Synthesis of a ^{13}C-Labeled Oligomer: Solid-State NMR and Theoretical Studies

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Main-chain thermotropic liquid crystalline polymers (LCPs), which consist of rigid mesogens and flexible spacers, produce different liquid crystalline states depending on the chemical structures of the constituent units and on the chemical bonds connecting the units. LCPs containing an ester functional group in a mesogenic unit have long been the subject of studies of intermolecular interactions. Many theoretical and experimental works have examined the planarity between the benzene rings and adjacent carbonyl group, or the location of bond rotation above the phase transition (solid-to-liquid crystal).[1,2] Many publications have already reported syntheses, structures, and properties of the LCPs.[3,4] More recent characterizations of structure and chain conformation have been carried out using different analytical methods, such as X-ray diffractometry,[5] small angle neutron scattering,[6] transmission electron microscopy,[7] and FT-IR,[8] solid-state ^{2}H NMR,[9] and ^{13}C NMR[10] spectroscopy. Of these, high-resolution solid-state NMR spectroscopy is the most powerful method for characterizing the detailed structure and molecular motion of the constituent units. In particular, it can be used to analyze the chain conformation, orientation, and intermolecular interactions, such as hydrogen bonding, of carbons or other nuclei in the mesogens, spacers, and their connecting units in all possible states of LCPs.

Therefore, high-resolution solid-state ^{13}C NMR spectroscopy was used to determine the properties and structure of this **12-4** oligomer. ^{13}C chemical shifts of carbonyl carbons in **12-4** (Figure 1) are especially important, accounting for the possibility of hydrogen bonding between the carbonyl oxygen near the ethyl terminal and one of the hydrogen atoms of the poly(ethylene oxide) (PEO) chain.[11] We must unambiguously assign the two free C=O groups, because this will correctly identify which C=O group participates in the hydrogen bonding. In addition, the behavior of the other C=O group, which is in the mesogen part, reflects the phase transition temperature. However, it is not easy to distinguish the chemical shifts of C4 and C15 in high-resolution solid-state NMR spectra. To assign the chemical shifts correctly, we synthesized **12-4** oligomer ^{13}C-labeled in position C4 to clarify the assignment.

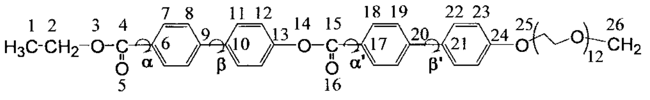
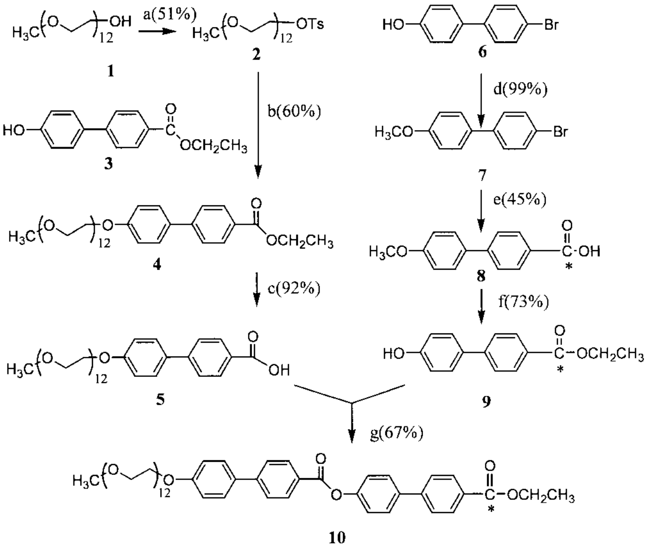


Figure 1. Schematic diagram and numbering of atoms for **12-4** oligomer.



Scheme 1. Synthesis of ^{13}C-labeled **12-4** oligomer. (a) TsCl, pyridine, (b) NaH, **3**/DMSO, 60 °C, (c) NaOH/MeOH-H_2O, reflux, (d) NaH, CH_3I/DMF, (e) i) Mg/THF, ii) $^{13}CO_2$(g), (f) BBr_3/CH_2Cl_2, 0 °C, (g) DIPC, DPTS/CH_2Cl_2.

10 was synthesized from polyethyleneglycol monomethyl ether (**1**, M_w = 700) and 4-bromo-4'-hydroxyl biphenyl, as shown in Scheme 1. Using a known procedure[3], the tosylate of 1 was coupled with **3** and then hydrolyzed to **5**. The hydroxyl group of **6** was protected with a methoxy group before the Grignard reaction followed by carboxylation with ^{13}C-labeled carbon dioxide ($^{13}CO_2$) to give **8**. The methoxy group was removed from **8** with BBr_3 and the carboxylic group was transformed to the ethyl ester **9**. Esterification of acid **5** with alcohol **9** was performed under mild conditions using diisopropylcarbodiimide (DIPC) and *N,N*-dimethylaminopyridine *p*-toluenesulfonate (DPTS). The structure of **10** was confirmed by comparing the ^{1}H NMR spectrum[12] with that of unlabeled **10**.[3]

The ^{13}C MAS (magic angle spinning) spectra in Figure 2 were acquired with a Bruker DSX400 system at 9.4 Tesla and 130 °C, which is near the phase transition temperature (135.2 °C) obtained from DSC measurement.[3] The spin rate, pulse length, and pulse repetition delay were 4.7 kHz, 2 μs, and 1s, respectively, and 180-217 transients were accumulated.

Comparison of experimental and theoretical spectra can be

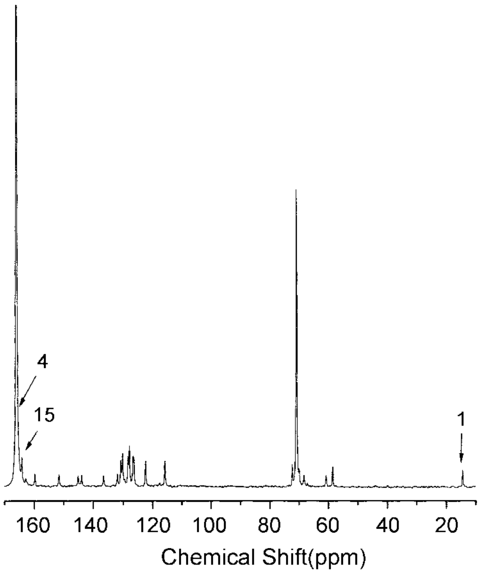


Figure 2. MAS ^{13}C NMR spectrum of labeled **12-4** oligomer at 130 °C.

very useful for understanding the basic chemical shift/molecular structure relationship. *Ab initio* NMR calculations are now feasible and accurate enough to be useful for understanding the relationship between the chemical shift and molecular structure. The calculated ^{13}C chemical shifts appear to be of sufficient accuracy to aid in experimental peak assignment.[13] The isotropic ^{13}C chemical shifts were calculated to determine the structure and assign the experimental peaks using the HF-GIAO/6-31G**//HF/6-31G* and B3LYP-GIAO/6-31G**//HF/6-31 G* approaches. Table 1 lists selected dihedral angles and GIAO theoretical isotropic ^{13}C chemical shifts relative to TMS obtained at the Hartree-Fock and DFT (Density Functional Theory) levels of theory for **12-4** oligomer. To simplify the calculation, only one out of 12 PEO units is adopted. Table 1 shows that the benzene rings of the biphenyl groups are not coplanar, with a dihedral angle of about 45°, while the ring-ester linkages are coplanar with dihedral angles of about 0°. Moreover, the calculated isotropic ^{13}C chemical shift of C4 is bigger than that of C15 in both the HF-GIAO and B3LYP-GIAO results. These trends are in good agreement with experimental results.

Table 1. Selected Dihedral Angles and the Calculated and Experimental Isotropic ^{13}C Chemical Shifts of 12-4 Using GIAO

	dihedral angle(deg)			
	α' (5,4,6,7)	α' (15,16,17,18)	β (8,9,10,11)	β' (19,20,21,22)
	0.39	135.21	0.51	-44.16
Method	δ_{iso} (ppm)			
	C1	C4	C15	
HF/6-31G*	15.848	158.752	157.480	
HF/6-31G**	15.864	160.216	158.895	
B3LYP/6-31G*	14.849	151.314	150.713	
B3LYP/6-31G**	14.842	153.231	152.578	
Expt.	14.202	166.265	164.241	

In conclusion, in solid NMR spectroscopy, the observed ^{13}C chemical shift and line width of each carbon reflect the conformation and dynamics of molecules and largely depend on temperature. Based on the firm assignment of the C4 and C15 chemical shifts in this study, the analysis of their isotropic ^{13}C NMR chemical shift and line broadening versus temperature will help to determine conformational and dynamics changes during the LC phase transition (solid-to-liquid crystal). Moreover, comparing experimental values with the NMR parameters calculated from the geometric structures[14] described as a function of α, β, α', and β', the structure of the **12-4** oligomer at each temperature can be searched systematically. This is in progress.

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12. ^{1}H NMR ($CDCl_3$) of 10: δ 1.42 (t, 3H, $CH_2\underline{CH_3}$, J = 7.2 Hz), 3.37 (s, 3H, CH_3O), 3.50-3.75 (m, 44H, OCH_2), 3.90 (t, 2H, $O\underline{CH_2}CH_2OPh$, J = 5.1 Hz), 4.20 (t, 2H, $OCH_2\underline{CH_2}OPh$, J = 5.1 Hz), 4.41 (q, 2H. $O\underline{CH_2}CH_3$), 7.04 (d, 2H, Ar-H, J = 8.7 Hz), 7.35 (d, 2H, Ar-H, J = 8.8 Hz), 7.60-7.70 (m, 4H, Ar-H,), 7.63-7.80 (m, 6H, Ar-H), 8.12 (d, 2H, Ar-H, J = 8.5 Hz), 8.25 (d, 2H, Ar, J = 8.4 Hz).
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