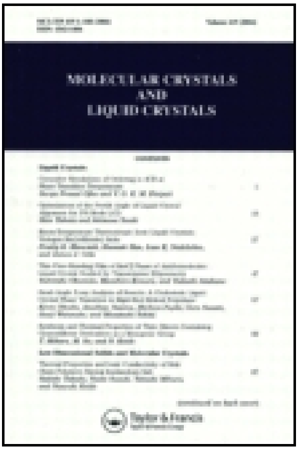

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D-NMR Study on Orientation of D-Labeled Benzyl Group in PBLG Liquid Crystal

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D-NMR Study on Orientation of D-Labeled Benzyl Group in PBLG Liquid Crystal†

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D-NMR was clearly observed from the concentrated dichloromethane solution of PBLG (0.346 gr/ml), in which helical PBLG polymers form a cholesteric state in case of no magnetic field. The observed spectrum was decomposed into a singlet and five doublets, among which the doublet having smallest separation was stronger than the singlet and the rests. Since the doublets originate from the quadrupolar splitting of the Zeeman level of deuteron, the observed doublets mean the partial alignments of the benzyl groups in the liquid crystalline state. The order parameters were estimated as 0.0040, 0.025, 0.072, 0.10, and 0.13 from the observed splittings of the five doublets and $e^2qQ = 167$ KHz for a static C—D bond. The singlet means complete averaging of the quadrupolar splitting due to a rapid motion. By rotating the sample about the axis perpendicular to the magnetic field, the observed separation of the strongest doublet was changed immediately after the rotation and reached to the former equilibrium value after ca. several minutes of the residence time. A dependence of the instantaneous separation upon the rotation angle, θ, was well approximated by $|3\cos^2\theta - 1|$. The spin-lattice relaxation times of both the singlet and the strongest doublet were found to be same. This fact suggests that rates of the molecular motions are almost same in the states corresponding these peaks. A model for the motion of the side chain end is proposed to explain the results consistently.

1 INTRODUCTION

It is known[1] that poly-γ-benzyl-L-glutamate (PBLG) molecules have solid helical structures in dichloromethane solvent and show cholesteric textures in a concentrated solution. The order parameters of the helical axis was deter-

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†Presented at the Eighth International Liquid Crystal Conference, Kyoto, July 1980.

mined[2] and various information is accumulated on this system.[1] However, little is known on degree of order and molecular motion of the side-chains of PBLG in this texture, except for a pioneer work by Samulski.[3, 4] Thus, it seems to be interesting to find out how much orientation of the side chain is different from the ordered orientation of the helical axes of PBLG molecules and also how mobile the side-chains being under intramolecular constraint caused by the covalent bonds with the main chain. In order to carry on this kind of experiments one has to determine a local order as well as a local mobility of the side chain of PBLG in a choresteric phase.

Spin-labeling technique[5] combined with ESR measurement was proved to be most useful for determination of such local order and mobility. However, this spin labeling technique has one disadvantage. Guest molecules should be introduced in a system and introduction of these foreign molecules may perturb the system. One may say that such perturbation could be negligible if concentration of the guest molecules is taken as less as possible. It is true if a bulk property is measured for a system containing a negligible concentration of the labeling molecules. Information obtained by magnetic resonance is actually collected from the guest molecules, around which the system is perturbed considerably. Thus, it is most desirable to use guest molecules, which produce the least disturbance to a system. Deuterium labeling is much more superior to the paramagnetic labeling used for ESR measurements on this point. Replacement of hydrogen atoms in a molecule with deuteriums causes actually no significant perturbation on the system. On the other hand it is well established that D-NMR is a very useful method to find out how a C—D bond is aligned in a magnetic field.[3-4, 6-8] By labeling a particular part of a molecule with deuterium one can obtain information on local orientation as well as mobility of the deuterized part of the molecule selectively.

2 EXPERIMENTAL

d_7-PBLG, in which the benzyl side chains are selectively deuterated, was prepared from polymethyl glutamate by ester exchange with deuterated d_7-benzyl alcohol in our laboratory. Deuteration of the benzyl group was checked by observation of D-NMR chemical shifts corresponding to phenyl and methylene groups, which were observed from d_7-PBLGs in coiled forms in a trifluoroacetic acid solution. Molecular weight of the used d_7-PBLG was found as 42,000 by the viscosity measurement. The concentration of the studied samples, which were dichloromethane solutions of the d_7-PBLG, were 0.340 gr/cc and 0.255 gr/cc, respectively. The concentrated dichloromethane solutions of PBLG with these concentrations were known to be of a cholesteric phase in the temperature range from 40°C to 30°C. The phase of the samples were confirmed by the optical measurement. It is also known[1] that the cholesteric phase of the concentrated solution of PBLG is destroyed and converted into a ne-

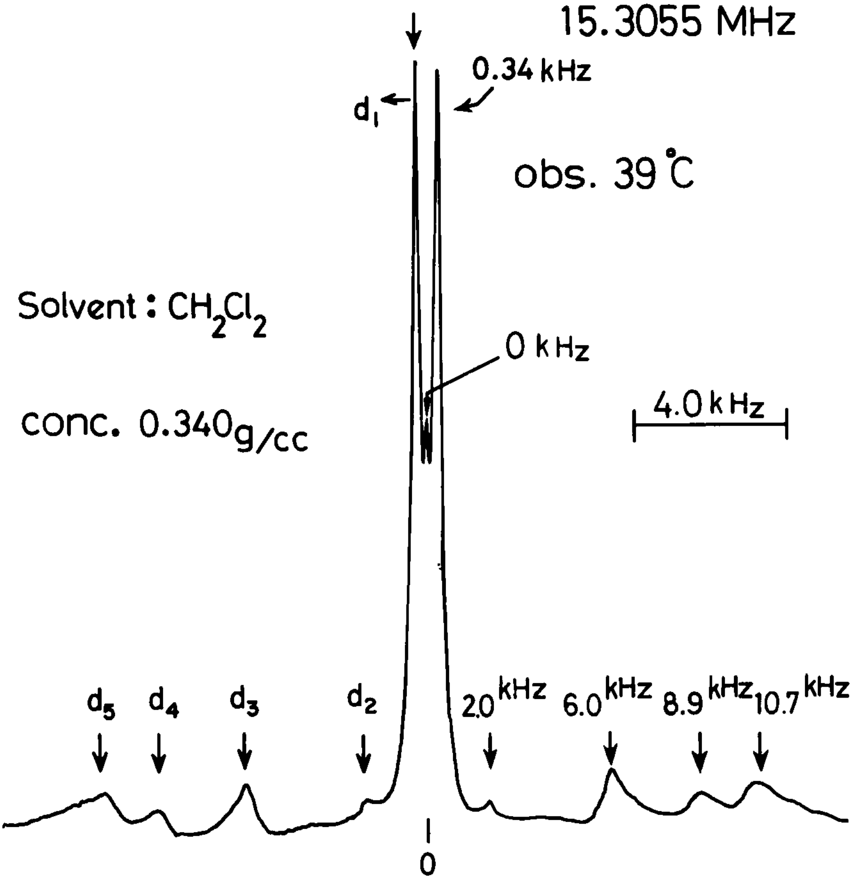

FIGURE 1 D-NMR spectrum of d_7-PBLG in CH_2Cl_2 solvent (conc. 0.340 gr/ml) observation temperature was 39° C.

matic phase under a high magnetic field, ca. 2.4 K Gauss, which was used for D-NMR in these experiments. JEOL FX100 Multinuclei Spectrometer was used for observation of D-NMR in a range of 15 MHz.

3 RESULTS

3.1 Observed spectra

An example of D-NMR spectrum observed from the d_7-PBLG in dichloromethane solvent is shown in Figure 1. In this trace there are apparently five doublets, one of which is very strong, and one singlet at the center of the spectrum. This spectrum is almost same to that reported by Samulski[3] except for two different points. In his spectrum there are four doublets and the doublet marked with d_2 in Figure 1 is lacking. The second is no appearance of the sin-

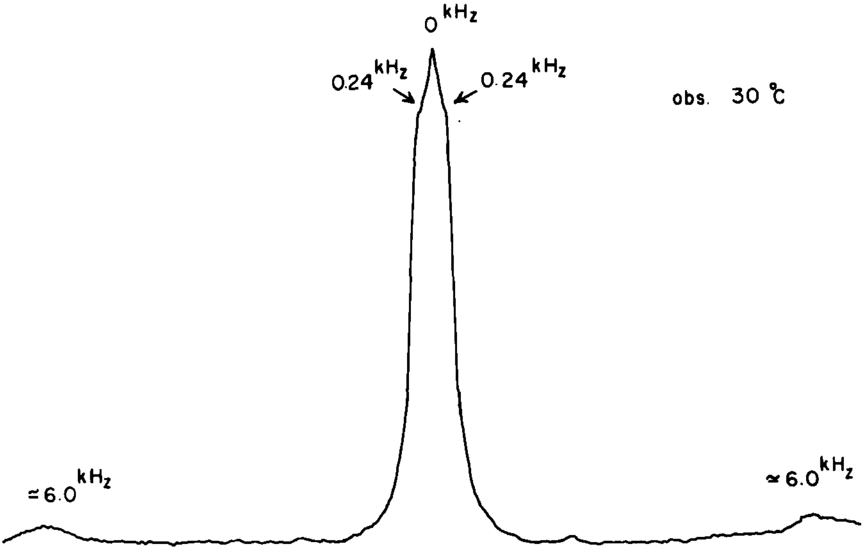

FIGURE 2 D-NMR spectrum observed at lower temperature (30° C) from the same sample showing the spectrum in Figure 1.

glet in his spectrum. A spectrum shown in Figure 2 was obtained from the same sample at 30° C, which is about 10° lower than the former observation. No clear doublets appeared in the spectrum and shoulders of the central peak suggest an existence of a smeared doublet. A spectrum observed at 39° C from a less concentrated (conc. 0.255 gr/ml) solution is shown in Figure 3. In this spectrum the central peak is enhanced and the intensities of all the doublets are suppressed.

3.2 Dependence of the doublet separation upon angles deviating from the magnetic field

After observing the spectrum shown in Figure 1, the sample tube was rotated about an axis perpendicular to the magnetic field by a fixed angle θ. Immediately after this rotation, the splitting of the strongest doublet was observed. The observed splittings were plotted against the rotation angles, and the result is shown in Figure 4. This angular dependence is well approximated by $(3\cos^2\theta - 1)$ equation, as shown with solid line. In this experiment the separations were measured in several seconds after each rotation and the orientation towards magnetic field was recovered by some degree before each measurement. Poor agreements between the results and the theoretical line in the neighborhood of the magic angle is due to enhanced experimental errors caused by sensitive angular dependence in this region.

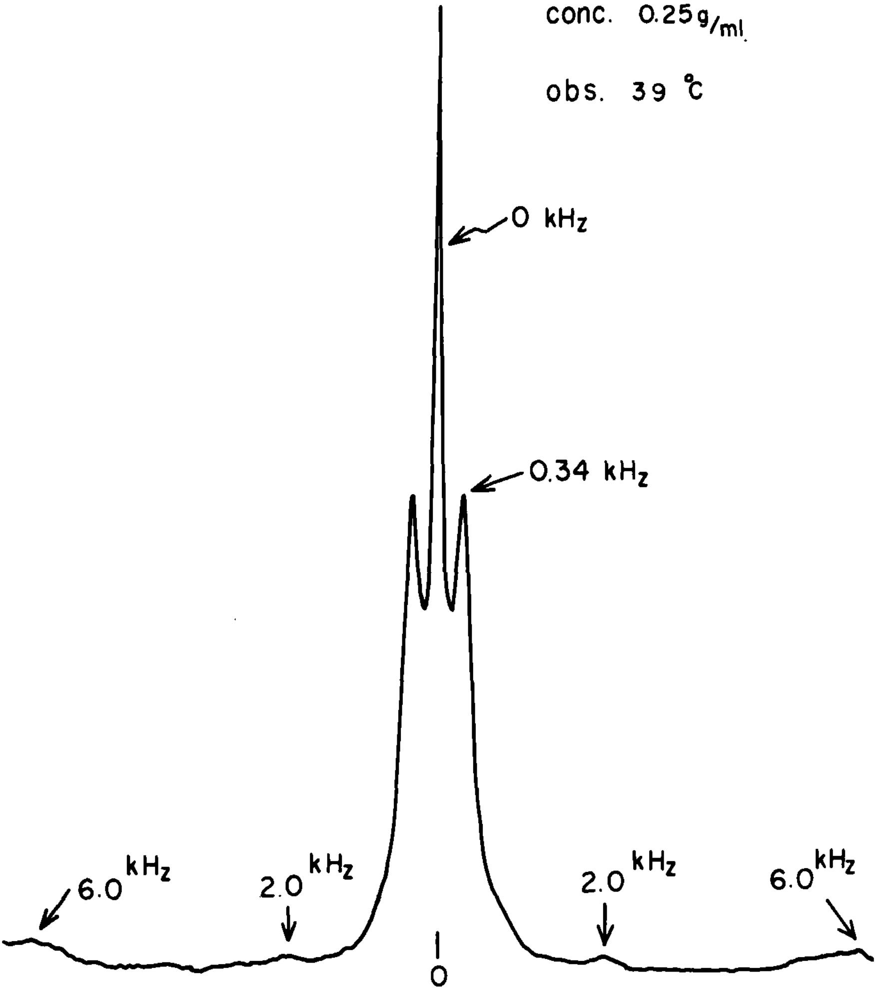

FIGURE 3 D-NMR spectrum observed at 39° C from a less concentrated solution (conc. 0.25 gr/ml) of d_7-PBLG in CH_2Cl_2.

3.3 Residence time dependence of the doublet splitting

The line-shape of the strongest doublet in the spectrum in Figure 1 varied with the residence time of the solution in the magnetic field after the rotation of the sample tube. Similar residence time dependence was observed for a *d-d* splitting of proton resonance of dichloromethane as the solvent. Figure 5 shows the residence time dependence of the separations of the two doublets; one is the quadrupolar doublet of the deuterated benzyl group and the other is the dipolar doublet of the solvent molecules. It is worthy to note that both separa-

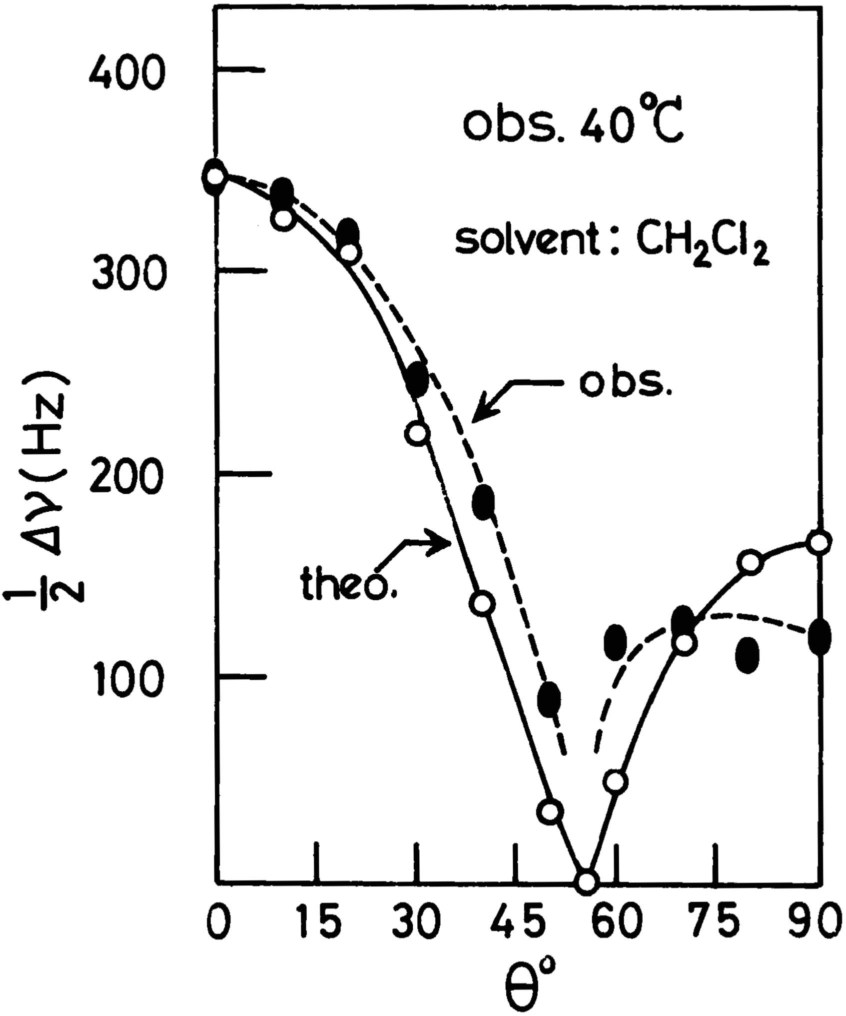

FIGURE 4 Separation of the strongest doublet in Figure 1 against the angle deviation from the magnetic field. Filled circles: observed. Solid line: ($3\cos^2\theta - 1$) dependence.

tions after the rotation recover their original separations at almost the same time of the residence, namely ca. 100 sec.

3.4 ^2D-T_1 measurements of d_7-PBLG

Spin-lattice relaxation times of D-NMR were measured for both the central singlet and the strong doublet in the spectrum in Figure 1. Semi log plots of the recoveries of the intensities at τ m sec. after each 180° pulse are shown in Figure 6. The recoveries of the doublet and the singlet are represented with a

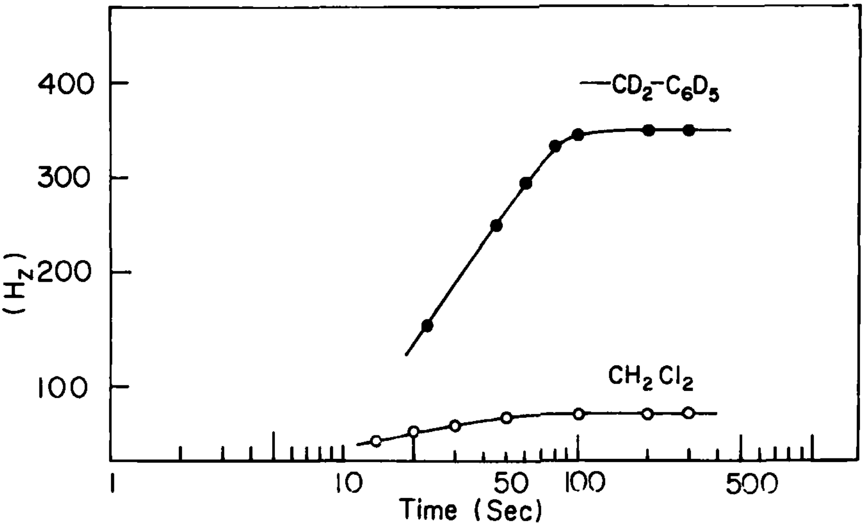

FIGURE 5 Residence time dependence of the separations after the rotation of the sample tube. The separations of the strongest doublet are shown with filled circles and doublet separations in ^{1}H-NMR of solvent CH_2Cl_2 are represented with open circle.

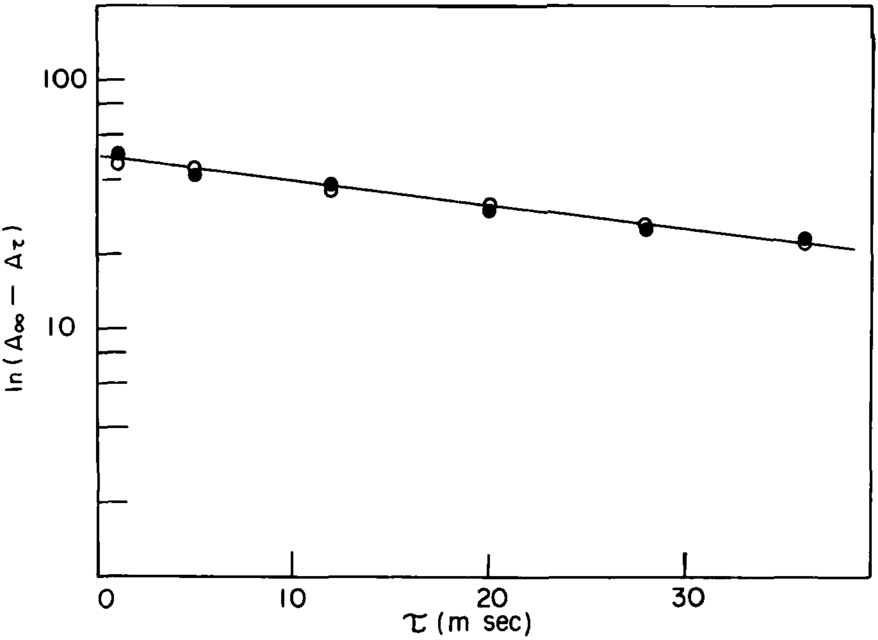

FIGURE 6 Semi log plots of recoveries of the intensities of both the doublet and the singlet against time τ. The open circles represent the recovery of the doublet, the filled circles do for the singlet.

single straight line within an error, as shown in the figure. The spin-lattice relaxation times for these two components are estimated approximately 40 m sec. It is worthy to note that the spin-lattice relaxation time of the doublet is equal to that for the singlet, which results from complete averaging of the quadrupolar splitting.

4 DISCUSSION

The quadrupolar splitting of D-NMR, $\Delta\nu_Q$, is related to an order parameter, S, of a C—D bond in a liquid crystal through a following equation[9] in case of axial symmetry,

$$\Delta\nu_Q = \frac{3}{4}\frac{e^2qQ}{h}S \tag{1}$$

where e^2qQ/h is the quadrupolar splitting constant in which q is the electric field gradient along the C—D bond. Assuming such a simple circumstance and 167 kHz for the e^2qQ/h value of the C—D bond[10] one may estimate the order parameters from the observed splittings of the five doublets in the spectrum shown in Figure 1. The results are listed in Table I. The order parameters determined are much lower than that ($S \approx 0.5$)[1] of the helical axis of PBLG molecules in a similar texture. Especially the order parameter derived from the strong doublet (d_1) is quite different from that of the helical main-chain but rather close to that ($S = 2.82 \times 10^{-3}$)[3] for the free toluene-d_8 in PBLG liquid crystal. This suggests that the benzyl groups resulting in this strong doublet are as mobile and less oriented as the free molecules in the liquid crystal phase, although all the benzyl groups are constrained by the chemical bonds with the highly oriented PBLG main-chain. This is also supported by the fact that the splitting of this strong doublet is nearly equal to that of benzyl alcohol-d_7 dissolved in an oriented PBLG—CH_2Cl_2 solution,[3] in which the dissolved benzyl-alcohol molecules are almost freely mobile. In the case of that a direc-

TABLE I

Order parameters determined from the observed splittings of quadrupolar doublets in the spectrum shown in Fig. 1.

	$\Delta\nu$ (kHz)	S
d_1 (strongest doublet)	0.681	0.0040
d_2	4.15	0.025
d_3	12.1	0.072
d_4	17.8	0.10
d_5	21.4	0.13

e^2qQ/h is assumed to be the 167 kHz[9] for C—D bond.

tor, *n*, is titled by an angle α from the magnetic field, the quadrupolar splitting is modified as the following expression

$$\Delta\nu_Q = \frac{3}{4}\frac{e^2qQ}{h}(3\cos^2\alpha - 1)\cdot S \tag{2}$$

Experimental results on the splittings obtained after the rotation of the sample tube were found to be expressed by the $(3\cos^2\theta - 1)$, which is the same modification of the Eq. (2). This means that the local director, n_l, to which the order parameter derived from the strong doublet is referred, is aligned along the magnetic field before the rotation. This parallel alignment of the local director for the benzyl group also suggests that the benzyl group showing the strong doublet is aligned being free from the static intramolecular constraints, which was theoretically derived by Scheraga *et al.*[11]

The spin-lattice relaxation time T_1 of the strong doublet is equal to that of the singlet resulting from a complete averaging of the quadrupolar splitting. This equality indicates that the benzyl groups responsible for the strong doublet are very much mobile as that for the singlet, although some degree of the order in the orientation is still survived for the benzyl groups showing the doublet. Higher mobility of the groups at the side-chain end of PBLG in the liquid crystal phase has been also concluded by T_1 measurements in ^{13}C-NMR.[12] Based on these T_1-measurements of D and ^{13}C-NMRs one may conclude that the benzyl groups at the side-chain ends are highly mobile. The most probable mode of such a highly mobile motion for the phenyl groups at the side-chain ends is a rotation about the axis along the chemical bond connecting the pheny to the methylene. Under such a rotational motion with the high rate the quadrupolar tensors along the C—D bonds in the phenyl group are dissolved into two components, one is parallel to and the other is perpendicular to the rotational axis. (cf. Figure 7) The latter components for all C—Ds in the phenyl are completely averaged out due to the rapid rotation. Thus, the orientations for all C—Ds are now parallel to the para-C—D direction, and this is probably the reason why this doublet is the strongest among the other doublets. And the order parameter determined from the strong doublet is a fluctuation of this component of the quadrupolar tensor along the rotational axis of the phenyl groups at the end of the side chain.

The conclusions derived from this experiment are summarized as follows:

1) The phenyl groups at the side chain ends undergo very rapid rotational motion.

2) The local order parameter derived from the strong doublet is that for the orientation of the *eqQ* component parallel to the rotational axis of the phenyl.

3) The local order of the side-chain ends are much more smaller than that of the helical axis of PBLG molecules in the liquid crystal but close to that for the free molecules dissolved in an oriented PBLG solution.

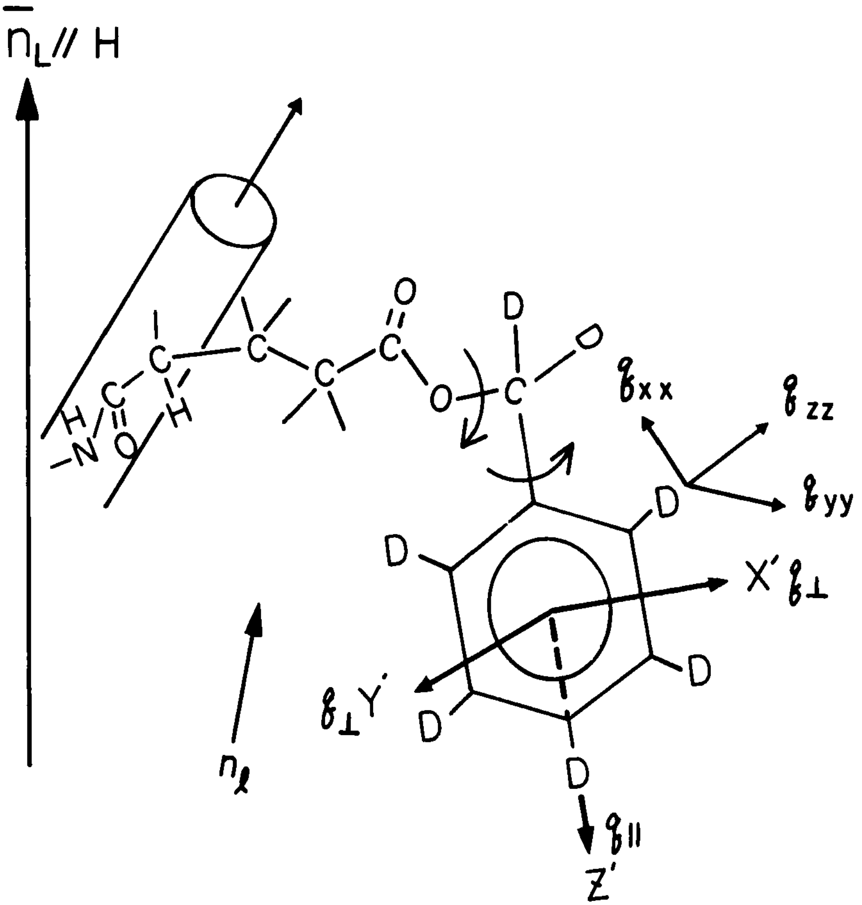

FIGURE 7 Conformation of a benzyl side chain of PBLG in a liquid crystal phase. In case of rapid rotation of phenyl group at an end of a side chain, quadrupolar interaction tensor along a C—D bond is effectively dissolved into component, $q_{\|}$, parallel to the rotational axis and two others, $q_{\perp}$, perpendicular, which are averaged out by the rotation. The local director, n_l, to which fluctuation of the $q_{\|}$ orientation is referred, is defined.

4) The local director for the benzyl groups at the side chain ends is oriented being free from the main-chain orientation and approximately parallel to the magnetic field, although the phenyls are under the constraints caused by the chemical bonds with the PBLG main chains.

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