Order Determinations in Liquid Crystals by Dynamic Director NMR Spectroscopy

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Liquid−crystalline polymers (LCPs) constitute an important class of macromolecules with numerous applications as ultrastrong materials and nonlinear optical devices.[1] A defining characteristic of these polymers is their ability to organize into aligned domains when molten or dissolved in suitable solvents and preserve this order upon freezing or coagulation. NMR can play an important role in the design of LCP-based materials by enabling the quantification of macromolecular order in their fluid phases.[2] So far studies of this kind have involved deuterium,[3] a quadrupolar probe which although sensitive demands site-specific isotope enrichment. Recently we have shown that order determinations in synthetic LCPs can also be reliably executed by analyzing the anisotropic displacements observed via natural abundance ^{13}C NMR,[4] a simple approach that provides simultaneous information for all inequivalent sites in the monomer. Unfortunately, as the chemical complexity of a polymer grows, such ^{13}C NMR experiments become impractical due to the difficulty to ascribe each nematic resonance to a particular chemical site. The present Communication describes a new spectroscopic approach for bypassing these limitations, based on a combination of NMR measurements and discrete reorientations of the nematic director achieved by mechanical means.

The type of spectral difficulties that may be encountered in natural abundance LCP studies are illustrated in Figure 1 on *poly*(pentamethylene-diphenoxyterephthalate) (**1**), a main-chain thermotropic polyester first synthesized by Lenz and co-workers that shares several features of interest with commercial analogues.[5] ^{13}C resonances appearing in both the high-resolution solid state and the molten isotropic NMR spectra of **1** can be readily assigned to individual sites based on standard substituent chemical shifts. NMR spectra recorded between the melting and clearing points, however, present resonances significantly shifted from these δ_{iso} frequencies due to the onset of liquid crystallinity. Although these liquid crystal displacements $\Delta\delta = \delta_{lc} - \delta_{iso}$ carry valuable information about the sites order parameters, the ambiguities that arise upon attempting to establish the chemical origin of the nematic peaks (and thus their $\Delta\delta$ values) preclude their reliable use in order analyses. Assigning ^{13}C NMR spectra for low molecular weight nematics becomes feasible with the aid of rapid sample spinning at an angle β, as this enables the discrimination of individual isotropic and anisotropic chemical shift contributions.[6] Although reminiscent of coherent averaging, the goal of nematic variable-angle-spinning (VAS) is not modulating spin interactions but achieving a deviation between the orientations of the director ***D*** and the external field B_o. Once this is accomplished rapid rotational diffusion discriminates between anisotropic and isotropic interactions, scaling the former by $P_2(\cos\beta) = (3\cos^2\beta - 1)/2$ while leaving the latter unaffected. Despite the success of VAS procedures toward analyses of low molecular weight nematics,[6] their application to structural polymers such as **1** faces a number of complications. These include the limited range of β angles that can be explored by virtue of the ***D*** randomization usually occurring when $\beta > 54.7°$ and of irradiation constrains associated to conventional VAS assemblies, the inherently large ^{13}C line widths characterizing LCPs, the relatively extreme temperatures or pressures at which nematic phases arise for structural thermotropics, and the high viscosities of these fluids.

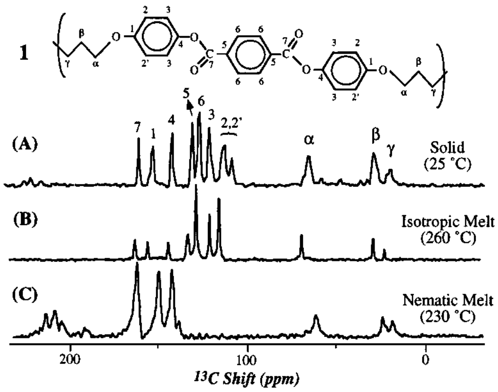

Figure 1. ^{13}C NMR spectra recorded for **1** in the solid phase (A), in its isotropic melt (B), and as a nematic (C). The polyester was prepared by condensing under N_2 4,4′-dihydroxy-1,6-diphenoxypentane with terephthaloyl chloride in tetrachloroethane/pyridine[5a] and characterized by elemental analysis, polarized microscopy, and DSC. NMR measurements were carried out at 7.1 T using a laboratory-built spectrometer, a dynamic-angle-spinning probe built around a 5 mm Doty stator for the solid experiments, and a high-temperature fixed-solenoid probe incorporating a sample container coupled to a stepping motor for the fluid state acquisitions. The solid measurements employed cross polarization, dipolar decoupling (70 kHz), and sample spinning at 7 kHz; fluid spectra were collected using 5 μs $\pi/2$ excitations, NOE, and WALTZ-16 decoupling. Differences between the intensities of protonated and nonprotonated ^{13}C resonances in the solid and fluid phases originate from distortions introduced by the NOE.

In view of these complications, we decided to explore an alternative route capable of discriminating iso- and anisotropic ^{13}C shifts over an extended angular range while avoiding the spinning of the liquid crystal altogether. Our scheme exploits the relatively long director relaxation times and high viscosities of LCPs, to achieve a scaling of the spin anisotropies with the aid of discrete ***D*** reorientations in and out of its equilibrium position. Events in these experiments thus begin with an initial relaxation delay during which both spins and nematic are allowed to equilibrate in B_o; this is followed by an NMR pulse sequence applied in synchrony with well defined ***D*** reorientations implemented with the aid of a stepping motor and concluded with a return of the sample to its initial orientation in preparation for a new scan (Figure 2A). The relaxation time of the nematic imposes a limit to the duration that ***D*** may remain away from equilibrium, but for most synthetic LCPs as well as for numerous biological liquid crystals and monomeric smectics these times exceed 10^{-1} s and are consequently compatible with a majority of NMR pulse sequences. In fact for numerous LCPs these

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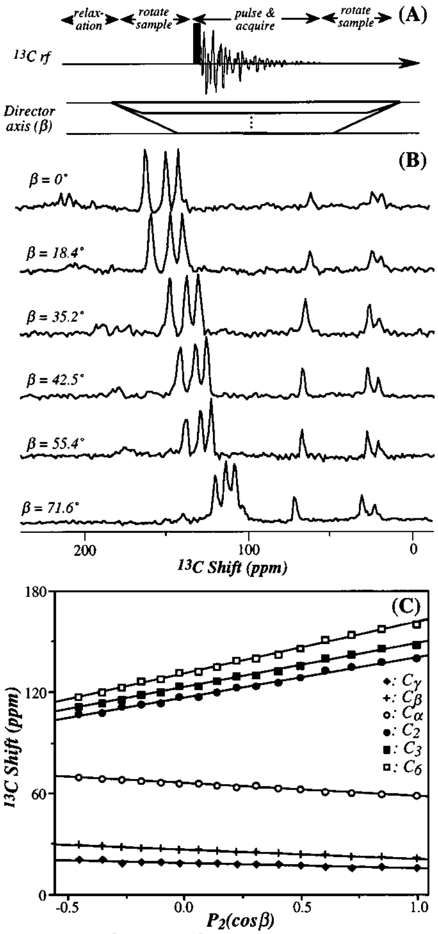

Figure 2. (A) Basic dynamic director NMR strategy. (B) Dynamic director ^{13}C NMR spectra of **1** in its nematic phase collected at the indicated β angles. Samples throughout these experiments were rotated away from equilibrium inside a static radio frequency solenoid positioned perpendicular to B_o using a parabolic acceleration/deceleration profile. In no cases were samples kept in a $\beta \neq 0°$ state for over 100 ms; by comparison, the experimental time measured for the **D** relaxation was in the order of 10 s. The absence of reorientation-induced disturbances in the nematic was further confirmed by the identical appearances of the $\beta = 0°, 180°$ spectra. (C) Linear dependence observed for the scaled dynamic director shifts of the protonated ^{13}C sites in **1** as a function of $P_2(\cos\beta)$.

Table 1. ^{13}C NMR Parameters for **1** [a]

site[b]	δ_{iso}[c] (solid)	δ_{iso}[d] (isotropic melt)	δ_{iso}[e] (nematic)	$\Delta\delta$[e] (nematic)	S_{local}[f]
1	155	154.5	153.5	+49.5	0.6
2	116	114.0	116.0	+24.5	0.7
3	123	119.0	121.5	+26.5	0.7
4	144	142.5	144.5	+54.0	0.6
5	133	131.5	*g*	*g*	*g*
6	129	127.0	129.0	+30.5	0.6
7	163	161.5	162.5	+45.0	
α	67	67.0	66.5	−7.5	
β	31	26.5	26.5	−5.5	
γ	24	20.0	19.5	−3.0	

[a] In ppm's downfield from TMS. [b] Assignment as in Figure 1A. [c] ±1 ppm (25 °C). [d] ±0.5 ppm (260 °C). [e] ±0.5 ppm (230 °C), from dynamic director data. [f] Local order parameters determined for the aromatic carbon sites. [g] Ambiguous measurement due to poor S/N.

director relaxation times are in the order of several minutes,[7] thus demanding long preequilibration periods during which the nematic is allowed to align in B_o prior to beginning the data acquisition. Director relaxation also defines the maximum ratio between the times that ***D*** may be allowed to spend on and off its equilibrium position; even for relatively low molecular weight polymers such as **1** ($M_W \approx 1$ kD) we found that when this duty cycle is kept below 5% extensive signal averaging is possible without any apparent disturbances in the nematic alignment.

Figure 2B illustrates a basic application of this dynamic director approach, involving the acquisition of ^{13}C NMR spectra as a function of different angles β between ***D*** and B_o. From these data it is possible to accurately extract the individual isotropic and anisotropic ^{13}C contributions to the resonances, using either a linear least-squares fit (Figure 2C) or a bidimensional processing analogous to the one employed in 2D variable-angle correlation spectroscopy.[8] The isotropic values available from these displacements reveal the chemical origin of each nematic resonance (Table 1), while their shift anisotropies enable the estimation of average local order parameters. To extract such ordering information, it is also necessary to know the magnitudes and orientations of the individual ^{13}C chemical shift tensors as well as the averaging occurring in the liquid crystal due to rapid interconversions between rotational isomers. The principal shielding components for **1** were measured using 2D VAS isotropic-anisotropic correlation NMR,[8] a technique that can clearly resolve individual powder patterns for the various chemical sites in the monomer (Supporting Information). The principal axes of these tensors were then oriented within a molecular reference frame using reliable literature guidelines.[9] Ambiguities arose, however, upon considering the conformational averaging occurring in the polymer. Although an all-trans configuration might be energetically favored by the alkyl spacers, such arrangement would deprive the main polymer chains from linearity and thus severely disturb the overall nematic order. Evidence that carbons in the alkyl spacers are actually undergoing fast conformational interconversions is provided by the liquid crystal ^{13}C NMR data, which show decreasing anisotropic displacements for methylene carbons positioned further away from the aromatic mesogens and no systematic differences (e.g., γ-gauche effects) between the isotropic $-CH_2-$ shifts in the ordered and random phases. A similar behavior has been reported for another main-chain nematic by ^{2}H NMR.[3a] Due to the ensuing uncertainty in spacer dynamics, we limited the calculations to local order parameter estimations for the mesogenic groups. These S_{local} parameters equal the overall macromolecular nematic order times a scaling factor $\langle P_2(\cos\alpha)\rangle$ depending on the average angle that each aromatic group subtends with respect to the nematic director. The resulting figures are summarized in Table 1; the relatively large uncertainities of these parameters (±0.05) reflect the error margins with which the individual static shielding tensors could be measured. It is worth noting that these S_{local} values are incompatible with all-trans alkyl chain conformations, whose geometries would otherwise lead to unreasonable polymeric order parameters larger than 1.

These initial results illustrate the potential of dynamic director NMR to the interpretation of natural abundance LCP spectra. In many respects this technique complements the analytical power of established VAS methods by facilitating studies under extreme conditions, extending the range of accessible director angles to the entire $0° \leq \beta \leq 360°$ interval, and providing a way of dealing with highly viscous systems. We also found dynamic director experiments useful for characterizing molecular distributions and director relaxation in lyotropic LCPs and smectics; a complete report on these investigations will be presented in an expanded publication.

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