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SQUID Studies of Main-Chain Polymer Liquid Crystals and a Rotational Isomeric State Treatment of the Data

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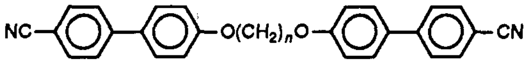
ABSTRACT: The magnetic susceptibilities of some ether-type liquid-crystalline polymers such as $-[\mathrm{PhOC(O)PhO(CH_2)_{\mathit{n}}OPhC(O)OPhO(CH_2)_{\mathit{n}}O}]_x-$ (Ether-PLC-*n*) with $n = 9$ and 10 have been measured by a SQUID magnetometer. Variations of $\Delta\chi$ at the isotropic to nematic transition were found to occur more gradually as compared with those observed for the dimer liquid crystals. The $\Delta\chi$ values estimated for the stable nematic state were analyzed according to the RIS scheme developed in the previous work. The order parameters of the mesogenic core axis S_M were elucidated for the nematic conformation derived independently from the ^{2}H NMR analysis. The same treatment has been extended to include ester-type main-chain liquid crystals such as $-[\mathrm{Ph(CH_3)N(O)NPh(CH_3)OOC(CH_2)_{\mathit{n}}COO}]_x-$ (Ester-PLC-*n*) with $n = 7$ and 10, for which experimental data are available from Esnault et al.'s work. For both Ether- and Ester-PLCs, the values of S_M estimated from SQUID were found to be reasonably consistent with those obtained by the other measurements.

Introduction

Thermodynamic properties of liquid crystals comprising a rigid mesogenic core and a flexible spacer in a repeating unit have been extensively studied.[1] These main-chain type liquid crystals often exhibit a distinct odd–even effect in various thermodynamic quantities at the nematic–isotropic (NI) transition temperature. The orientational order parameter of the mesogenic core axis is also known to oscillate with the number of methylene units *n*. In these liquid crystals, the order–disorder transition of the mesogenic core is coupled with conformational changes of the flexible spacer. The conformational rearrangement of the flexible spacer taking place at the transition should give rise to a significant contribution to physical properties.

In a previous work,[2] we have reported the results of SQUID studies of ether-type dimer liquid crystals such as



with $n = 9$ and 10. These compounds are known to exhibit stable nematic liquid-crystalline states. The observed magnetic susceptibility data have been analyzed within the framework of the rotational-isomeric-state (RIS) approximation. For these dimer liquid crystals, the molecular axis (z) was defined along the line connecting the centers of the mesogenic cores situated at the terminals. The observed anisotropies of the diamagnetic susceptibility, $\Delta\chi$, can then be related to the order parameters by

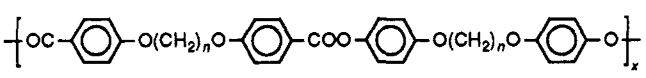
$$\Delta\chi = \Delta\chi_0 S_{zz} + (1/2)(\langle\chi_{xx}\rangle - \langle\chi_{yy}\rangle)(S_{xx} - S_{yy}) \tag{1}$$

where

$$\Delta\chi_0 = 3(\langle\chi_{zz}\rangle - \chi_{\mathrm{iso}})/2 \tag{2}$$

corresponds to the anisotropy of the susceptibility for the state in which the z axes are perfectly aligned along the director. In these expressions, $\langle\chi_{xx}\rangle$, $\langle\chi_{yy}\rangle$, and $\langle\chi_{zz}\rangle$ represent the components of the molecular susceptibility tensor averaged over all allowed conformations, and χ_{iso} is the magnetic susceptibility in the isotropic state. When molecules are cylindrically symmetric, contribution from the biaxiality term $(S_{xx} - S_{yy})$ may be ignored. The orientational order of the molecular axis S_{zz} may be estimated from eq 1, provided that the $\Delta\chi_0$ value is known. In the previous example, the nematic conformation deduced from the RIS analysis[3] of ^{2}H NMR quadrupolar splitting data was adopted for the estimation of $\langle\chi_{zz}\rangle$. The order parameters of the mesogenic core axis S_M elucidated in this manner were shown to be consistent with those directly observed by the ^{2}H NMR method.

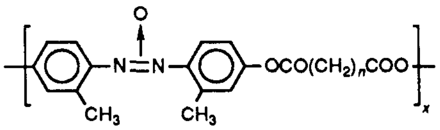
In this work, similar studies have been extended to include some ether-type main-chain polymer liquid crystals such as



Ether-PLC-*n*

with $n = 9$ and 10. As shown above, the mesogen and flexible spacer are joined by the ether linkage. The magnetic susceptibility studies for the $n = 10$ polymer and related model compounds have been previously reported by Sigaud, Yoon, and Griffin,[4] who employed a Faraday balance for the determination of $\Delta\chi$ values. Here we report the results of measurements by using a SQUID apparatus.

Recently, Esnault, Galland, Volino, and Blumstein[5] reported the results of extensive studies on the main-chain liquid-crystalline polyesters such as



Ester-PLC-*n*

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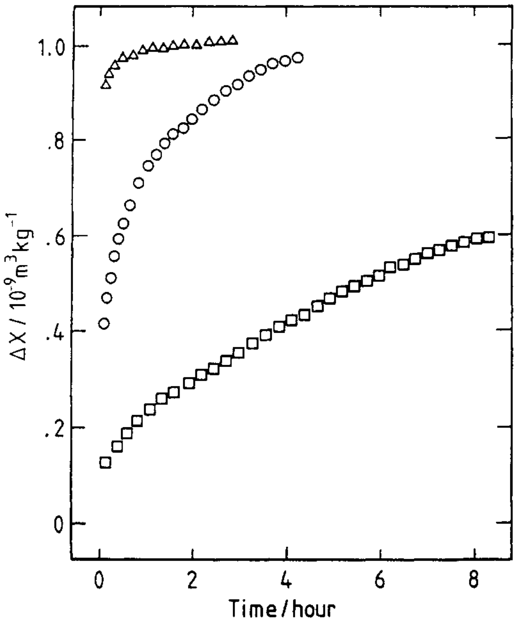

Figure 1. Recovery curves of the anisotropy of the magnetic susceptibility for Ether-PLC-10 observed at 458 K. Magnetic field strengths: 0.5 T (□), 2.0 T (○), and 5.0 T (△).

with n = 7 and 10 by a combined use of SQUID and ^{1}H and ^{2}H NMR techniques. It has been concluded that the biaxiality of these polyesters tends to be enhanced as the chain length increases. In this work, we benefit by use of these data to test our scheme for Ester-PLCs. The results of SQUID measurements have been successfully related to the orientational order determined by the ^{2}H NMR method. Contributions arising from the biaxiality term are shown to be relatively unimportant in eq 1.

Synthesis and Measurements

Ether-PLC-n samples were prepared according to the solution polyesterification technique prescribed by Jin et al.[6] Both n = 9 and 10 PLC samples exhibited an enantiotropic nematic behavior by their polarizing microscopic examination. Phase-transition temperatures, T_{KN} and T_{NI}, determined by the DSC measurements are as follows: Ether-PLC-9, K 400 N 446 I; Ether-PLC-10, K 437 N 479 I. The transition temperatures of PLC-9 are slightly lower than those reported previously.[3]

The magnetic susceptibility measurements were performed by using a SQUID magnetometer (S.H.E. Corp. VTS 909) equipped with an inset especially designed for high-temperature experiments.[7] An approximately 50 mg of sample was charged in a Cryolite glass bulb for each run. Experiments were carried out by cooling the sample from the isotropic phase under an N_2 atmosphere. To determine the contribution of the glass bulb, experiments were performed, prior to the real measurements, for an unloaded bulb as a function of temperature. The signals observed for the empty bulb were subtracted from the raw susceptibility data.

Experimental Results

Shown in Figure 1 are the isothermal recovery curves of $\Delta\chi$ for Ether-PLC-10 under constant magnetic fields, the numerical values being indicated in the legend to the figure. In these measurements, samples initially heated to the isotropic melt were brought into a nematic state by rapidly lowering the temperature to 458 K in the SQUID apparatus. When the field strength is 5 T, $\Delta\chi$ attains its asymptotic value within 1 h (the uppermost curve). With a lower field strength such as 2 T, several hours are required to reach saturation. The rate slows down drastically at 0.5 T.

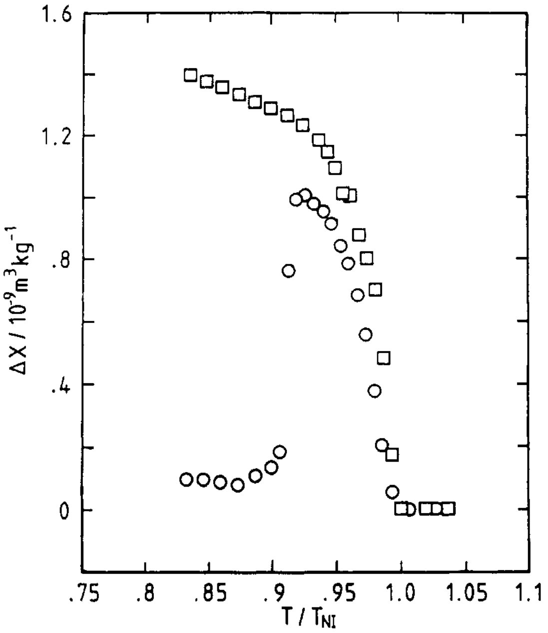

Figure 2. Observed anisotropies of the susceptibility $\Delta\chi$ plotted against the reduced temperature T/T_{NI} for Ether-PLC-n: n = 9 (○) and n = 10 (□).

After these pilot experiments, the anisotropies of the susceptibility $\Delta\chi$ were measured under a magnetic field strength of 5 T as a function of temperature by gradually cooling the sample from the isotropic state. The results obtained for the two Ether-PLC samples are compared in Figure 2, where the observed $\Delta\chi$ values are plotted against the reduced temperature $T_{red}(=T/T_{NI})$. In the isotropic phase, the values of $\Delta\chi_{iso}$ remain nearly invariant with temperature within the experimental error. The observed values are 7.839 and 7.743 × 10^{-9} m^3 kg^{-1}, respectively, for Ether-PLC-9 and -10. These values are lower by about 5% than those calculated according to the bond additivity rule by using Flygare et al.'s data:[8] 8.129 and 8.183 × 10^{-9} m^3 kg^{-1} in the corresponding order. The values of $\Delta\chi$ exhibit a sudden increase at the transition from the isotropic to the nematic phase. The rate of increase with temperature is, however, somewhat more gradual in comparison with those usually observed for monomer or dimer liquid crystals. Such a reduction in the rate is probably due to the presence of some nematic–isotropic biphasic equilibrium region around the transition point. The $\Delta\chi$–temperature profile is very different between the n = 9 and 10 PLCs. The curve for n = 10 continues to increase even after the commencement of solidification, indicating that the orientational order remains persistently in the sample. On the contrary, the plot for n = 9 decreases sharply around the transition temperature T_{KN}. The latter behavior is similar to those commonly observed among low molecular weight liquid crystals including dimers.[2]

In Figure 2, an accurate assessment of the $\Delta\chi$ value that serves to estimate the order parameter S_{zz} near T_{NI} is quite difficult. The termini of the biphasic region were separately estimated from the DSC diagram by cooling the sample from the isotropic melt: the temperatures thus estimated are T_{red} = 0.94 for n = 9 and 0.96 for n = 10. Correspondingly, we obtained values of $\Delta\chi$ = 0.979 and 1.005 × 10^{-9} m^3 kg^{-1} for the nematic state of n = 9 and 10, respectively. For the latter PLC, the magnetic susceptibility data have been previously reported by Sigaud et al.[4] Their measurements were carried out by employing a Faraday balance at the field strength of 2 T. The value of $\Delta\chi$ was estimated to be 0.942 × 10^{-9} m^3 kg^{-1} at 476 K, being slightly lower than the present estimate.

Table I
Structural Parameters Used in the RIS Analysis

bond	length/Å	bond angle	angle/deg
		Ether[a]	
O–C	1.40	$\angle C^{Ph}OC$	120
C–C	1.53	$\angle OCC$	112
		$\angle CCC$	112
		$\angle CCH$	109
		$\angle C^{*}OC^{Ph}$	118[b]
		$\angle C^{Ph}C^{*}O$	111[b]
		Ester[c]	
O–C*	1.35	$\angle C^{Ph}OC^{*}$	125[d]
C*–C	1.53	$\angle OC^{*}C$	111.4
		$\angle C^{*}CC$	112

[a] Reference 2. [b] Reference 4. [c] Reference 12. [d] Reference 18.

Table II
Components of the Bond or Group Susceptibility Tensors[a]

	χ_{11}	χ_{22}	χ_{33}
benzene[b]	−34.9	−34.9	−94.6
C*=O*[c]	−1.3	2.2	−13.0
C–O[d]	−7.2	−6.7	−3.8
C–C[e]	−7.9	−0.2	−0.2
C–H[e]	−5.6	−3.1	−3.1

[a] Expressed in units of 10^{-6} erg G^{-2} mol^{-1}.[8] [b] Axes 1 and 2 are defined in the plane of the phenyl ring. [c] Axis 1 is defined along the bond and axis 2 in the plane of the pendant bonds. [d] Axis 1 is defined along the bond and axis 2 in the plane of the bond pair jointed by O. [e] The given bond is identified with axis 1.

The experimental values of $\Delta\chi$ for Ester-PLC-n have been reported by Esnault et al.[5] The values estimated from the $\Delta\chi/S_M$ vs temperature curve are 0.880 and 1.225 $\times 10^{-9}$ m^3 kg^{-1} for $n = 7$ and 10, respectively. These values are adopted for the RIS analysis of Ester-PLCs in the following section.

RIS Analysis

Geometrical parameters used in the estimation of $\Delta\chi_0$ are summarized in Table I, where the carbonyl carbons are distinguished by an asterisk. In this work, the conformation of the ester groups was fixed in trans. The rotational states for the C^{Ph}–$C^{*}O$ and $C^{*}O$–C^{Ph} bond in the mesogenic core part of Ether-PLC were taken to be ±6° and ±65°, respectively.[9] The moiety C^{Ph}–OC was taken to be coplanar with the preceding phenylene ring. For the $C^{Ph}O$–CC bond, values of 0° and ±100° were adopted. The rotational states of the OC–CC bond were assumed to occur at 0° and ±117.0°.[10] For Ester-PLCs, we have examined two possible orientations of the ester group with respect to the attached phenylene ring:[5,9,11] i.e., the rotational states about the C^{Ph}–OC^{*} bond were taken to occur at either ±65° or ±90°. For the following OC^{*}–CC bond, the rotational states have been estimated to be 0° and ±122.7°.[12] We adopted conventional values of 0° and ±112.5° for the internal CC–CC bond of the spacer.[13,14]

According to Flygare et al.,[8] the magnetic susceptibility tensor of a molecule can be evaluated as the sum of contributions from the constituent bonds or groups. Values of the bond (group) magnetic susceptibility tensors required for the description of Ether- and Ester-PLCs were taken from the literature and are listed in Table II, where $\chi_{\alpha\alpha}$'s indicate the principal components of the χ tensor. The transformation of tensors was performed according to the procedure described by Jernigan and Flory[14,15] in their treatment of the optical anisotropy of chain molecules. For the mesogenic core of Ether-PLC, OPhCOOPhO, the tensor can be estimated by the sum such as

$$\chi_{meso} = 3\chi_{CO} + 2\chi_{phenyl} + \chi_{CC} + \chi_{C^{*}O^{*}} + \chi_{C^{*}O} \qquad (3)$$

with χ values listed in Table II. The tensors associated with the methylene unit $(CH_2)_i$ may be treated in the coordinate system defined on the C_i–C_{i+1} bond. According to the rule, contribution from the C_n–H bond of the terminal methylene group is expressed in the frame fixed on the C_n–O bond.

The magnetic susceptibility tensor of the mesogenic unit for Ester-PLC, $OPh(CH_3)N(O)NPh(CH_3)O$, may be easily derived starting from the χ tensor of p-azoxyanisole. Thus

$$\chi_{meso} = \chi_{PAA} + 2\chi_{CC} - 2\chi_{CH} - 2\chi_{CO} \qquad (4)$$

where a value of $\chi_{PAA} = (-172, -164, -105) \times 10^{-6}$ erg G^{-2} mol^{-1} has been reported from the analysis of a monocrystal of p-azoxyanisole (PAA),[16] and the other χ tensors required are listed in Table II. For the two carbonyl units, $C^{*}O^{*}$–C_1 and $C^{*}O^{*}$–O, their tensors are expressed in the reference frames fixed on the C^{*}–C_1 and C^{*}–O bonds, respectively. The methylene units constituting the flexible spacer of Ester-PLC may be treated in the same manner as described above for Ether-PLC.

Following the previous treatment,[3] the molecular axis was defined along the direction parallel to the line connecting the centers of two adjacent mesogenic cores (cf. Figure 1 of ref 3). For simplicity, the center of the mesogenic core was assumed to lie at a distance of 5 Å along the C^{Ph}–O bond from the oxygen atom joining the flexible spacer. Accordingly the molecular axis should be defined for each spatial configuration of the spacer. In this scheme, the inclination (ψ) of the mesogenic core axes with respect to the molecular axis provides an important criterion for the estimation of the nematic fraction.

For a given configuration (k), the magnetic susceptibility tensor may be generally expressed as[14,15]

$$\begin{aligned}\chi_k &= T_0\chi_1 T_0^{t} + T_0 T_1 \chi_2 T_1^{t} T_0^{t} + \ldots \\ &= \sum_{j=1} T_0 (T_1^{j-1}) \chi_j (T_1^{j-1})^{t} T_0^{t}\end{aligned} \qquad (5)$$

where T_0 is responsible for the transformation of the reference frame from bond 1 to the molecular axis, T_j ($j > 1$) transforms the coordinate system from bond j to bond $j - 1$, T_j^{t} denotes the transpose of T_j, and T_1^{j-1} represents the serial product comprising $j - 1$ factors. The zz component of the magnetic susceptibility tensor averaged for the nematic phase can be obtained by

$$\langle \chi_{zz} \rangle = \sum_k \zeta_k \chi_{zz} / \sum_k \zeta_k \qquad (6)$$

where ζ_k represents the statistical weight of the kth configuration.

Under a nematic environment, the orientational distribution of mesogenic cores may be restricted within certain fractional ranges of the inclination angle ψ. In the previous ^2H NMR analysis of main-chain liquid-crystalline polymers, simulations of the spectra were carried out for the ensemble of conformers selected from the (ψ_1, ψ_2) map, where the numerical subscripts denote two successive mesogenic cores along the chain. In the simulation, conformational statistical weight parameters σ_i assigned to every rotatable bond were adjusted so as to reproduce the observed quadrupolar splittings. The best fit set of conformations and their statistical weight parameters define the nematic ensemble. The statistical weight of a given conformation (ζ_k) occurring in the nematic state can be estimated as a serial product such as $\zeta_k = (\prod \sigma_i)_k$. The nematic conformation derived in this manner may be

Table III
$\Delta\chi_0$ Values and the Order Parameters Estimated for PLCs

	ether		ester	
	$n = 9$	$n = 10$	$n = 7$	$n = 10$
$\Delta\chi_0$	1.16	1.17	0.99	1.54
S_{zz}	0.85	0.57	0.89	0.80
S_M	0.48	0.53	0.49	0.69
$S_{M,obs}$	0.39[a]	0.69,[a] 0.75,[b] 0.60[c]	0.48[d]	0.75[d]

[a] Reference 3. [b] Reference 17. [c] Reference 4. [d] References 5 and 19.

adopted in the calculation of ensemble average $\langle\chi_{zz}\rangle$ defined in eq 6. The value of $\Delta\chi_0$ required for the estimation of the order parameter S_{zz} can then be obtained by using eq 2, χ_{iso} being readily available according to the bond additivity rule. The order parameter S_{zz} may be related to that of the mesogenic core by

$$S_M = S_{zz}P_2(\cos\psi) \qquad (7)$$

where

$$P_2(\cos\psi) = (3\langle\cos^2\psi\rangle - 1)/2 \qquad (8)$$

is the intramolecular correlation term, which can be easily evaluated for a given nematic conformation.

Results of Calculations

Ether-PLC. The RIS analysis of the ^{2}H NMR spectra for these PLCs has been previously reported. The results indicate that the conformations of the flexible spacer are largely restricted in the nematic state: ψ_1, $\psi_2 < 40°$ for both PLCs with $n = 9$ and 10. In this treatment, the rotation around the ether C^{ph}O–CC bond jointing the mesogenic core to the spacer has been fixed in trans in order to reduce the burden required for the computer simulation. Such an assumption may be valid in the isotropic state, where a great deal of experimental data are available for relevant model compounds. In a liquid-crystalline state, however, some slight deviation from the fully trans conformation may be critical in the interpretation of the orientation-dependent properties. Revised calculations indicate that the fraction of the gauche form around the C^{ph}O–CC bond may be as high as a few percent for the $n = 10$ PLC system and negligibly small for the $n = 9$ PLC system. The values of $\Delta\chi_0$ listed in Table III are practically unaffected by such modifications in the treatment. It should be noted here that the analysis was carried out for the ^{2}H NMR data observed in the immediate vicinity of the NI transition. Accordingly, the temperature may be a few degrees higher than those for the SQUID data. The consequence of this difference will be discussed later.

Given in the following row of Table III are the S_{zz} values calculated from the $\Delta\chi_0$ values thus derived. The observed values of $\Delta\chi$ adopted in this estimation are given in the previous section. The $P_2(\cos\psi)$ terms defined in eq 8 have been estimated to be 0.57 for $n = 9$ and 0.93 for $n = 10$. The values of S_M obtained by eq 7 are compared with those estimated by the ^{2}H NMR method in Table III. In the RIS treatment of the ^{2}H NMR data, the ratios of the quadrupolar splitting $\Delta\nu$ to the order parameter $S_{M,obs}$ have provided a basis to elucidate the nematic conformation of the flexible spacer. Accordingly, the deviation of S_M from $S_{M,obs}$, i.e., 0.48 vs 0.39 for $n = 9$ and 0.53 vs 0.69 for $n = 10$ (cf. Table III), reflects the difference between the ^{2}H NMR and SQUID measurements. As pointed out above, the SQUID data were obtained at somewhat lower temperatures than those of ^{2}H NMR. The difference may be attributable at least partially to this source. For the $n = 10$ PLC, the values of $S_{M,obs}$ reported by the other groups[4,17] are also cited in Table III.

In the treatment described above, contribution from the biaxiality term has been entirely ignored (cf. the second term of eq 1). The effect arising from this term may be estimated as follows. The first factor includes a conformational average $(1/2)(\langle\chi_{xx}\rangle - \langle\chi_{yy}\rangle)$, which can be easily calculated by knowing the nematic fraction: thus, 0.37 and 0.08×10^{-9} m^3 kg^{-1} for $n = 9$ and 10, respectively. Then, even when $S_{xx} - S_{yy}$ is as high as 0.1, the contribution of the second term remains ca. 4% for $n = 9$ and 1% for $n = 10$ in eq 1. With such modification, the calculated values of S_{zz} will be lowered by 0.04 and 0.01 from those listed in Table III. The effect is therefore well within the error limit of measurements.

Ester-PLC. The RIS analysis of the ^{2}H NMR data reported by Esnault et al.[5] has been attempted according to the procedure previously described. A brief summary of the results is given in the Appendix. The nematic fractions were found in the range ψ_1, $\psi_2 < 50°$ for the $n = 7$ PLC and ψ_1, $\psi_2 < 35°$ for the $n = 10$ PLC. In this treatment, the order parameter S_{zz} was found to vary sensitively with bond angle $\angle$C^{ph}OC*: a reasonable value of S_{zz} was obtained only in the range $\angle$C^{ph}OC* > 125°, somewhat higher than that (116.7°) conventionally adopted.[18] The values of $\Delta\chi_0$ elucidated by using $\angle$C^{ph}OC* = 125° are listed in Table III. As stated earlier, the calculation of $\Delta\chi_0$ was attempted for two values of the ester orientation, C^{ph}–OC*. The difference was found to be less than 1% between the two choices of the rotation angle, i.e., ±65° and ±90°. In Table III, the results derived from the latter value are listed. The calculations of S_{zz} and S_M are straightforward from eqs 1 and 7 within the assumptions adopted in this treatment. The values of $P_2(\cos\psi)$ required for the estimation of S_M were given in the Appendix. The order parameters thus calculated are shown in the following rows of the table. In the analysis described in the Appendix, the order parameters $S_{M,obs}$ derived from the ^{1}H NMR measurements[5,19] were used in combination with the ^{2}H NMR data. In spite of such complexities in the choice of experimental data, the differences between S_M and $S_{M,obs}$ are rather small, indicating that the results derived from the NMR and SQUID measurements are quite consistent.

The biaxiality factors $(1/2)(\langle\chi_{xx}\rangle - \langle\chi_{yy}\rangle)$ were calculated to be 0.280 and 0.253×10^{-9} m^3 kg^{-1} for $n = 7$ and 10, respectively. If we adopt a value of 0.07 for the remaining factor $S_{xx} - S_{yy}$ as estimated by Esnault et al.,[5] the contribution from the second term amounts to ca. 2% in eq 1. The effect on S_{zz} is negligibly small.

Concluding Remarks

In the previous studies of dimer liquid crystals, the role of the flexible spacer was examined. Although the major part of the contribution to $\Delta\chi_0$ originates from the orientation of mesogenic cores, the effect of the spacer is also shown to be substantial. In the main-chain liquid crystals, the flexible spacer assumes a dual role: (1) effect on the orientational correlation between the terminal mesogenic core units and (2) contribution to $\Delta\chi_0$ through the conformational anisotropy of the spacer. To estimate the contribution of the spacer explicitly, calculations of $\langle\chi_{zz}\rangle$ were also performed for a model in which all χ tensors of the spacer were assumed to be null. In this model, all χ_{zz} contributions arise from the terminal mesogenic core units, the role of flexible spacers being restricted to item 1 mentioned above. The results of these calculations indicate that the flexible spacer contributes an appreciably large portion of $\langle\chi_{zz}\rangle$: i.e., for Ether-PLC-*n*, 36% ($n = 9$) and 42% ($n = 10$); and for Ester-PLC-*n*, 27% ($n = 7$) and 39% ($n = 10$). The $\Delta\chi_0$ values may be further estimated from eq 2 in combination with χ_{iso} calculated for the same model. We obtain, for Ether-PLC-*n*, $\Delta\chi_0 = 1.32$ ($n = 9$) and 2.00 ($n = 10$) and, for Ester-PLC-*n*, 1.01 ($n = 7$) and 1.63 ($n = 10$), units being 10^{-9} m^3 kg^{-1}. The increment amounts to ca. 13–14% for Ether-PLC and 2–6% for Ester-PLC relative to the $\Delta\chi_0$ values listed in Table III. The former values are close to those previously estimated for the ether-type dimer liquid crystals.

Finally, we emphasize that the conformational cooperativity along the flexible spacer plays an important role in determining the orientational characteristics of main-chain PLCs, including dimers.

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Appendix

Estimation of the Nematic Conformation for Ester-PLC. A RIS Analysis on the ^{2}H NMR Data of Esnault et al. The results of ^{2}H NMR studies on Ester-PLC carrying deuterated spacers have been reported by Esnault et al.[5] The spectra observed for the $n = 7$ and 10 polymers exhibit qualitatively a similar profile, comprising two doublets designated as $\Delta\nu_1$ and $\Delta\nu_4$. While the larger quadrupolar splitting ($\Delta\nu_1$) corresponds to the α–CD bond, the contributions from the remaining CD$_2$ groups are all included in $\Delta\nu_4$. The values of the splittings obtained from the spectra are as follows: $\Delta\nu_1 = 56.0$ and $\Delta\nu_4 = 30.2$ kHz for $n = 7$ and $\Delta\nu_1 = 85.3$ and $\Delta\nu_4 = 65.3$ kHz for $n = 10$, respectively. The order parameters S_M for the orientation of the mesogenic cores were estimated from the dipolar splitting data derived from the ^{1}H NMR measurements. The values of $S_{M,obs}$ were calculated according to the formula given by Esnault et al.: $S_{M,obs} = 0.48$ for $n = 7$ and 0.75 for $n = 10$.[5,19]

According to the RIS scheme set forth previously,[3] the ratio

$$\Delta\nu_i/S_M = C(3\langle\cos^2\phi_i\rangle - 1)/(3\langle\cos^2\psi\rangle - 1) \quad \text{(A1)}$$

is free from the order parameter of the molecular axis S_{zz} and depends only on the spatial configuration of the spacer. In this expression, C $(=(3/2)e^2qQ/h)$ designates the quadrupolar coupling constant, ϕ_i represents the angle between the *i*th CD bond and the molecular axis, and ψ denotes the inclination of the mesogenic core axis with respect to the molecular axis. The nematic conformations and their statistical weights may be elucidated by simulation so as to reproduce the ratios $\Delta\nu_i/S_M$ experimentally obtained. For the sake of computer time, configurations that do not conform to the nematic ordering were discarded: for $n = 7$, $\psi_1, \psi_2 > 50°$ and, for $n = 10$, $\psi_1, \psi_2 > 35°$. Thus, conformations in the colony with larger ψ values were dismissed. For the nematic conformation, the second-order interactions $g^{\pm}g^{\mp}$ were assumed to be entirely suppressed. The geometrical parameters adopted in this analysis are listed in Table I.

Table IV
Bond Conformations of the Flexible Spacer for Ester-PLCs: Trans Fractions Estimated for the Nematic Phase

bond	$n = 7$	$n = 10$
C^*–C_1	0.80	0.72
C_1–C_2	0.49	0.81
C_2–C_3	0.30	0.63
C_3–C_4	0.51	0.85
C_4–C_5		0.60
C_5–C_6		0.87

The results for $n = 7$ were found to vary sensitively with bond angle $\angle C^{ph}OC^*$. Experimental values could be satisfactorily reproduced only for the range $\angle C^{ph}OC^* > 125°$. Use of a conventional value $\angle C^{ph}OC^* = 116.7°$ failed to achieve agreement between the calculation and experiment. In contrast, the results of simulation for $n = 10$ were comparatively insensitive to the $\angle C^{ph}OC^*$ angle. In consideration of these results, we have adopted a value of $\angle C^{ph}OC^* = 125°$ in Table I.[18] The bond conformations of the spacer estimated in this manner are summarized in Table IV, where the carbon atoms are numbered from one terminal to the midpoint of the spacer. For $n = 10$, the results of calculation vary rather insensitively with the conformation around bonds C_2–C_3 and C_4–C_5. Corresponding to the nematic conformation estimated above, the values of $P_2(\cos\psi)$ were calculated to be 0.55 and 0.86 for $n = 7$ and 10, respectively. The orientational order parameters S_{zz} obtained therefrom are 0.89 for $n = 7$ and 0.80 for $n = 10$. These values of S_{zz} are somewhat higher than those estimated for Ether-PLCs.

References and Notes

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