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Deuterium NMR analysis of main-chain polymer liquid crystals

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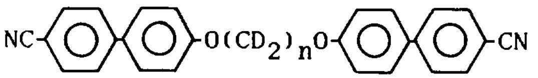
SUMMARY

Deuterium NMR measurements have been performed for main-chain polymer liquid crystals having structures such as $\{\phi\text{-OC(O)-}\phi\text{-O(CD}_2)_n\text{O-}\phi\text{-C(O)O-}\phi\text{-O(CH}_2)_n\text{O}\}_x$ with $n = 9, 10$. D-NMR spectra obtained in the nematic mesophase are compared with those previously reported for the dimer liquid crystals of the type $\text{NC-}\phi\text{-}\phi\text{-O(CD}_2)_n\text{O-}\phi\text{-}\phi\text{-CN}$ with $n = 9, 10$. Although resolutions are relatively poor in the polymer spectrum, the general profiles of the spectra were found to be similar to those of the corresponding dimer. The results of the RIS analysis suggest that the spatial configurations of the spacer are nearly identical between the dimer and polymer. It has been concluded that the observed enhancement in the quadrupolar splittings should arise largely from a higher orientational ordering of the molecular axis in the polymeric system.

INTRODUCTION

Main-chain polymer liquid crystals (PLC) comprising a rigid mesogenic core and a flexible spacer in a repeating unit often exhibit a distinct odd-even effect in various thermodynamic quantities at the nematic-isotropic (NI) transition temperature. In these liquid crystals, the order-disorder transition of the anisotropic mesogen is coupled with conformational changes of the flexible spacer.[1-3] Determination of the conformation permitted in the nematic mesophase is of primary importance in understanding the molecular mechanism of such transitions. The deuterium NMR method has been proved to be useful for this purpose. The quadrupolar splittings observed in the mesophase represent the average orientation of the deuterium labeled bond.

In a previous communication,[4] we have reported the deuterium NMR spectra and some preliminary results of the analysis for dimer liquid crystals (DLC) such as



$\text{NC-}\phi\text{-}\phi\text{-O(CD}_2)_n\text{O-}\phi\text{-}\phi\text{-CN}$

(I-n)

with $n = 9$ and 10. Observations carried out just below T_{NI} yielded the spectra of well-defined peaks: the sample with $n = 9$ exhibited four splittings in the relative intensity ratio of 4:2:1:2 starting from the outside signal, while the spectrum of $n = 10$ was found to consist of three splittings in the ratio 2:2:1. In both samples, the outermost peaks include

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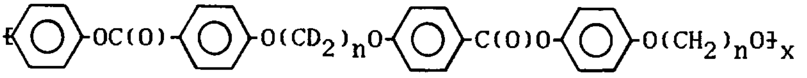
*To whom offprint requests should be sent contribution from the α- and β-CD bonds. The RIS analysis of the spectra has been carried out according to the procedure previously established.5)

In this paper, a similar treatment has been extended to polymer liquid crystals such as


(II-n)

with n = 9 and 10. Some physical properties of these polymers including D-NMR spectra have been reported by Yoon et al.3) These polymers form a reasonably stable nematic mesophase below 200 °C: thus the temperature range is suitable for the NMR investigation. As indicated above, PLC II comprises two flexible spacers in a repeating unit. The difference between these two spacers arises from the arrangement of the ester group incorporated in the mesogenic core. In this study, we introduced deuterons only in one kind of spacers in order to enhance the resolution in the D-NMR spectroscopy. Our compounds differ slightly from those of Yoon et al. who used samples deuterated at both spacers.

In both compounds I and II, the flexible spacer is jointed by the ether linkage with the mesogenic cores. Since these compounds bear a common structural feature in the spacer, we may expect similar odd-even characteristics with n between these two series of liquid crystals.

EXPERIMENTAL

PLC II samples were prepared by the ester exchange reaction according to the prescription given by Van Luyen et al.6) The polymers formed were purified by reprecipitation from a mixture of phenol (60%) and 1,1,2,2-tetrachloroethane (40%) by addition of acetone. The thermodynamic data obtained by using DSC are summarized in Table I, where values reported in literatures are also included.

The D-NMR spectra were recorded on a JEOL JNM-GSX-270 spectrometer. Measurements were carried out under a complete proton decoupling and non-spinning mode.

Table I. Thermodynamic Properties of PLC II-n at the NI Transition

n	$[\eta]^a$	T_{NI}	ΔH^b	ΔS^b	ref.
	dl g^{-1}	°C	kcal$(mru)^{-1}$	cal $K^{-1}(mru)^{-1}$	
9	0.62	200	1.12	2.37	this work
		189	0.92	2.0	3
		200			6
10	0.46	204	2.46	5.15	this work
		215	1.56	3.2	3

[a] The intrinsic viscosities measured in a mixture of phenol (60%) and 1,1,2,2-tetrachloroethane (40%) at 30 °C.

[b] For the repeating unit depicted in the text, these values must be doubled.

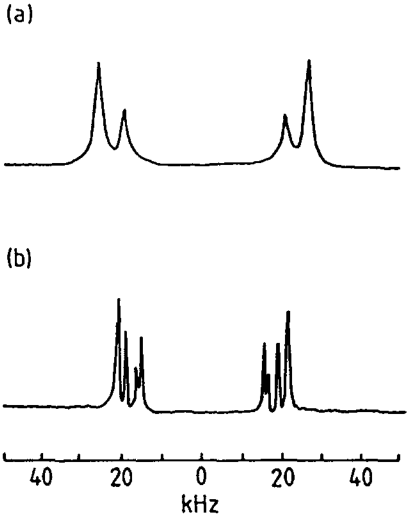


Figure 1. D-NMR spectra of (a) PLC II-9 (188 °C) and (b) DLC I-9 (172 °C).

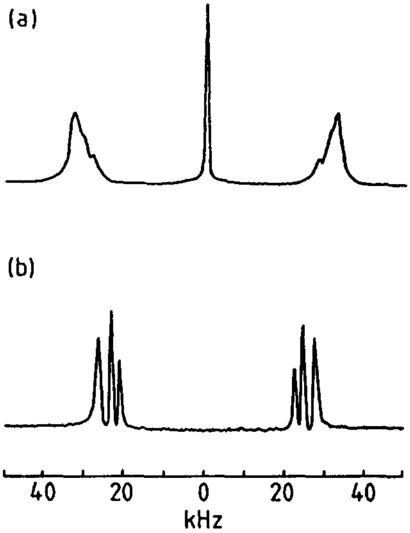


Figure 2. D-NMR spectra of (a) PLC II-10 (199 °C) and (b) DLC I-10 (184 °C).

RESULTS AND DISCUSSION

The D-NMR spectra observed for polymers II-9 and II-10 are shown in Figures 1 and 2, respectively. In these diagrams, the spectra obtained previously for dimers I-9 and I-10 are also included for comparison. Because of the tempatature limit of the JEOL apparatus, we were obliged to run our measurements below 200 °C. Sample II-10 has therefore never reached its T_{NI} in the NMR magnet. A sharp peak appearing in the center of the spectrum indicates that some poorly aligned domain still remains under the experimental condition. For II-9, the NI transition takes place below 200 °C. In this sample, the molecules can be easily aligned in a mono domain by lowering the temparature from the isotropic state. The dimer samples are less viscous, and therefore the resolution of the signal is better in Figures 1b and 2b. The observed quadrupolar splittings are somewhat larger for the polymer than those for the corresponding dimer, indicating that the orientational order is higher in the polymeric system. The general profiles of the peaks are, however, quite similar between the dimer and polymer for a given n. The four splittings observed for I-9 in Figure 1b are transformed into two doublets with broad peaks for II-9 in Figure 1a. The peak intensity ratio varies from 4:2:1:2 to 2:1. With n = 10, polymer II-10 exhibits a doublet with two shoulder peaks. The fine profiles observed for the dimer (Figure 2b) are largely lost in the polymer spectrum (Figure 2a), but the two figures still have much in common.

The RIS simulations were iterarively carried out until the observed D-NMR spectra were satisfactorily reproduced. Following the previous treatment, the molecular axis was defined by the vector connecting the centers of two adjacent mesogenic cores. The statistical weight parameter set obtained for the dimer was adopted as the initial set in the simulation of the corresponding polymer spectrum. From the nematic fraction thus elucidated, bond conformation probabilities can be easily estimated. The trans fraction (f_t) obtained for the individual bonds of the spacer are listed in Table II, where the constituent carbon atoms are numbered from the ether terminal. For the O-C_1 bond, f_t = 1.0, and thus the value is not given in the table. Conformations for the bonds other than those listed can be deduced by symmetry. With n = 9, values of f_t tend to increase slightly for all of the C-C bonds on going from the dimer to the polymer. When n = 10, the profile of the D-NMR spectrum varies rather insensitively with the conformation around the bonds such as C_3-C_4 and C_5-C_6. As pointed out by Yoon et al.[3], these bonds tend to align parallel with the mesogenic core axis in the nematic conformation. Considering the fact that the observations were carried out at temparatures close to the NI transition, conformational statistical weights of these bonds were set equal to the values usually adopted in the unconstrained state. The results shown in Table II suggest that the spatial configurations of the spacer are nearly identical between the dimer and polymer. The observed enhancement in the quadrupolar splittings (cf. Figures 1 and 2) should be attributed to a higher orientational ordering of the molecular axis in the polymeric system. The details of the analysis will be reported in the forthcoming paper.

Table II. The Trans Fraction Estimated for the Individual C-C Bonds in the Nematic Phase

bond	dimer		polymer	
	I-9	I-10	II-9	II-10
C_1-C_2	0.54	0.42	0.57	0.36
C_2-C_3	0.74	0.92	0.77	0.97
C_3-C_4	0.50	0.50	0.51	0.48
C_4-C_5	0.64	0.86	0.67	0.91
C_5-C_6	——	0.50	——	0.48

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