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Nematogens containing oxyethylene units at a lateral or terminal position and their mixtures with salts

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Nematogens containing oxyethylene units at a lateral or terminal position and their mixtures with salts

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Short terminal polyoxyethylene chains may be introduced into mesogens containing lateral substituents such as two hexyloxy chains or a crown-ether fragment. These compounds have a large nematic range near room temperature and can dissolve large amounts of the salt $LiBF_4$ without destroying the nematic arrangment. In the nematic phase, the ions are ordered and the quadrupolar splitting associated with these ions can allow this ordering to be monitored. Increasing the salt concentration does not seem to change the ordering of the individual ions. The ^{13}C thermal evolution of the field-induced chemical shift in the oxyethylene (OE) units with or without salt does not show any real difference, indicating that the interaction between the ions and the mesogen is small. This means that there is very little change in conformation in the OE unit when adding salt to the mesogen.

1. Introduction

For many applications, room temperature liquid crystals are needed and the choice of the chain type, and its length and position within the core, is of major importance in reducing the melting temperature. In conventional mesogens, alkyl or alkoxy chains are used as terminal fragments [1]. The chain conformation in the solid phase of these compounds is usually *trans* and the crystal cohesion which contributes to the value of the melting temperature is mainly due to core–core interactions. Thus, in a series the melting temperatures can be modified by increasing the chain length, with the accompanying consequence of strongly decreasing the mesophase stability due to the enhancement of the conformational disordering along the chain. A nice alternative way to decrease these core–core interactions in the solid phase is to introduce flexible fragments at a lateral position. In the solid and in the nematic phase of these compounds, the lateral flexible substituents adopt a mean conformation more or less parallel to the mesogenic core in such a way that this peculiar arrangement does not perturb to a large extent the anisotropic packing needed for the mesophase stability [2–4]. The lateral chains are less disordered than terminal chains, in accordance with their peculiar conformation along the core. As a consequence, in a homologous series, the melting temperatures can be adjusted by changing the number of carbons within the terminal and/or lateral chains without affecting too much the nematic range [5–7].

Nematogens containing the oxyethylene unit have two interesting properties; they can dissolve ionic material and they still present a mesophase. In addition, it has been established that polyoxyethylene ether (POE) chains are good candidates for ionic conduction [8–10]. Therefore, adding POE chains to a mesogenic structure can lead to monodirectional conductivity properties. In the literature, some mesogenic structures are quoted which incorporate the POE chains as terminal flexible substituents [11–14]. However, increasing the length of a terminal POE chain usually leads to very ordered phases. Nevertheless, this tedious problem can be counterbalanced by introducing a terminal POE chain into a dilaterally substituted compound which can lead to a

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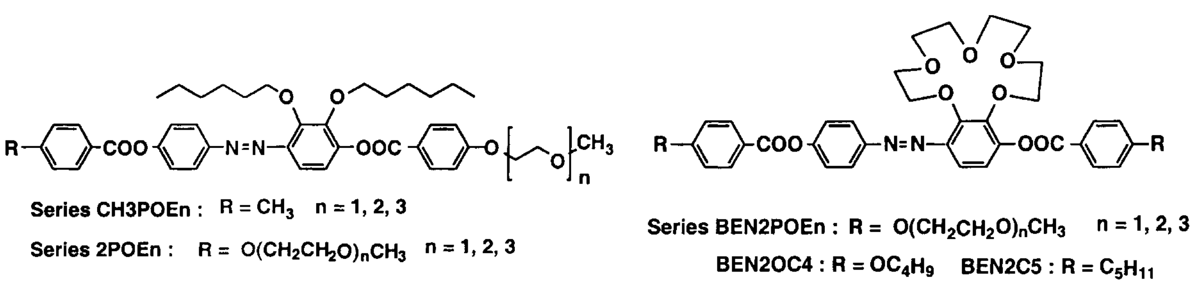


Figure 1. Different synthesized series containing lateral and terminal oxyethylene units.

low melting nematic [15]. In addition, we have reported that the OE units can be advantageously introduced in the form of a lateral or terminal crown-ether ring [16].

Thus, in order to obtain low melting nematogens containing the POE fragment, we describe the synthesis and mesomorphic properties of several compounds possessing the same core, containing four aromatic rings and laterally substituted by two hexyloxy chains or a crown-ether lateral ring, and having POE terminal chains which contain 1, 2 or 3 OE units. Variable amounts of salt will be dissolved in some of the compounds and the correlated effect on the mesomorphic properties will be discussed.

In order to evaluate the interaction between the salt and the mesogen, ^{13}C, ^{7}Li and ^{11}B NMR studies of the low melting compound 2POE3 were undertaken. The effect of dissolving a salt on the ordering of the mesogen itself is monitored by analysing the ^{13}C chemical shift anisotropy of the carbon atoms linked to an oxygen atom. The ordering of the ions will be studied by the quadrupolar splittings of ^{11}B and ^{7}Li.

2. Results and discussion

2.1. *Synthesis*

The general synthetic scheme for the compounds containing 1, 2 and 3 OE units in the terminal chains and a lateral crown ether is summarized in figure 2. As an example, we describe the synthesis of BEN2POE3. 3-Hydroxybenzo-15-crown-5 was prepared by selective etherification of 1,2,3-trihydroxybenzene in ethanol following the Pedersen procedure [17]. *p*-Toluic acid was esterified with *p*-nitrophenol using the DCC method in dichloromethane [18]. The nitro group in this compound was selectively reduced using the $NiCl_2/NaBH_4$ reducing system [19]. After acidification, the crude precipitated amine hydrochloride was dried under vacuum

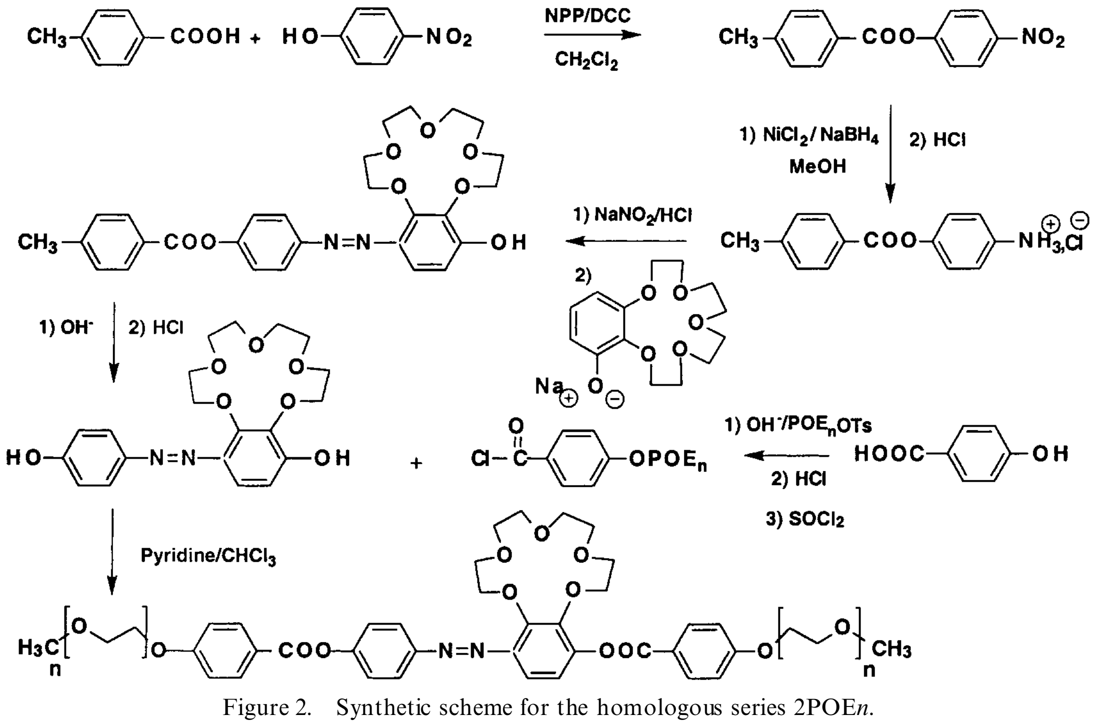


Figure 2. Synthetic scheme for the homologous series 2POE*n*.

and then used for the diazotization step without further purification. The coupling was performed at room temperature in PEG 200 solvent, by slowly adding the diazonium salt to the crown-ether phenate. After acidification and extraction with dichloromethane, the crude phenol was chromatographed with ethyl acetate/dichloromethane (50/50) as eluent. The second hydroxy function was generated by saponification of the ester in ethanol. After solvent evaporation, water was added and the pH adjusted to 7; this resulted in the precipitation of the diphenol. In the next step, the diphenol was esterified with the appropriate 4-substituted benzoyl chloride in $CHCl_3$/pyridine (50/50) as solvent. The final mesogen was chromatographed twice with CH_2Cl_2/MeOH (90/10) mixture as eluent on silica gel (60–220 mesh). Products were recrystallized from $CHCl_3$/ethanol mixture until constant transition temperatures were obtained.

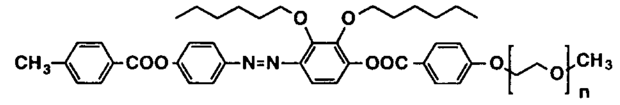
The mixtures with salt ($LiBF_4$) were obtained by dissolving both materials in dry THF. The solvent was then evaporated with mechanical stirring at the boiling point of THF. Then, the mixtures were kept in an oven at 100° for several days.

2.2. *Transition temperatures of the mesogens*

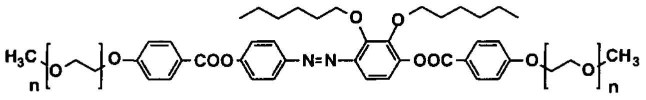
The phase transitions were observed and characterized using an Olympus polarizing microscope fitted with an FP 82 Mettler heating stage, and an FP 85 Mettler DSC. The transition temperatures are given in the table. All the compounds exhibit an enantiotropic liquid crystal phase as shown in figure 3.

The first two series in this graph possess two hexyloxy lateral chains and differ by the number of oxyethylene units in the terminal chains. We have shown recently in conventional mesogens that the replacement of carbons by oxygen atoms within the terminal chain decreases the melting and clearing temperatures, keeping the nematic range quite unaffected [15]. Replacing the terminal methyl group in the CH3POE*n* series by a second POE chain does not greatly affect nematic range. In fact, for the compound containing three units in each chain, a 50°C nematic range is observed very near to room temperature. It can also be noticed that the clearing temperatures show a steep decrease when increasing the number of OE units in the 2POE*n* series. Adding more than one unit in the terminal chains of 2POE3 would destroy the nematic phase. Thus, it would be necessary to increase the thermodynamic stability of the mesophase by replacing the two lateral chains by a lateral ring [6], as we will discuss in the next paragraph, or by increasing the length of the rod [1].

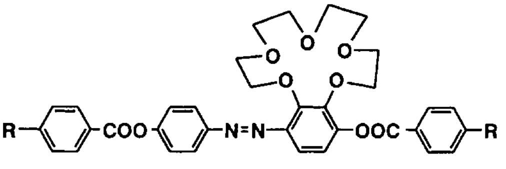
Table. Transition temperatures (in °C) of some related compounds having one or two POE terminal chains or a lateral crown-ether. The values were measured on heating scans (heating rate 10°C min^{-1}).



Compound	Cr	→	N	→	I
CH3POE1	●	67	●	165.5	●
CH3POE2	●	50	●	122	●
CH3POE3	●	20	●	106	●



Compound	Cr	→	N	→	I
2POE1	●	98	●	182	●
2POE2	●	40	●	124	●
2POE3	●	30	●	80	●



Series BEN2POEn : R = $O(CH_2CH_2O)_nCH_3$ n = 1, 2, 3

Series BEN2R : R = C_5H_{11} or OC_4H_9

Compound	Cr	→	Sm	→	N	→	I
BEN2POE1	●	154			●	224	●
BEN2POE2	●	134			●	162	●
BEN2POE3	●	51	●	72	●	115	●
BEN2OC4	●	133			●	232	●
BEN2C5	●	83			●	177	●

The BEN2POE*n* series contains a lateral crown-ether and two terminal POE chains and this series can be compared with the 2POE*n* series. The lateral crown ether does not destroy the nematic ordering even if the lateral fragment protrudes markedly from the rod-like shape. This ring contains nearly the same number of atoms as the two hexyloxy chains in the 2POE*n* series. This protruding ring has the ability to increase the interactions between molecules in the solid phase and thus to increase the melting temperature. However, it also increases the thermodynamic stability of the mesophase. The liquid crystal range presents an odd–even effect as BEN2POE2 possesses a shorter range than the two other compounds within the series. Increasing the chain length does not perturb the relative packing in the liquid crystalline and solid phases as observed in the 2POE*n* series, and accordingly the phase range is as large for the compounds containing 6 or 2 units in the terminal chains. We may expect to retain some liquid

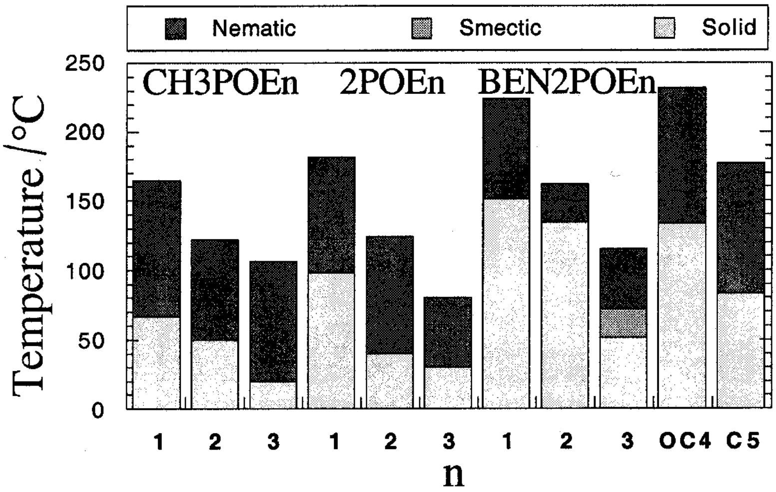


Figure 3. Stacked plot for the transition temperatures in compounds containing terminal or lateral OE units.

crystal properties if these chains are made longer, even if the mesophase type is going to change due to the segregation between the chains on one side and between the crown-ethers on the other side. We can also compare BEN2POE2 with the two compounds having a terminal butoxy or pentyl chain. The absence of the oxygen atom attached to the ring decreases the transition temperatures strongly without greatly affecting the nematic range.

2.3. *Phase diagrams of the salt–mesogen mixture*

We used polarizing optical microscopy to check for the presence of insoluble materials. Insoluble materials, which can be attributed to insoluble $LiBF_4$ salt, appear, respectively, with 0.2 and 0.8 molar equivalents of $LiBF_4$ in the mixtures with 2POE1 and 2POE2. This behaviour is reflected in figure 4 by the almost constant clearing temperatures and ΔS_{NI} observed for these concentrations and thereafter (indicated by a vertical arrow).

Usually, for compounds containing alkyl or alkoxy terminal chains, $\Delta S_{NI}/R$ increases with the number of carbons in the chain due to the increase in conformational entropy on going from the ordered liquid crystal phase to the isotropic liquid [20]. For the pure compounds, the opposite behaviour is observed, the entropy decreases slighty when the number of OE units in the POE chain is increased. This may stem from the lateral chains which space the molecules and make the terminal chains conformationally disordered in the nematic phase. Adding some salt has the same effect on the $\Delta S_{NI}/R$ values, certainly due to the fact that the ions increase the disorder in the nematic phase of the POE chains.

2.4. *^{7}Li and ^{11}B NMR measurements on the dissolved salt*

^{7}Li ($I = 3/2$) and ^{11}B ($I = 3/2$) NMR spectra were obtained for 2POE3 mixed with 0.1 and 0.4 molar equivalents of $LiBF_4$ using a Bruker AM-250 NMR

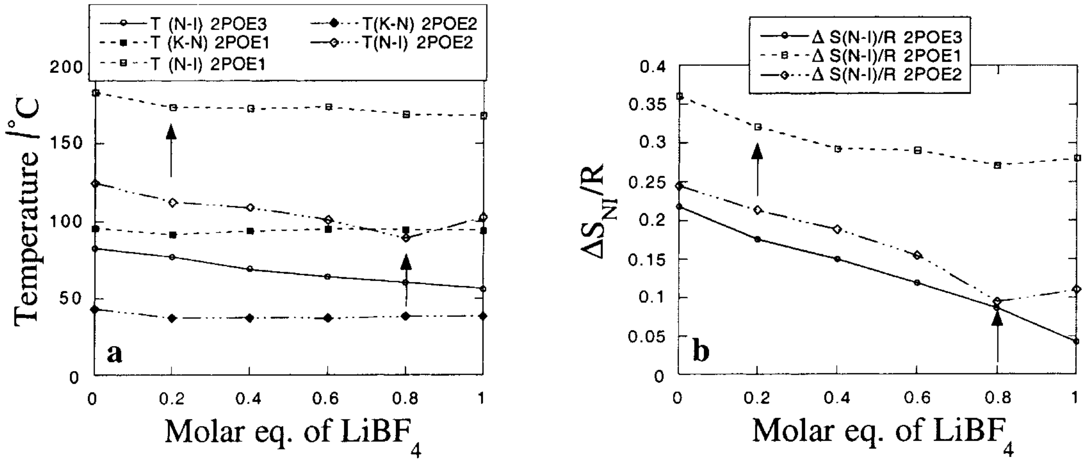


Figure 4. Phase diagram (*a*) and $\Delta S_{NI}/R$ plot (*b*) for 2POE3, 2POE2 and 2POE1 with increasing x, the molar equivalent of $LiBF_4$ salt. The absolute error in the $\Delta S_{NI}/R$ values increases with the amount of salt from 1% ($x = 0$) to 15% ($x = 1$).

spectrometer at $B_o = 5.88$ T on the static sample. The spectra were recorded with decreasing temperature from the isotropic liquid. In the isotropic liquid, due to the fast tumbling of the ions, the averaged electric field gradient is zero and for both nuclei a single line is observed. When entering the nematic phase, the anisotropic molecular packing of the phase creates a non-symmetrical environment leading to a polarization of the electronic cloud. The averaged electric field gradient is no longer zero and in the spectrum three equally spaced lines are observed [21, 22]. In addition, the ^{11}B central line is split into a quintet structure due to its dipolar and J couplings ($T = 2D + J$) with the four fluorine atoms. It is found that the ratio between these two splittings is constant when the temperature is changed and is equal to 275 ± 15. This indicates that both quantities are sensitive to the same ordering factor.

Figure 5(*a*) presents the observed quadrupolar splitting between two adjacent lines plotted as a function of the reduced temperature for both nuclei at two different concentrations; figure 5(*b*) shows the ratio between the quadrupolar splittings between the two nuclei.

Figure 5 requires several comments: (i) the splittings of both ions increase when decreasing the reduced temperature; (ii) the splittings of the lithium ion seem to be more concentration dependent than those of the tetrafluoroborate anion; (iii) the ratio of the splitting between the B and Li decreases with temperature and is concentration dependent.

It is well known that the polymer POE dissolves salt by complexing the cations as a polydentate ligand. With the lithium ion, it seems that only one strand is involved in the complexation. This strand is forced into a crown-ether-like conformation which needs at least five oxygen atoms and so five OE units [23]. This type of complexation is not possible for short POE chains as there are insufficient oxygen atoms on one chain to complex the cation. In our compounds, the lithium cation may certainly be in interaction with two or more terminal chains.

The question arises whether the quadrupolar splitting variation with temperature gives some information on the interaction between the ions and the nematogen? To a crude approximation, we can assume that the distortion of the ion and its ordering are dependent on the ordering of the phase itself. Hence the increase in the splitting will probe the increase in the ordering of the ion. This change in the ordering with temperature can be expressed through a Haller [24] type dependence. Thus the observed splitting can be expressed as a function of the reduced temperature as:

$$\Delta\nu = \Delta\nu_o{}^*(1 - T/T^\dagger)^F. \qquad (1)$$

$\Delta\nu_o$ can be seen as the limit of the observed splitting and F the way the splitting reaches its limit. $T^\dagger$ is a temperature slightly higher than T_{NI}. For C–H fragments within the molecule, it has been shown that in the Haller equation a higher F value indicates a more rigid fragment [25]. It is found for a salt proportion of 0.1 molar equivalents that the F value for Li^+ ion is larger (0.32 ± 0.04) than for the BF_4^- ion (0.12 ± 0.05), which certainly indicates that the lithium ion is far less free to move and is more efficiently ordered by the phase itself than the tetrafluoroborate anion; this F value can be related to the partial complexation of the lithium ion with the oxygen atoms inside the terminal chains. These F values change slightly when the salt concentration increases. It is interesting to note that the F value of Li^+ decreases (0.26 ± 0.04), whereas the F value of the BF_4^- ion is more or less constant (0.13 ± 0.04) for the mixture containing 0.4 molar equivalents of salt. This behaviour may be an indication that the complexation of the lithium is on average less efficient when the number of lithium ions is increasing whereas the number

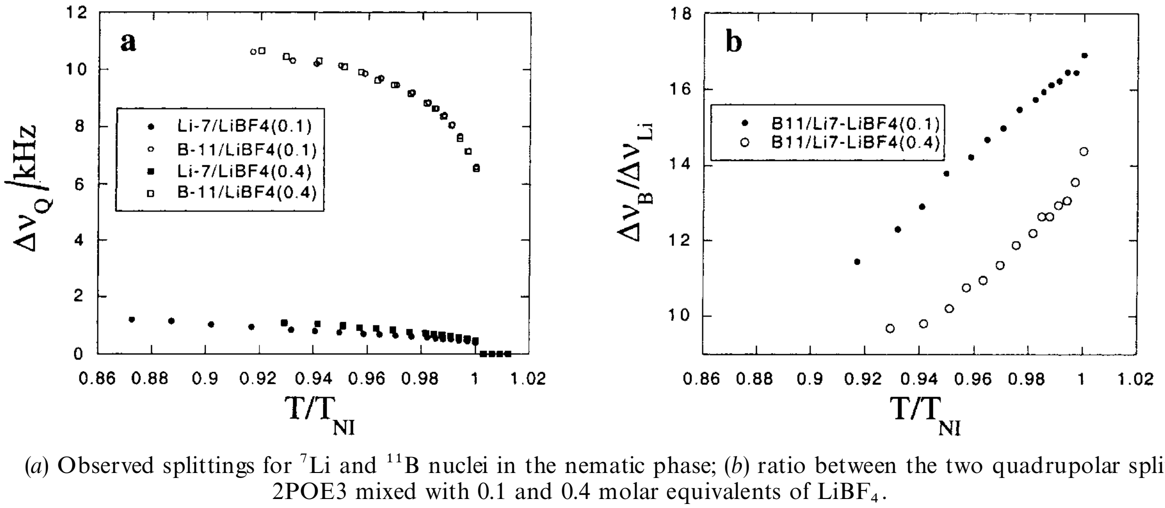


Figure 5. (*a*) Observed splittings for ^7Li and ^{11}B nuclei in the nematic phase; (*b*) ratio between the two quadrupolar splittings in 2POE3 mixed with 0.1 and 0.4 molar equivalents of $LiBF_4$.

of complexing oxygen atoms is maintained constant. The ratio between the two splittings is temperature and concentration dependent. This is due mainly to the difference in the *F* values.

2.5. ^{13}C *NMR measurements in the nematogen*

We have compared by ^{13}C NMR the ordering behaviour of pure 2POE3 and its mixture with 0.2 molar equivalents of $LiBF_4$. Does the salt interact strongly with some part of the mesogen, in particular with the POE chain? The answer is of importance, as the conductivity of ions in POE chains is described as a change of complexation site involving a change in the conformation of the POE chain around the lithium ions. This conformation changes between a crown-ether-like conformation when complexed, to a normal helicoidal conformation when the chain is not in interaction with the cation [26–28]. This question may be answered using ^{13}C NMR as we can obtain, in principle, the anisotropy of the chemical shift for every individual carbon within the molecule.

For this purpose, we have studied the anisotropic chemical shifts in the nematic phase of 2POE3, for which the transition temperatures are within the temperature probe limitations. These experiments were performed using a Bruker DSX-300 NMR spectrometer at $B_o = 7.05$ T on the static sample. The 1D spectra were obtained near the isotropic–nematic transition using a single pulse, and using a standard CP sequence with strong decoupling for lower temperatures. To avoid rf overheating, a 15 s delay time was used. The temperature calibration was made by observing the nematic to isotropic transition. Two spectra, with and without salt, are presented in figure 6 at the same reduced temperature ($T/T_{NI} = 0.983$); they look very similar, even if the linewidth of the peaks seems to increase on salt addition. However, the chemical shift anisotropies do not reflect any important change in conformation of the PEO chains which indicates that the ions and the mesogen interact weakly.

The chemical shifts are rather sensitive to the environment and the change in the chemical shift on entering the nematic phase is an average over different factors: the probability of finding a conformation, the ordering matrix of the C–H fragment involved in that conformation, and the chemical shift tensor of the observed carbon in that conformation. The interaction between the ions and the nematogen can modify each of these factors. To decipher these different factors is difficult, but an empirical relationship for the alignment-induced shift ($\delta_N - \delta_{iso}$) of the aliphatic carbons in the nematic phase has been expressed as [29]:

$$\delta_N - \delta_{iso} = b + aS_{C\text{-}H} = b + aS_o(1 - T/T^{\dagger})^F. \quad (2)$$

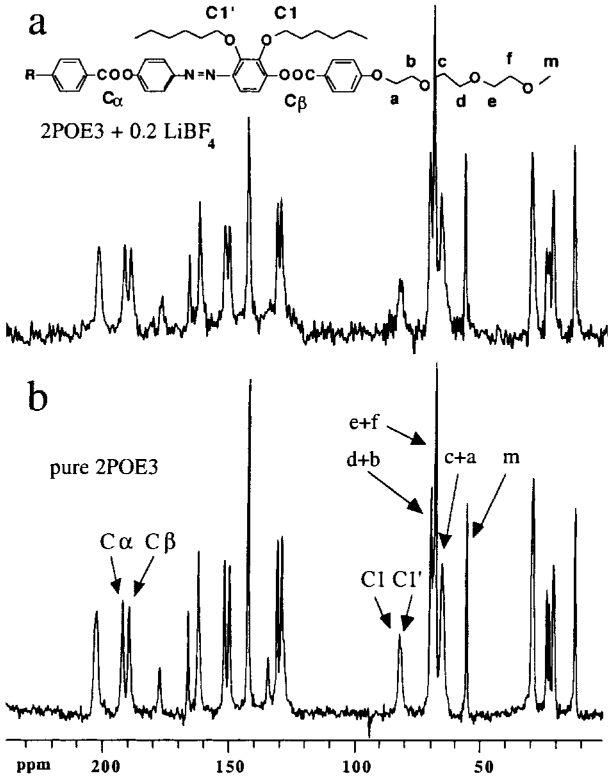


Figure 6. Proton decoupled ^{13}C spectrum in the nematic phase of (*a*) 2POE3 mixture with 0.2 molar equivalent of $LiBF_4$ at 75.475 MHz and the oxygenated carbons in the structure labelled; (*b*) pure 2POE3. Acquisition parameters: single pulse, pulse width = 3 μs, recycle delay = 15 s, number of scans = 256, $T/T_{NI} = 0.983$.

Here *a* and *b* involve the chemical shift tensor components in the axis system chosen to define the order parameter, and were found to vary with temperature in short POE chains indicating a change in the differently populated conformations for the OE unit [15]. In that unit, the *gauche*- and *trans*-conformations do not have the same tensor components. S_o is the limit of the bond order parameter of the fragment relative to the director. The chemical shift should be sensitive to the partial complexation if this involves a change in the conformational population.

In order to have a clearer view of the lack of interaction between the salt and the mesogens, we chose to compare (figure 7) the fragments containing the oxygen atoms: (*a*) the two carboxyl groups of the core, (*b*) the CH_2O of the lateral chains and (*c*) the CH_2O of the terminal POE chains. These signals in (*a*) and (*b*) present a non-negligible anisotropy and may give some indication about the change of the ordering and particularly the change in the position of the molecular long axis of the molecule. The CH_2O and CH_3O signals of the two POE terminal chains probe the change in the conformation of the chain when adding the salt. The assignment of

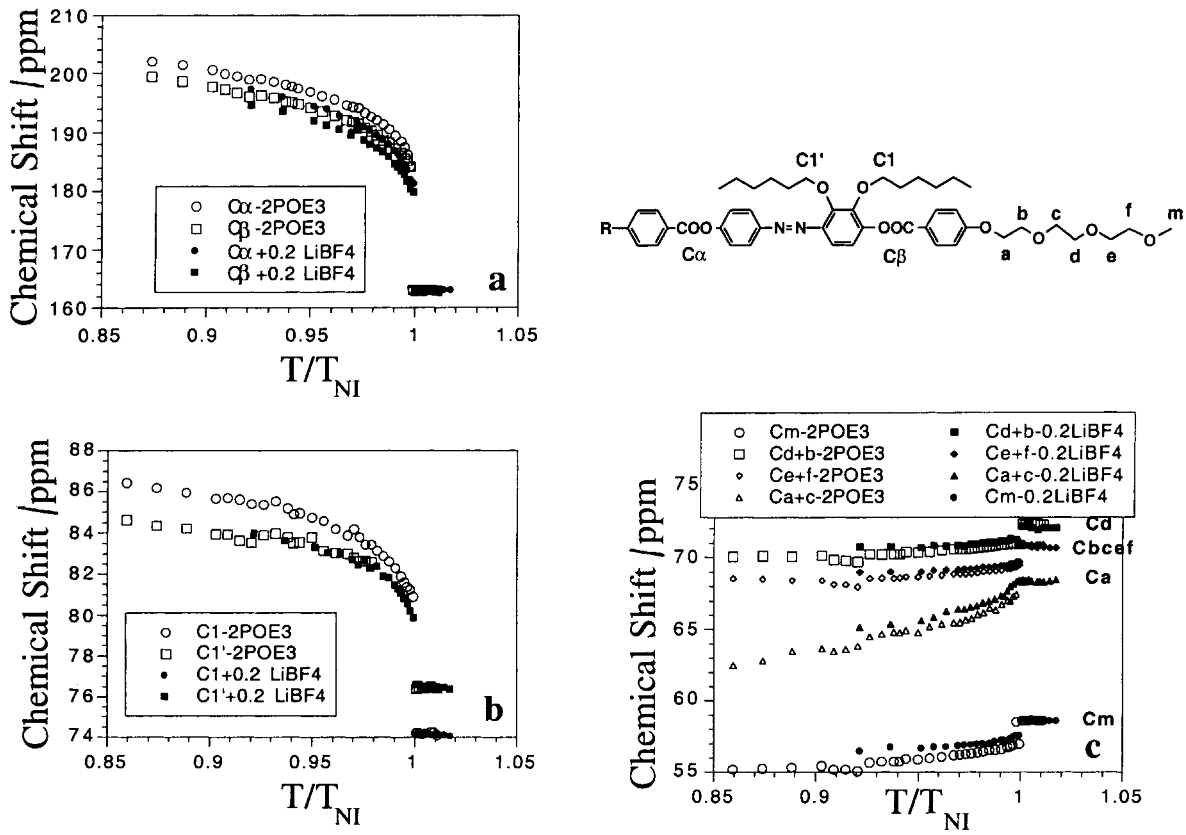


Figure 7. Temperature dependence of the ^{13}C chemical shifts in the static sample of 2POE3 (*a*) for the carboxyl carbons, (*b*) for the CH_2O in the lateral chains and (*c*) for the POE chain carbons.

the different signals is made according to our previous study [15] and is given on the spectra of figure 6. It can be noted that the molecule is not symmetrical; the signals of the two chains overlap and this precludes a fine analysis of the chemical shift evolution.

However, it is clear from figure 7 that the chemical shifts have similar variations with and without salts. Going from the isotropic melt to the nematic phase, the usual large positive jump in the chemical shifts is observed for the two carbonyl carbons and for the two first carbons C1′ and C1 in the lateral chains (in the mixture, a single line is observed for these carbons due to the increase in the linewidth). This large positive jump has been associated with the folding back of the lateral chains that induces a positive order parameter for these carbons [30]. On the contrary, carbons belonging to a terminal chain or to the far part of the lateral chains experience a negative jump due to the peculiar mean orientation of their C–H bonds with respect to the molecular long axis. In figure 7, we can note that the signal corresponding to the first carbon (Ca+ Cc) in the two first OE units presents a larger chemical shift anisotropy than for the second one in the same respective units (Cb+ Cd).

The similar chemical shift anisotropies experienced by the different parts of the molecule tend to prove that the interactions between ions and the mesogens are weak with no evident modification of the molecular long axis and no drastic change of the ordering of the different fragments under study. The analysis of the *F* values is difficult or impossible for the chains because of the superposition of the signals. Nevertheless on the carbonyl carbons and on the OCH_2 lateral carbons a small but significant decrease of the *F* values is observed as for the ions themselves. Thus, the ordering perturbation induced by the dissolution of the ions is rather weak due certainly to the small size of these ions.

Longer chains, terminal or lateral crown-ethers will certainly present a different behaviour on dissolving salts. The possibility of getting a more effective complexation will certainly have an impact on the ^{13}C chemical shifts anisotropy and work is in progress in that direction.

3. Conclusion

The introduction of a short terminal POE chain on a laterally substituted molecule leads to low melting nematogens. The OE units can be incorporated in an open chain or in a lateral crown-ether. The compounds with a lateral crown-ether lead to higher clearing and melting temperatures than those obtained for open chain compounds. These compounds containing OE units can dissolve a large amount of ionic material and still possess a large nematic range.

^{13}C NMR in the nematic phase of a mixture of a nematogen containing two POE chains with $LiBF_4$ indicates that there are very little changes in the carbon chemical shifts, showing that the interaction between the ionic species and the nematogen does not involve a change in the conformation of the POE chains. ^{7}Li and ^{11}B NMR probe the ordering of the ions. When decreasing the temperature, the increase in the ordering is steeper for the lithium cation than for the tetrafluoroborate anion. This may be an indication that, if ions are associated in pairs, the lithium cation is relatively more in interaction with the POE chains.

References

[1] Gray, G. W., 1974, *Liquid Crystals and Plastic Crystals* (Chichester: Ellis Horwood).

[2] Weissflog, W., and Demus, D., 1984, *Cryst. Res. Tech.*, **19,** 55.

[3] Allouchi, H., Belaaraj, A., Cotrait, M., Lafontaine, E., Judeinstein, P., and Bayle, J.-P., 2000, *Liq. Cryst.*, **27,** 1087.

[4] Perez, F., Judeinstein, P., Bayle, J.-P., Allouchi, H., Cotrait, M., and Lafontaine, E., 1996, *Liq. Cryst.*, **21,** 855.

[5] Berdaguè, P., Perez, F., Bayle, J.-P., Ho, M. S., and Fung, B. M., 1995, *New J. Chem.*, **19,** 383.

[6] Perez, F., Judeinstein, P., and Bayle, J.-P., 1995, *New J. Chem.*, **19,** 1015.

[7] Perez, F., Judeinstein, P., Bayle, J.-P., Roussel, F., and Fung, B. M., 1997, *Liq. Cryst.*, **22,** 711.

[8] Armand, M., 1990, *Adv. Mater.*, **2,** 278.

[9] Meyer, W. H., 1998, *Adv. Mater.*, **10,** 439.

[10] Aihara, Y., Sugimoto, K., Price, W. S., and Hayamizu, K., 2000, *J. chem. Phys.*, **113,** 1981.

[11] Lee, M., and Oh, N. K., 1996, *J. mater. Chem.*, **6,** 1079.

[12] Neumann, B., Sauer, C., Diele, S., and Tschierske, C., 1996, *J. mater. Chem.*, **6,** 1087.

[13] Hsiue, G. H., Wu, J. L., and Chen, J. H., 1996, *Liq. Cryst.*, **21,** 449.

[14] Kang, Y.-S, Zin, W. C., Lee, D. W., and Lee, M., 2000, *Liq. Cryst.*, **27,** 1543.

[15] Rayssac, V., Judeinstein, P., Bayle, J.-P., Kuwahara, D., Ogata, H., and Miyajima, S., 1998, *Liq. Cryst.*, **25,** 427.

[16] Leblanc, K., Berdaguè, P., Judeinstein, P., and Bayle, J.-P., 2001, *Liq. Cryst.*, **28,** 265.

[17] Pedersen, C. J., 1967, *J. Am. chem. Soc.*, **89,** 7017.

[18] Hassner, A., and Alexanian, V., 1978, *Tetrahedron Lett.*, **46,** 4475.

[19] Nose, A., and Kudo, T., 1981, *Chem. Pharm. Bull.*, **29,** 1159.

[20] Imrie, C. T., and Taylor, L., 1989, *Liq. Cryst.*, **6,** 1.

[21] Samulski, E. T., 1985, *Polymer*, **26,** 177.

[22] Leblanc, K., Berdaguè, P., Rault, J., Bayle, J.-P., and Judeinstein, P., 2000, *Chem. Commun.*, 1291.

[23] Müller-Plathe, F., and van Gunsteren, V. F., 1995, *J. chem. Phys.*, **103,** 4745.

[24] Haller, I., 1975, *Prog. solid state Chem.*, **10,** 103.

[25] Magnuson, M. L., Fung, B. M., and Bayle, J.-P., 1995, *Liq. Cryst.*, **19,** 823.

[26] Tadokoro, H., Yoshihara, T., Chatani, Y., and Murahashi, S. J., 1964, *Makromol. Chem.*, **73,** 109.

[27] Takahashi, Y., Sumita, I., and Tadokoro, H., 1973, *J. polym. Sci.*, **11,** 2113.

[28] Mujica, V., Malaver, M., and Ruette, F., 1999, *J. phys. Chem. A*, **103,** 89.

[29] Guo, W., and Fung, B. M., 1991, *J. chem. Phys.*, **95,** 3917.

[30] Bayle, J.-P., Ho, M. S., and Fung, B. M., 1993, *New. J. Chem.*, **17,** 345.