL chains incorporated inside the different host matrices α-CD and γ-CD, with reduced $T_{1\rho}$(^{13}C)'s observed for PCL in the latter. Either the cooperative motions that are possible for side-by-side parallel PCL chains in the γ-CD/PCL inclusion complex are facilitating their kilohertz motions, or because their protons are in closer proximity than those of single PCL chains and α-CD, $T_{1\rho}$(^{13}C) relaxation by mutual proton spin flips is enhanced. Although we observe that the higher frequency (megahertz) motions of isolated PCL chains in the complexes probed by T_1(^{13}C) relaxation measurements are similar to the motions of amorphous polymers, we could not observe the minimum in $T_{1\rho}$(^{13}C) as a function of temperature, which can generally be observed for amorphous polymers.[31]

Information about the molecular dynamics of polymers can also be obtained from the NMR line shapes. The lines are broadened by the combination of chemical shift anisotropy, homo- and heteronuclear dipolar couplings, and, for deuterium, quadrupolar couplings.[14,15] If the polymer dynamics are fast compared to the line width, then a motionally averaged line shape will be observed. Deuterium NMR is often used for these studies because the deuterium line shape is extremely sensitive to both the rate and amplitude of atomic fluctuations.[32] It is also possible to monitor the chain dynamics using the proton line shapes. Broad lines are observed in the proton spectra, mostly because of the strong proton−proton dipolar couplings (60 kHz). The proton chemical shift range is 10 ppm (4 kHz), so the individual lines are not resolved, but they can be observed indirectly in 2D NMR experiments using wideline separation (WISE) NMR.[20] A major advantage of the WISE experiment over the direct measurement of the proton line shapes is that the proton line widths are correlated with the carbon chemical shifts, so it is possible to measure the proton line shapes for each resolved carbon resonance in the spectrum.

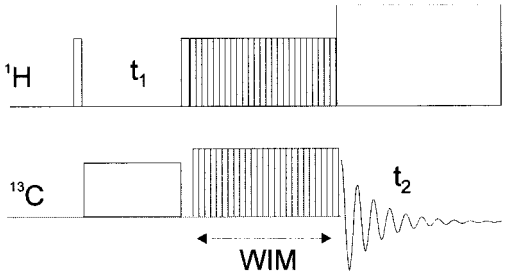

Figure 8. Pulse sequence diagram for 2D WISE NMR with windowless isotropic mixing during cross-polarization. Carbon decoupling is turned on during the t_1 period to remove the broadening from heteronuclear dipolar couplings.

We recently introduced a modified version of WISE in which the cross-polarization step is replaced with windowless isotropic mixing (WIM).[13] The advantage of the WIM/WISE experiment (Figure 8) is that the WIM quenches spin diffusion during the cross-polarization.[19,21] This means that the proton line widths can be directly related to the dynamics of individual protons, rather than the average values for the entire chain that is measured using the original WISE experiment.[20] We have used the pulse sequence with carbon decoupling during the t_1 period to remove the line broadening from carbon−proton dipolar couplings.[33]

Figure 9 shows the proton line shapes obtained from cross sections through the 2D WISE spectrum for the C1 carbon of α-CD and the PCL methylene carbons *a*, *e*, and *c*/*d* in the inclusion complex. Broad lines (26−41 kHz) are observed for PCL in the proton dimension, showing that the polymer chains are restricted in the inclusion compounds but more mobile than rigid organic solids. We observe large line width differences between some of the PCL peaks, showing that the dynamics are not identical for all parts of the chains.

Table 5. Proton Line Widths for α-Cd, γ-CD, Polycaprolactone, and Their Inclusion Complexes Measured by 2D WIM/WISE NMR

	line width (kHz)[a]							
	α-CD				polycaprolactone			
sample	C1	C4	C2, C3, C5	C6	a	b	c, d	e
α-CD	45	46	45	59				
α-CD/PCL	44	47	40	45	41	33	30	26
γ-CD	45	46	45	59				
γ-CD/PCL	46	40	40			34	26	34
PCL					62	51	54	52

[a] The reported line widths are the full width at half-maximum.

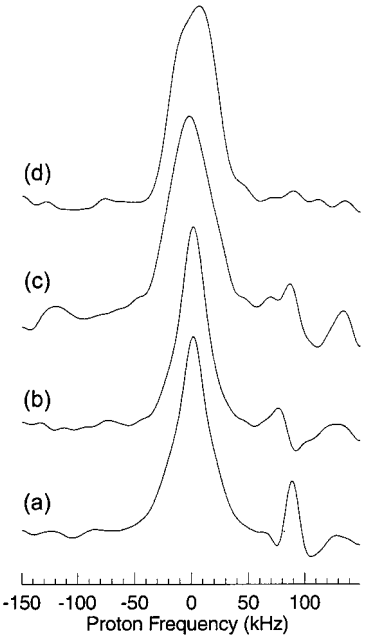

Figure 9. Cross sections through the 2D WIM/WISE spectrum for the α-CD/polycaprolactone inclusion complex at the frequency of the polycaprolactone carbons at (a) 24 ppm, (b) 29 ppm, (c) 64 ppm, and (d) the α-CD carbons at 101 ppm.

Table 5 lists the full width at half-maximum for pure α-CD and γ-CD, semicrystalline PCL, the crystalline α-CD/PCL, and γ-CD/PCL inclusion complexes. For pure α-CD, the line widths for all the carbons except C6 are about 45 kHz. The larger line width for C6 is most likely due to the fact that this is a methylene carbon, and the geminal protons (which are separated by 1.78 Å) have very strong dipolar interactions. The line widths for all the carbons of γ-CD are exactly the same as those of α-CD, reflecting that the dynamics of pure CDs in the dipolar decoupling range are not affected by the number of glucose units. Broader lines (51−62 kHz) are observed for the protons in semicrystalline PCL.

The line widths for PCL in the inclusion complex with α-CD are reduced relative to semicrystalline PCL. The methylene nearest the carbonyl group (*e*) shows the largest reduction in line width, from 52 kHz in semicrystalline PCL to 26 kHz in the inclusion complex. The methylenes at the center of the PCL monomer (*c, d*) are reduced from 54 kHz in the crystal to 30 kHz in the complex. The methylene nearest the ester oxygen (a) shows the smallest change in line width (51 to 41 kHz). This demonstrates that the chain is not uniformly restricted in the channel but that some methylene groups are more mobile than others. There is also a large change in line width for the α-CD C6 carbon upon formation of the complex. For the γ-CD/PCL inclusion complex, since there is significant overlap of methylene carbon *a* with the C6 carbon of γ-CD, we are only able to test the proton line widths of methylene carbons *b*, *c*/*d*, and *e* of PCL chains and C1, C2/C3/C5, and C4 carbons of γ-CD. There is not much change in the proton line widths of γ-CD upon complex formation. The proton lines of included PCL chains are much narrower than those of semicrystalline PCL chains, and the methylene groups do not exhibit uniform mobility either.

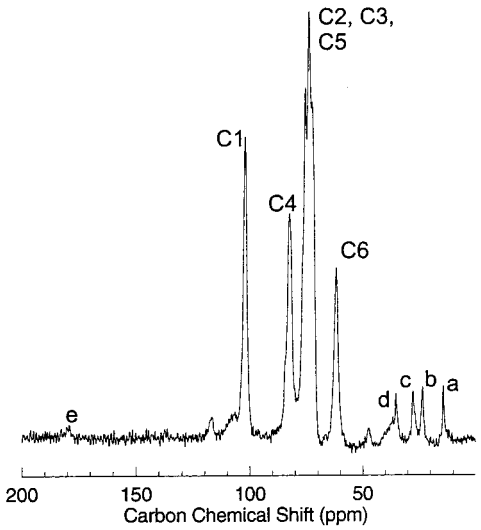

Figure 10. Carbon CPMAS spectrum of the α-CD/valeric acid inclusion complex.

X-ray diffraction is one of the most important methods for identifying and classifying the inclusion complexes formed with α-CD's.[1] Several different types of structures have been identified, including channel-type, herringbone cage-type, and brick cage-type crystal structures. The X-ray pattern for α-CD/PCL inclusion complex closely resembles that observed for the inclusion compound formed between valeric acid (VA) and α-CD,[5] which has been identified as a channel-type structure.[16] We have studied the NMR properties of the α-CD/VA inclusion compound to measure how the structure and dynamics of included small molecules compare with their polymer counterparts.

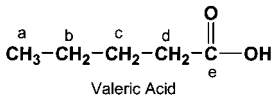

Figure 10 shows the CPMAS spectrum of the α-CD/VA inclusion complex. The four small peaks at 35.2, 27.6, 23.4, and 14.3 ppm are assigned to the methylene and methyl carbons of the valeric acid, and the signal at 179.1 ppm is assigned to the carbonyl. The chemical shifts for the α-CD carbons in the α-CD/VA inclusion complex are similar to those for the inclusion complex with PCL.

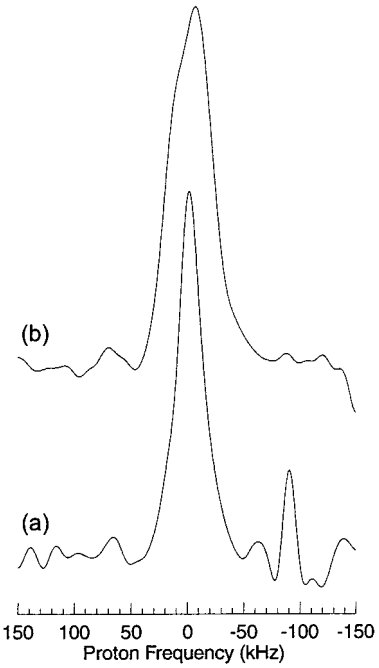

Figure 11. Cross sections through the 2D WIM/WISE NMR spectrum of the α-CD/valeric acid inclusion complex at the frequency of the (a) valeric acid carbon at 25 ppm and (b) the α-CD carbon at 101 ppm.

Table 6. Proton $T_{1\rho}$ Relaxation Times for α-CD and the Valeric Acid-α-CD Inclusion Compound

	$T_{1\rho}$ (ms)	
samples	α-CD	valeric acid
α-CD	4.9	
α-CD/valeric acid	8.4	8.1

We have measured the proton $T_{1\rho}$ relaxation times for the α-CD/VA inclusion complex to explore how magnetization exchange in the α-CD/small molecule complex compares with the polymer inclusion complexes. The results of the relaxation studies are listed in Table 6. In contrast to the α-CD/PCL complexes, identical relaxation times are measured for both α-CD and VA. This shows that there is efficient spin diffusion between the α-CD host and the small molecule guest. VA is a liquid at ambient temperature, so it is not possible to measure the solid-state proton $T_{1\rho}$ relaxation times. We note that the relaxation time for α-CD in the complex is increased relative to pure α-CD, which also suggests that there is efficient guest−host spin diffusion.

We have used WIM/WISE NMR to study the molecular dynamics of the α-CD/VA inclusion compound for comparison with the polymer complex. Some typical results are shown in Figure 11, which compares the line shapes for the α-CD C1 carbon and the valeric acid methylene carbon *c* at 25.7 ppm. Again, we note that there is a large difference in the line widths for the host and the included small molecule. The widths (Table 7) for the α-CD are similar to those observed for the polymer complex. For VA in the complex, the line widths for the methylenes nearest the carbonyl are most restricted, and the methyl group has the smallest line width. This result is expected because the dipolar interactions are partially averaged by methyl group rotation.

Discussion

Polymer inclusion compounds are of interest for a number of possible applications, including the fabrication of high-strength materials and novel composites.[7] CDs are particularly interesting as host materials because they are readily available, there are several types of CDs with a range of pore sizes, and they can accommodate a variety of polymers.[4−7] Since only a single chain can fit in the α-CD cavity, these inclusion complexes are a way to measure the single-chain conformational, dynamic, optical, and electrical properties of polymers in the solid state. On the other hand, γ-CD is large enough to accommodate two side-by-side parallel chains. By comparing the NMR observations of PCL chains in the α-CD and γ-CD channels with identical NMR observations of semicrystalline bulk PCL polymers, we can gain some insight into the relative contributions made to the properties of ordered, bulk polymers by the inherent behavior of single, segregated and stretched polymer chains, the interaction between immediately adjacent chains, and overall cooperative interchain interactions.

Solid-state NMR has emerged as an important method for polymer characterization, since NMR can be used to study the structure, dynamics, and length scale of mixing. In the current studies we used proton relaxation times and the 2D heteronuclear correlation experiment to measure magnetization exchange between the polymer in the channel and the host material, and we have used carbon spin−lattice relaxation, carbon spin−lattice relaxation in the rotating frame, and 2D wide-line separation NMR to measure the dynamics of semicrystalline PCL and its CD inclusion complexes.

The structures of the PCL inclusion complex with CDs have been studied by several methods, including DSC, FTIR, and X-ray diffraction.[5,6] The X-ray data are consistent with the formation of channel-type inclusion complexes, and the carbon chemical shifts suggest that the polymer adopts an extended all-trans conformation in the channels.

Solid-state NMR utilizing proton spin diffusion is one of the most effective ways to measure the length scale of mixing in polymer blends[23] and for measuring domain sizes in phase-separated and semicrystalline polymers.[14,15] A quantitative interpretation of the spin diffusion in terms of the length scale of phase separation is possible because spin diffusion has been calibrated on block copolymers with well-defined morphologies.[34,35] In contrast to other well-mixed polymer systems, the α-CD/PCL inclusion complex shows incomplete spin

Table 7. Proton Line Widths for α-CD and the Valeric Acid-α-CD Inclusion Compound Measured by 2D WIM/WISE NMR

	line width (kHz)[a]							
	α-CD				valeric acid			
samples	C1	C4	C2, C3, C5	C6	a	b	c	d
α-CD	45	46	45	59				
α-CD/valeric acid	44	46	42	47	15	34	24	33

[a] The reported line widths are the full width at half-maximum.

diffusion between the polymer and the host matrix. α-CD has a 4.9 Å channel, and the available evidence strongly suggests that there is a channel-type complex formed, so that the polymer is expected to be within spin diffusion distance of the α-CD. We believe this inefficient spin diffusion can be related to fundamental differences in the proton density in the inclusion complexes relative to the more extensively studied polymer blends, semicrystalline polymers, and phase-separated materials.

Proton spin diffusion over length scales as long as 200 Å is the result of many individual magnetization transfer steps. The rate of spin diffusion depends on polymer chain dynamics and the proton density and can be estimated as[36]

$$D = \frac{13a^2}{T_2}$$

where a is the average distance between adjacent protons and T_2 is the spin−spin relaxation time. The rate of spin diffusion in glassy polymers, such as polystyrene and poly(methyl methacrylate), appears to be well-described by a single spin diffusion coefficient.[35] For mobile polymers the spin diffusion coefficients scale with the T_2.[37−39]

We believe that the fundamental difference between most materials and the polymer inclusion complexes is that the proton density is not uniform. There is a high density of protons along the polymer chain and in the α-CD that can promote efficient spin diffusion. In most solid polymers there are van der Waals contacts between chains that cause the protons from neighboring chains to be in close contact. The polymer in the inclusion complex is constrained by chain connectivity to occupy the center of the channel. It may be that this forces the PCL and the α-CD protons to be more distant than they would be in normal organic solids, and this greater separation is the reason that we do not see efficient spin diffusion between the polymer and the host. However, since there are two side-by-side, parallel PCL chains incorporated inside the γ-CD channels, the distance between the included PCL chains and γ-CD may be somewhat closer, leading to more efficient spin diffusion between the polymer and the guest. Modeling studies are currently underway to evaluate this hypothesis. We recognize that this explanation is somewhat speculative and that other explanations, such as rapid axial motions about the chain axis that might reduce the PCL−CD dipolar couplings, cannot be rigorously excluded without additional experiments. The small molecule inclusion complexes do not have the long-chain constraint to occupy the center of the channel since the guest does not span many α-CD molecules. In fact, a 1:1 stoichiometry is observed[16] in the case of the α-CD/VA complex, and we observe efficient spin diffusion between the host and the guest.

The two-dimensional (2D) heteronuclear correlation (HETCOR) experiment is a powerful means to measure spin diffusion rates, to probe miscibility in a polymer blend,[24] and to investigate the intermolecular interactions in miscible polymer blends.[18] By applying this experiment with 10 ms mixing time to the inclusion complexes, we can clearly observe the diffusion of proton spins between the polymer and hosts in the complexes. It is more straightforward and powerful than the proton $T_{1\rho}$ experiment. The results show that there is incomplete spin diffusion between the polymers and α-CD, but complete spin diffusion between the polymers and γ-CD in the complexes, which are consistent with the results of proton $T_{1\rho}$ experiments. This experiment also provides a straightforward method to verify the formation of the complex structure.

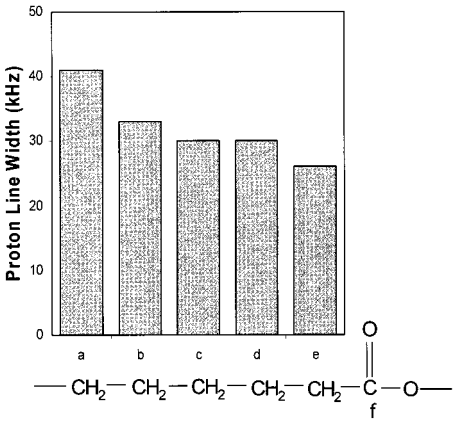

Figure 12. Plot of the proton line widths measured by 2D WIM/WISE NMR for each polycaprolactone methylene in the α-CD/polcaprolactone inclusion complex (see Table 5 and Figure 7).

The chain dynamics of PCL measured from the proton line shape in the inclusion complex differ from those observed for the semicrystalline material. The chains are relatively rigid in semicrystalline PCL, and we measured proton line widths on the order of 51−54 kHz using 2D WIM/WISE NMR spectroscopy. In the inclusion complex we find that the line widths are greatly reduced, showing that the polymer in the channel is not rigid but experiences local atomic fluctuations. Furthermore, using the WIM/WISE method,[13] we can measure the line widths for neighboring methylene units along the chain without the complications of spin diffusion. The results show that the line widths correlate with position along the chain. This is illustrated in Figure 12, which shows a plot of the line width vs position along the chain in polycaprolactone. The line width is greatest for the methylene nearest the main chain oxygen (41 kHz) and systematically decreases toward the other end of the monomer, where a line width of 26 kHz is observed for the methylene nearest the carbonyl group. We believe this difference in line width may arise from interactions between the polymer chain and the α-CD. The most likely explanation for this behavior is hydrogen bonding between the polycaprolactone backbone oxygens and the hydroxyl groups in α-CD, as suggested by FTIR data.[5] However, we do not observe such a gradient in proton line widths for pairs of PCL chains included in γ-CD (see Figure 13), which most likely reflects the increased cooperative nature of the motion of side-by-side, parallel PCL chains.

The small molecule inclusion complex formed between α-CD and VA shows different spin diffusion behavior but similar dynamics. The line widths for the VA are similar to those observed for PCL in the complex, showing that the small molecule is not rigidly held in the inclusion complex but experiences large-amplitude fluctuations that are fast on the time scale of the dipolar couplings (60 kHz). That overall rotation of VA about its backbone is not occurring in its α-CD inclusion complex is implied by the commensurate VA and PCL observed line widths, which would be expected to be much narrower for VA if it was rotating.

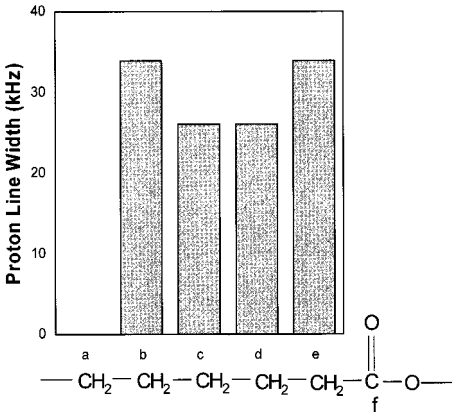

Figure 13. Plot of the proton line widths measured by 2D WIM/WISE NMR for each polycaprolactone methylene in the γ-CD/polcaprolactone inclusion complex (see Table 5).

In summary, we have used solid-state NMR to probe the structure and dynamics of the α- and γ- inclusion complexes with PCL and compared with the α-CD channel complex formed with the model compound VA. The α-CD inclusion complex with PCL differs from other materials in that there is not an even distribution of protons, so that spin diffusion is inefficient when the PCL chains have to occupy the center of α-CD channels, but efficient for pairs of PCL chains in γ-CD channels due to the closer distance between the guest and the host. Unlike polymers, small molecules are not constrained to the center of the channel and show efficient spin diffusion. Complex formation is driven by intermolecular interactions, and these interactions exert an effect on the chain dynamics, with those portions of the chain nearest the main chain oxygen being the most restricted for the α-CD complex. However, we did not observe such a dynamic gradient for pairs of PCL chains in the γ-CD complex, which may be due to the increased cooperative nature of the motion of side-by-side, parallel PCL chains.

References and Notes

(1) Szejtli, J. *Chem. Rev.* **1998**, *98*, 1743.
(2) Saenger, W. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 344.
(3) Schneider, H. J. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1417.
(4) Harada, A.; Kamachi, M. *Macromolecules* **1990**, *23*, 2821.
(5) Huang, L.; Allen, E.; Tonelli, A. E. *Polymer* **1998**, *39*, 4857.
(6) Huang, L.; Allen, E.; Tonelli, A. E. *Polymer* **1999**, *40*, 3211.
(7) Tonelli, A. E. *Polym. Int.* **1997**, *43*, 295.
(8) Sozzani, P.; Bovey, F. A.; Schilling, F. C. *Macromolecules* **1991**, *24*, 6764.
(9) Sozzani, P.; Behling, R. W.; Schilling, F. C.; Bruckner, S.; Helfand, E.; Bovey, F. A.; Jelinski, L. W. *Macromolecules* **1989**, *22*, 3318.
(10) Shin, I. D.; Huang, L.; Tonelli, A. E. *Macromol. Symp.* **1999**, *138*, 21.
(11) Vasanthan, N.; Shin, I. I. D.; Tonelli, A. E. *Macromolecules* **1994**, *27*, 6515.
(12) Tonelli, A. E.; Lu, J.; Shin, I. D.; Mirau, P. A. *PMSE Prepr. (Am. Chem. Soc.)* **2000**, *82*, 163.
(13) Qiu, X.; Mirau, P. *J. Magn. Reson.* **2000**, *142*, 183.
(14) Bovey, F. A.; Mirau, P. A. *NMR of Polymers*; Academic Press: New York, 1996.
(15) Schmidt-Rohr, K.; Spiess, H. W. *Multidimensional Solid-State NMR and Polymers*; Academic Press: New York, 1994.
(16) McMullan, R. K.; Saenger, W.; Fayos, J.; Mootz, D. *Carbohydr. Res.* **1973**, *31*, 37.
(17) White, J. L.; Mirau, P. A. *Macromolecules* **1994**, *27*, 1648.
(18) Burum, D. P.; Bielecki, A. *J. Magn. Reson.* **1991**, *94*, 645.
(19) Caravatti, P.; Braunschweiler, L.; Ernst, R. R. *Chem. Phys. Lett.* **1983**, *100*, 305.
(20) Schmidt-Rohr, K.; Clauss, J.; Spiess, H. W. *Macromolecules* **1992**, *25*, 3273.
(21) Caravatti, P.; Bodenhausen, G.; Ernst, R. R. *Chem. Phys. Lett.* **1982**, *89*, 363.
(22) Gidley, M. J.; Bociek, S. M. *J. Am. Chem. Soc.* **1988**, *110*, 3820.
(23) McBrierty, V.; Douglass, D.; Kwei, T. *Macromolecules* **1978**, *11*, 1265.
(24) Kaplan, S. *Macromolecules* **1993**, *26*, 1060.
(25) Lu, J.; Mirau, P. A.; Tonelli, A. E. *Prog. Polym. Sci.*, in press.
(26) Comotti, A.; Simonutti, R.; Catel, G.; Sozzani, P. *Chem. Mater.* **1999**, *11*, 1476.
(27) Kawaguchi, Y.; Nishiyama, T.; Okada, M.; Kamachi, M.; Harada, A. *Macromolecules* **2000**, *33*, 4472.
(28) Schaefer, J.; Stejskal, E. O.; Buchdahl, R. *Macromolecules* **1977**, *10*, 384.
(29) Schaefer, J.; Stejskal, E. O.; Steger, T. R.; Sefcik, M. D.; McKay, R. A. *Macromolecules*, **1980**, *13*, 1121.
(30) VanderHart, D. L.; Garroway, A. N. *J. Chem. Phys.* **1979**, *71*, 2773.
(31) Kevin, S. J.; Whittaker, A. K. *Macromolecules* **1997**, *30*, 3560.
(32) Wendoloski, J.; Gardner, K.; Hirschinger, J.; Miura, H.; English, A. *Science* **1990**, *247*, 431.
(33) Tekely, P.; Palmas, P.; Mutzenhardt, P. *Macromolecules* **1993**, *26*, 7363.
(34) Cai, W. Z.; Schmidt-Rohr, K.; Egger, N.; Gerharz, B.; Spiess, H. W. *Polymer* **1993**, *34*, 267.
(35) Clauss, J.; Schmidt-Rohr, K.; Spiess, H. W. *Acta Polym.* **1993**, *44*, 1.
(36) Cheung, T.; Gerstein, B. *J. Appl. Phys.* **1981**, *52*, 5517.
(37) Mellinger, F.; Wilhelm, M.; Spiess, H. W. *Macromolecules* **1999**, *32*, 4686.
(38) Carr, H. Y.; Purcell, E. M. *Phys. Rev.* **1954**, *94*, 630.
(39) Meiboom, S.; Gill, D. *Rev. Sci. Instrum.* **1958**, *29*, 6881.

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