Chapter 4

PMRD Investigations of Nematic Phases of Single Component and Binary Mixture of 4O.m Liquid Crystals

4.1 Introduction

Liquid crystals (LC) are usually formed by long molecules with a rigid core. In the formation of LC phase rigid core plays the significant role. There are evidences where long molecular conformations which are flexible without any rigid core don’t exhibit liquid crystal phase of thermotropic kind (Gray 1979). Further it is observed that the liquid crystal properties are very sensitive to molecular structure. Even minor changes in the rigidity or flexibility of the molecules could lead to dramatic effects on the polymorphism exhibited by these systems. From chemical studies it has long been known that the end-chains of the molecules play a significant part in the stability of the mesophases. The nematic-isotropic transition temperature and a number of other properties (e.g. the order parameter, the excess specific heat, the transition entropy, the splay elastic constants, etc.) show a pronounced alternation as the number of carbon atoms in the end-chain is changed. One such effect is the odd-even effect. Many experimental results were reported on different homologous series, mainly by changing the chain length systematically and observing differing physical properties. Investigations on different homologous series are carried out with typical objectives such as:

i. effects of molecular structure on polymorphism;

ii. changes in molecular static/dynamical parameters with additional molecular parameters, as one runs through the homologous series;

iii. discovery of suitable mesogenic phases for different technological applications; and finally,
iv. to look for physical systems to test the validity of theoretical models built to explain static and dynamic features of liquid crystals.

4.2 Review of Literature on nO.m Liquid Crystals

Alkyloxybenzylidine alkylaniline (no.m series) are one of the families of liquid crystals which are well investigated. They have rich polymorphism and also the mesophases are in convenient temperature regions to work with. The first experimental result was reported by Smith and Gardlund (1973). They used calorimetry and optical microscopy, and reported transition temperatures and different mesophases for n=1 to 7 and m=4 to 8. Later Goodby et al. (1980), Takahashi et al. (1987a) and Takahashi et al. (1987b) did exhaustive study on odd-even effects of volume changes at I/N and N/S_A transitions and birefringence study of N/S_A transition in different homologous series of nO.m. Papisati and group (Pisipati et al. 1987, Alapati et al. 1988, Potukuchi 1989, Rannavare et al. 1987, Rannavare et al. 1988) used density, ultrasonic, calorimetry and ESR techniques, respectively, to study various transitions in nO.m series. High-resolution ac calorimetric measurements were carried out on 4O.7, 7O.6 and 7O.4 near the S_A to S_C transition by Miechle and Garland (1983). Apart from these, many experiments were also done on individual members of the no.m series. Magnetic birefringence studies on 9O.4 by Rosenblatt and Ho (1983), light scattering studies on 6O.9 by Mahmood et al. (1985), 6O.3 and 9O.4 by Potukuchi (1989) and dielectric studies on 4O.8 by Nagabhushan et al. (1988) are a few examples of such studies. Neutron scattering experiments were used to study the cooperative nature of the molecular motions in S_B and S_G phases of 5O.7 (Richardson et al. 1984) and molecular rotational motions in 4O.4, 4O.8 and 5O.6 (Mitra et al. 2000, Mitra et al. 2004).

Magnetic resonance technique is extensively used to investigate both molecular structure and dynamics in liquid crystals and were also carried out on a few homologous members of this series. Moore et al. (1980) carried out relaxation and line width measurements on alkoxyazoxybenzenes (PAA). Relaxation times and self diffusion coefficients were measured in a series of p-Alkonyl-Benzylidene-p Aminoazobenzenes by Kruger and Spiesecke (1973). Various relaxation measurements were made on homologous series p-alkoxybenzoic acids by Thompson et al. (1977). Proton spin relaxation dispersion studies were done on nematic homologous of PAA by Nagel et al. (1983). Studies on isolated systems were also reported: Limmer and group reported line width measurements on three nO.m compounds 5O.6, 7O.5 and 7O.6 (Limmer et al. 1984). Schmiedel et al. (1980) measured line shapes to get information on molecular order and intermolecular motions, ESR studies were also done by
4.2. Review of Literature on nO.m Liquid Crystals


Information on molecular dynamics can be obtained from nuclear magnetic relaxation measurements (*Wade 1977, Dong 1983, Norrido and Segre 1979, Vold and Vold 1989*). Blinc and Mugele (*Blinc et al. 1975, Blink 1976, Blinc et al. 1978, Mugele et al. 1980*) investigated the molecular dynamics in TBBA using $T_1$ relaxation dispersion. Recent proton $T_1$ relaxation studies on 4O.m series (varying m values from 2 to 9) include the work of *Venu (1985), Ravindranath (1991),* and *Sailaja (1994)* covering the frequency range of 5 MHz to 50 MHz. These studies showed that in 4O.2, 4O.8 and 4O.9 the ODF contribution is extending up to tens of MHz whereas in 4O.4 and 4O.5 self diffusion was the main mechanism mediating the relaxation above a few MHz while director fluctuations (ODF) were found to be confined to lower frequencies.

The study of molecular dynamics in liquid crystals was originally promoted by the interest in collective dynamic processes associated with orientational fluctuations of the local molecular order. NMR relaxation due to ODF as a manifestation of collective dynamics was first worked out for the nematic phase by Pincus (*Pincus 1969*) (characteristic $\omega^{\frac{1}{2}}$ Larmor frequency dependence for the spin-lattice relaxation time $T_1$) and later developed by several poineers (*Blink 1976, Vold and Vold 1988, Struppe and Noack 1996, Venu and Sastry 1998*). Theoretical expressions for these contributions to spin-lattice relaxation rate are given in Chapter 2. Experimentally $\omega^{\frac{1}{2}}$ dependence of ODF on $T_1$ was first verified in the kHz regime by (*Wolfel et al. 1975*). However these theoretical predictions were not substantiated until the revolutionary advent of field-cycling technique (*Noack 1986*) ruling out the early pneumatic sample shifting technique. Since then, field-cycling relaxometry has been applied to many different liquid crystalline compounds (*Schweikert and Noack 1989, Pusiol and Chavez 1999, Satheesh 2000, Phanikumar 2003, and references therein*).

Recently several single-component liquid crystals as well as liquid crystalline mixtures were studied using this technique (*Venu and Sastry 1999, Satheesh et al. 1999, Satheesh 2000, Phanikumar 2003*). Apart from the dominant ODF, self diffusion (SD) molecular reorientations (R), critical fluctuations near the transition temperatures (CF), diffusion assisted ODF and layer undulations (LU) are the other interesting mechanisms studied (*Pusiol and Chavez 1999, Phanikumar 2003*). These studies showed that MRD technique can be used to obtain qualitative information
regarding the elastic properties as well as about the presence of smectic clusters in nematic phases. These studies also brought out an interesting difference in the dynamic environment of the nematic phases with and without an underlying smectic phase. For example, observation of an interesting nematic state having small smectic clusters which do not grow as the temperature decreased, and hence not leading to the formation of smectic phase, is attributed to the chargetaristic elastic properties of the medium. (Satheesh et al. 1999). In this context, detailed PMRD on a chosen set of 4O.m compounds, with the objective of investigating the end chain length influence on the collective motions in different mesophases, and possible odd-even effects in the series should prove to be rewarding.

In the present work field-cycling NMR relaxometric investigations of molecular processes in 4O.2, 4O.3, 4O.4 and a binary mixture of 4O.2 and 4O.4 are carried out. In this chapter Section 4.3 deals with the \( R_1 \) dispersions in deep nematic phase while Section 4.4 is concerned with dispersions just below \( T_{IN} \).

### 4.3 PMRD Investigations of Nematic Phases of 4O.m Liquid Crystals

#### 4.3.1 Butyloxy Benzilidene Ethylaniline. (4O.2)

The first system of 4O.m series studied in this work is butyloxy benzilidene ethylaniline (4O.2). The system has the following structure and phase sequence (Murase 1971).

![Chemical Structure](image)

Figure 4.1:

\[
\begin{align*}
\text{K} & \quad 43^\circ\text{C} & \text{S}_B & \quad 51^\circ\text{C} & \text{N} & \quad 65.5^\circ\text{C} & \text{I}
\end{align*}
\]

It has a nematic phase over a temperature range of 14.5°C and an ordered smectic phase over 9°C.

#### 4.3.1.1 Experimental Results and Analysis

Spin-lattice relaxation rate \( (R_1) \) profile over the frequency range 50 kHz to 50 MHz at a mid nematic temperature 60°C is collected using fast field cycling NMR relaxometer and a home built, conventional field-variable pulsed NMR spectrometer as
explained in Sections 3.2 and 3.3 of Chapter-3. Fig. 4.2 illustrates the $R_1$ dispersion. The error in data is less than 3% and temperature stability is within 0.2°C. The spin lattice relaxation times ($T_1$) measured here are single exponential fits to the magnetization recovery. Data show dispersions over a wide frequency range (50 kHz-50 MHz). Earlier, temperature dependent relaxation data were collected at three different frequencies (9 MHz, 29.8 MHz and 40 MHz) (Sailaja 1994) and Fig. 4.3 depicts the temperature variation so obtained. It can be seen from this data that in the nematic phase relaxation times are essentially temperature independent ruling out self diffusion (SD) as the major contributing mechanism for relaxation. The possible mechanisms are thus the order director fluctuations (ODF) and reorientations (R). Data were analyzed considering ODF and R as the contributing mechanisms towards this relaxation. i.e.

$$R_{1Total} = R_{1ODF} + R_{1R}$$

(4.1)

$R_{1ODF}$ and $R_{1R}$ are given by Eqns. 2.35 and 2.55 respectively.

The motional parameters of both the mechanisms are extracted from the dispersion by means of a non-linear least squares fitting of the dispersion data to the Eqn. 4.1 using the procedure based on Levenberg-Marquart algorithm which was already explained in Chapter 2. $K_1$ and $K_2$ were fixed at $10^{-6}$ dyne and $K_3$ was varied in the fitting process. The data doesn’t show low frequency plateau indicating that the
Figure 4.3: Proton Spin lattice relaxation time $T_1$ as a function of temperature $T$ at three frequencies in 4O.2. Solid lines are drawn as a guide to the eye. The vertical lines denote the transition temperatures. $T_1$ is temperature independent in the nematic phase ($T > 55^\circ$C).

low frequency cut off of the ODF contribution is below the lowest frequency of study (50 kHz).

4.3.2 Butyloxy Benzilidene Propylailine (4O.3)

The second system studied in the series of 4O.m is butyloxy benzilidene propylaniline (4O.3), with one CH$_2$ group more compared to 4O.2. The system has the following phase sequence (Murase 1971)

![Phase diagram](image)

Figure 4.4:

$K$ 54.5°C  N  82.5°C  I

This system has nematic mesophase over a range of 30°C and no underlying smectic phase.
4.3.2.1 Experimental Results and Analysis

Spin-lattice relaxation measurements over four decades of frequencies (50 kHz - 50 MHz) were collected at two temperatures in the deep nematic phase (60°C and 70°C) and two temperatures near the I-N transition (\(\Delta T = 1°C\) and 0.5°C). Fig. 4.5 shows the PMRD profiles at four temperatures. Spin lattice relaxation times as function of temperature (Sailaja 1994) are shown in Fig. 4.6. The temperature dependent data read from the dispersions is plotted in Fig. 4.7. In the low frequency regime below 2 MHz relaxation rates are temperature independent. Strong temperature dependence is seen only at high frequencies. The proton spin relaxation dispersions obtained in nematic phase were analyzed considering three mechanisms mediating the relaxation namely ODF, SD and R according to Eqn. 2.10. i.e.

\[
R_{1\text{total}} = R_{1\text{ODF}} + R_{1\text{SD}} + R_{1\text{R}}
\]  

(4.2)

where \(R_{1\text{ODF}}, R_{1\text{SD}}\) and \(R_{1\text{R}}\) are given by equations 2.35, 2.52 and 2.55 respectively. Figs. 4.8 and 4.9 show the fitted dispersions.
Figure 4.6: Spin lattice relaxation time $T_1$ as a function of temperature $T$ at three frequencies in 4O.3. Solid lines are drawn as a guide to the eye. The vertical lines denote the transition temperatures.

Figure 4.7: Spin lattice relaxation time $T_1$ as a function of temperature $T$ at different frequencies in 4O.3. The lines joining the points are for eye guide.
The parameters $q_{zch}$ and $q_{pch}$ are found to be nearly equal at every temperature.
ODF is the dominating mechanism up to 2 MHz. Reorientations start contributing significantly to relaxation rate above 2 MHz frequency. Here SD contribution to the total relaxation seem to be relatively quite small. Motional parameters obtained from this analysis are tabulated in Table 4.1. The correlation time associated with reorientations is much smaller so that its contribution to the dispersion is practically found to be a constant C’. This contribution C’ showed weak temperature dependence. The cutoff frequencies and wavelengths of the ODF in this system are tabulated in Table 4.2.

4.3.3 Butyloxy Benzilidene Butylaniline (4O.4)

The third system studied in nO.m series is Butyloxy Benzilidene Butylaniline (4O.4). This has a phase sequence given by (Flannery and Haas 1970) as shown below.

\[
\begin{align*}
S_X & \quad 38.6^\circ C \quad S_B \quad 44.7^\circ C \quad S_A \quad 45.1^\circ C \quad N \quad 74^\circ C \quad I
\end{align*}
\]

This system has wide nematic phase and a very narrow range of S_A and S_B phases.

4.3.3.1 Experimental results and analysis

Spin-lattice relaxation measurements were carried out as explained for other samples in this series earlier, in the deep nematic phase at 60°C. Dispersion is shown in Fig. 4.11. Fig. 4.12 shows the temperature dependent relaxation data measured earlier at three frequencies (5 MHz, 15 MHz and 39.6 MHz) (Sailaja 1994). Relatively strong temperature dependence of relaxation times can be seen, compare to the other two members of the family discussed above. 4O.4 dispersions were analyzed following similar procedure as it was explained in case of 4O.3, considering three mechanisms mediating the relaxation namely ODF, SD and R (Fig. 4.11). Optimized analysis reveals that ODF is the dominating mechanism up to 1 MHz. Self diffusion dominates in the intermediate frequencies 1 MHz to 10 MHz. Reorientations contribute dominantly to relaxation rates at higher frequencies. The correlation time associated with reorientations is much smaller so that its contribution to the dispersion is taken as a constant C’. Motional parameters obtained from such analysis are tabulated in Table 4.1. The cutoff frequencies and wavelengths calculated are tabulated in Table 4.2.
4.3. PMRD Investigations of Nematic Phases of 4O.m Liquid Crystals

Figure 4.11: PMRD of 4O.4 in the nematic phase at 60°C.

Figure 4.12: Spin lattice relaxation time $T_1$ as a function of temperature $T$ at different frequencies. The lines joining the points are for eye guide.

4.3.4 Binary Mixture of 4O.2 and 4O.4

The analysis of data in the three 4O.m systems brings out certain contrasting comparisons. In 4O.2, there is an underlying $S_B$ phase below the nematic phase. From
Table 4.1 it is seen that there is no diffusion contribution to the relaxation process and the ODF contribution seems to suggest the lower cutoff wavelengths for ODF are comparable to molecular sizes. This inturn indicates the absence of smectic like organization. In 4O.3, there is a small contribution from SD as well, and analysis of ODF reflects the presence of lower wavelength cutoff values, which indicate the presence of clusters of smectic organizations. However, these clusters have comparable dimensions along & perpendicular to the director (so-called isotropic clusters for simple discription), and their size does not seem to grow with decrease in temperature. It may be noted that this system (4O.3) does not have an underlying smectic phase.

In 4O.4, the contributions of SD is even more, and the lower cutoff wavelengths of ODF suggest the presence of smectic clusters with unequal sizes in the two directions (so-called anisotropic clusters). Now the case of 4O.3 wherein there are (so-called) isotropic clusters of smectic organizations in the nematic phase and which do not change in their size with temperature is comparable to the earlier observation on 7BCB (4-Cyanophenyl-4'-n-heptylbenzoate). It was concluded that such a dynamic molecular organization in the nematic phase represents a frustrated phase where smectic clusters as seeds, do form, but can not grow in size, to finally condense into a smectic phase, due to sustainable elastic properties of the medium (Satheesh 2000). In the light of these observations on the three homologous members, it is felt that a binary mixture of 4O.2 and 4O.4 might be an interesting system to see if it exhibit this type of dynamic organization.

With this in mind a 1:1 (number of moles) mixture of 4O.2 and 4O.4 is prepared and studied using proton relaxometry. The phase sequence of this mixture is found using polarizing microscope, and is as shown below.

\[
S_x \quad 45.1^\circ C \quad N \quad 71.5^\circ C \quad I
\]

This system has wide nematic phase and an unspecified smectic phase.

### 4.3.4.1 Experimental Results and Analysis

Spin-lattice relaxation measurements were done as explained earlier, in the nematic phase at three temperatures (55°C, 60°C, and at 65°C). Dispersions are shown in Fig. 4.13. Fig. 4.14 shows the temperature dependent relaxation data at 40 MHz. Relaxation times as function of temperature in the nematic phase are shown in Fig. 4.15. Strong temperature dependence of relaxation times at high frequencies can be seen here too. As it was guided by the temperature dependence of relaxation rates the conditions used in the analysis of 4O.3 and 4O.4 are implemented in this case too. Figs. 4.16 to 4.18 show the fitted dispersions. Nonlinear least square method
of analysis reveals that ODF is the dominating mechanism up to 1 MHz. Self diffusion dominates in the intermediate frequencies 1 MHz to 10 MHz. Reorientations contribute dominantly to relaxation rates at higher frequencies. The data, however, show there is no frequency dependence to the relaxation contribution from reorientations, as has been in the case in 4O.3 and 4O.4, indicating that this situation corresponds to $\omega \tau_c \ll 1$ limit in the experimental frequency range. Therefore the relaxation contribution due to reorientations is taken as a constant ($C'$). Motional parameters obtained from such analysis are shown in Table 4.1. From the table it can be seen that the fits require inequality of the three elastic constants reflecting the elastic properties in this system. The cutoff frequencies and wavelengths calculated are provided in Table 4.2.

![Figure 4.13: PMRD profiles in the nematic phase in 1:1 mixture of 4O.2 and 4O.4.](image-url)
Figure 4.14: Spin lattice relaxation time $T_1$ as a function of temperature $T$ at 40 MHz.

Figure 4.15: Spin lattice relaxation time $T_1$ as a function of temperature $T$ at different frequencies in the mixture of 4O.2 and 4O.4. The lines joining the points are for eye guide.
4.3. PMRD Investigations of Nematic Phases of 4O.m Liquid Crystals

Figure 4.16: PMRD profile of 4O.2 and 4O.4 mixture in the nematic phase at 55°C.

Figure 4.17: PMRD profile of 4O.2 and 4O.4 mixture in the nematic phase at 60°C.
Figure 4.18: PMRD profile of 4O.2 and 4O.4 mixture in the nematic phase at 65°C.

<table>
<thead>
<tr>
<th>nO.m</th>
<th>T °C</th>
<th>$K_3$ $10^{-6}$dynes</th>
<th>$q_{zh}$ $10^8$cm$^{-1}$</th>
<th>$q_{pch}$ $10^8$cm$^{-1}$</th>
<th>$A_{ODF}$ $10^{-6}$s$^{-2}$</th>
<th>$B$ $10^{-12}$m$^2$s$^{-1}$</th>
<th>$D$ $10^9$s$^{-2}$</th>
<th>$C$ $10^9$s$^{-2}$</th>
<th>$\tau_R$ $10^{-9}$s</th>
</tr>
</thead>
<tbody>
<tr>
<td>4O.2</td>
<td>60</td>
<td>1.09</td>
<td>0.32</td>
<td>0.3</td>
<td>3.43</td>
<td>2.08</td>
<td>(0.1)</td>
<td>1.12</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(0.19)</td>
<td>(0.02)</td>
<td>(0.013)</td>
<td>(0.29)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4O.3</td>
<td>60</td>
<td>1.02</td>
<td>0.107</td>
<td>0.107</td>
<td>2.293</td>
<td>1.101</td>
<td>15.02</td>
<td>1.8*</td>
<td></td>
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<tr>
<td></td>
<td></td>
<td>(0.02)</td>
<td>(0.04)</td>
<td>(0.04)</td>
<td>(0.025)</td>
<td>(0.4)</td>
<td>(2.7)</td>
<td>(0.46)</td>
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</tr>
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<td></td>
<td>70</td>
<td>1.001</td>
<td>0.105</td>
<td>0.105</td>
<td>2.0954</td>
<td>1.271</td>
<td>15.5</td>
<td>1.47*</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(0.03)</td>
<td>(0.042)</td>
<td>(0.042)</td>
<td>(0.034)</td>
<td>(0.89)</td>
<td>(1.7)</td>
<td>(0.11)</td>
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<tr>
<td>4O.4</td>
<td>60</td>
<td>1.54</td>
<td>0.028</td>
<td>0.048</td>
<td>3.15</td>
<td>4.87</td>
<td>25.7</td>
<td>1.52*</td>
<td></td>
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<tr>
<td></td>
<td></td>
<td>(0.02)</td>
<td>(0.002)</td>
<td>(0.003)</td>
<td>(0.023)</td>
<td>(0.2)</td>
<td>(1.23)</td>
<td>(1.52)</td>
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<tr>
<td></td>
<td>55</td>
<td>1.38</td>
<td>0.062</td>
<td>0.027</td>
<td>2.98</td>
<td>3.097</td>
<td>12.78</td>
<td>1.75*</td>
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<tr>
<td></td>
<td></td>
<td>(0.03)</td>
<td>(0.002)</td>
<td>(0.001)</td>
<td>(0.02)</td>
<td>(0.03)</td>
<td>(0.5)</td>
<td>(0.05)</td>
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</tr>
<tr>
<td>4O.2</td>
<td>+</td>
<td>1.17</td>
<td>0.071</td>
<td>0.036</td>
<td>2.72</td>
<td>3.22</td>
<td>16.69</td>
<td>1.56*</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(0.02)</td>
<td>(0.01)</td>
<td>(0.001)</td>
<td>(0.02)</td>
<td>(0.03)</td>
<td>(0.5)</td>
<td>(0.05)</td>
<td></td>
</tr>
<tr>
<td>4O.4</td>
<td>65</td>
<td>1.03</td>
<td>0.048</td>
<td>0.039</td>
<td>2.47</td>
<td>3.78</td>
<td>19.95</td>
<td>1.37*</td>
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<td></td>
<td></td>
<td>(0.037)</td>
<td>(0.005)</td>
<td>(0.003)</td>
<td>(0.016)</td>
<td>(0.04)</td>
<td>(0.78)</td>
<td>(0.07)</td>
<td></td>
</tr>
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* in the limit $\omega \tau_r \ll 1$ it is taken as $C\tau_r = C'$

Table 4.1: Parameters extracted from the fits of proton spin-lattice relaxation rate dispersions in the nematic phase of 4O.2, 4O.3, 4O.4 and the mixture of 4O.2 and 4O.4. Data were fitted to equation 2.10 considering the contributions from ODF, SD, and R. Uncertainties in the parameters are enclosed in the parathesis.
### Table 4.2: Cutoff frequencies and wavelengths calculated from the parameters extracted.

<table>
<thead>
<tr>
<th>nO.m</th>
<th>T °C</th>
<th>$\nu_{zch}$ MHz</th>
<th>$\nu_{pch}$ MHz</th>
<th>$\lambda_{zcl}$ A</th>
<th>$\lambda_{pcl}$ A</th>
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<td>4O.3</td>
<td>60</td>
<td>37.3</td>
<td>36.6</td>
<td>58.58</td>
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<tr>
<td></td>
<td>70</td>
<td>34.8</td>
<td>34.8</td>
<td>60.1</td>
<td>60.1</td>
</tr>
<tr>
<td>4O.4</td>
<td>60</td>
<td>6</td>
<td>5.6</td>
<td>180</td>
<td>157</td>
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<td>4O.2</td>
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<td>4.1</td>
<td>2.1</td>
<td>193</td>
<td>246</td>
</tr>
<tr>
<td>4O.4</td>
<td>60</td>
<td>5.9</td>
<td>4.8</td>
<td>157</td>
<td>161</td>
</tr>
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<td>65</td>
<td>7.1</td>
<td>6.47</td>
<td>125</td>
<td>133</td>
</tr>
</tbody>
</table>

4.3.5 Discussion

The results show that ODF and R mechanisms essentially mediate the proton relaxation in the entire frequency range in 4O.2 (Fig. 4.2). The computed cutoff frequencies of director fluctuations are well outside the experimental frequency range. The upper cutoff frequency is thus greater than 50MHz and hence lower cutoff wavelength should be less than 50Å, indicating that the lower cut off wavelength of ODF modes is in the range of molecular size. It is known that typically the average size of the smectic clusters normally determine this lower cutoff wavelengths in the nematic phase, and such low values in 4O.2 (reaching molecular size) are indication of absence of smectic clusters in the medium (Venu and Sastry 1998, Venu and Sastry 1999). Similar trend was observed earlier in a few other liquid crystals, with only a nematic phase without underlying S_A. (Venu and Sastry 1999, Phanikumar 2003). 4O.2 however has an underlying smectic phase S_B, which is almost like crystalline organization. It is interesting that it seems to make a difference in the dynamic orgaization of the nematic medium, depending upon whether the underlying layered phase is S_A or S_B. The near temperature independence of relaxation data over the frequency range (Fig. 4.3) shows that ODF contribution as expected (Vold and Vold 1989) as well as R cotributions are essentially independent of temperature. This strongly suggest very low activation energy hindering the reorientational motions. Earlier studies (Rebeirio 1987, Satheesh 2000, Phanikumar 2003) also lead to similar conclusions. It appears that whenever the director fluctuations dominate NMR relaxation up to few tens of MHz, meaning that the director modes have wavelengths as shorts as molecular size (i.e. clean nematic phases with no smectic clusters), the reorientations experience very low hindrance. This seems to be consistent with the fact that the reorientations about short axis (which are the main type of reorientations contributing to the relaxation in nematic phases) are asymptotically compared to the ODF modes having length scales of the order of molecular size (Satheesh 2000). This compound also exhibits isotropic elastic properties (all the Frank elastic constants as
estimated from the fit of the experimental data being approximately the same).

4O.4 provides a contrasting situation. The self diffusion of the molecules (SD) is a dominating mechanism in the intermediate frequency range (Fig. 4.11) and director modes get cutoff around a few MHz (Table 4.2). Further the lower cutoff wavelengths of the director modes are anisotropic in the sense that they have different values in the directions parallel and perpendicular to the director. As per the above discussion, these lower wavelength cutoff values are assigned to corresponding average smectic cluster size in the medium (Satheesh 2000), then the present results indicate the presence of anisotropic smectic clusters in the nematic phase. The existence of the underlying SA phase makes the detection of such clusters in the nematic phase plausible. Further this compound exhibits anisotropic elastic properties ($K_3 > K_1$ and $K_2$) (Table 4.1).

The results of 4O.3 can now be compared with those of both the neighbors in the homologous series (4O.2 and 4O.4). Like in 4O.4, SD contributes to the relaxation in 4O.3 in the intermediate frequency range. Similarly the ODF modes in 4O.3 exhibit lower cutoff wavelengths, though smaller compared to 4O.4, of the order of 60Å both along the transverse and longitudinal directions (Table 4.2). That means 4O.3 exhibits isotropic smectic-like clusters comprising of a few molecules unlike in 4O.4. The results also indicate that the sizes of these clusters remain the same on lowering the temperature by 10°C (Table 4.2). Further, the elastic constants seem to be of equal magnitude in this compound (as in 4O.2). Concluding the observations on 4O.2 and 4O.4, it appears that an underlying SA phase and not SB leaves a signature in the high temperature nematic phase. There appear to be smectic organizations with anisottrpic sizes and the elastic coefficients are found to be unequal. Though 4O.3 shows smectic clusters, they don’t grow in sizes as the system is cooled. It is interesting to mention this observation in the context of the fact that a SA phase is not found at low temperatures in this compund. Similar behavior was observed earlier (Satheesh 2000) and such nematic phases were called frustrated nematic phases. These frustrated nematic phases are different from pure nematic phases (as in 4O.2), as well as nematic phases with underlying smectic phases (as in 4O.4). These studies further strengthen the earlier conclusions found between the nature and size of smectic organizations in nematic phase, and stability of low temperature smectic phases.

It is interesting to observe how a mixture of two compounds, 4O.2+4O.4 behave. Such a system with 1:1 molar ratio has shown anisotropic elastic properties (Table 4.1) as well as anisotropic and relatively (to 4O.3) larger smectic clusters (Table 4.2). Further these clusters grow in size as the sample is cooled. These results are
consistent with the fact that this mixture was found to have an underlying smectic phase. Thus, 50% mixture of 4O.2 and 4O.4 is not exactly like 4O.3.

4.4 PMRD Investigations of 4O.m Liquid Crystals Just Below $T_{IN}$

4.4.1 Experimental Results and Analysis

Just below $T_{IN}$ PMRD data at two different temperatures 81°C and 81.5°C for 4O.3 and 70°C and 70.5°C for the binary mixture of 4O.2 and 4O.4 are collected. $\Delta T_{IN}$ is 1°C and 1.5°C respectively in both the cases. Data were analyzed with a suitable model (Dong 1994), considering order parameter fluctuations (OPF), molecular self diffusion (SD) and molecular reorientations (R). The analysis was carried out using non-linear least square method based on Levenberg-Marquardt algorithm. Parameters extracted are tabulated in Table 4.3. Results of analysis of these data at each temperature are as follows.

4.4.1.1 4O.3

At $\Delta T_{IN} = 1$°C: Here the major contribution to relaxation is arising from nematic order parameter fluctuations (OPF) showing $\omega^{-0.5}$ dependence above 0.6 MHz. A plateau is observed below this frequency. The relaxation contribution due to translational diffusion (SD) is showing dispersion above 3 MHz. and is dominant up to 50 MHz. The contribution of R which is due to molecular reorientations around short axis is small and fast in the experimental frequency range of study. Here its contribution is constant over the frequency range of study (Fig. 4.19).

At $\Delta T_{NI} = 1.5$°C: Here the major contribution to the relaxation is again from OPF. Further the analysis show that the $\omega^{-0.5}$ region due to OPF relaxation modes is extending to lower frequencies. SD is seen to be important at higher frequencies above 5 MHz. Here SD contribution to total relaxation rate is less (13%) compared to $\Delta T_{NI} = 1$°C (25%). Here also molecular reorientations are fast in the experimental range of study (Fig. 4.19).
4.4. PMRD Investigations of 4O.m Liquid Crystals Just Below $T_{IN}$

Figure 4.19: PMRD of 4O.3°C below $T_{NI}$.

Figure 4.20: PMRD of 4O.3 1.5°C below $T_{NI}$.
4.4.1.2 Mixture (4O.2 + 4O.4)

At $\Delta T_{IN} = 1^\circ$C: Here the major contribution to relaxation is arising from nematic order parameter fluctuations (OPF) showing $\omega^{-0.5}$ dependence above 1 MHz. A plateau is observed below this frequency. The relaxation contribution due to translational diffusion (SD) is showing dispersion above 2 MHz. Its dominance is not seen throughout the frequency range of study up to 50 MHz. The contribution of R which is due to molecular reorientations around short axis is small and fast in the experimental frequency range of study. Here R is constant ($C'$) over the frequency range of study (Fig. 4.21).

At $\Delta T_{IN} = 1.5^\circ$C: Here the major contribution to the relaxation is arising from OPF. However the results of the analysis show that the $\omega^{-0.5}$ region due to OPF relaxation modes extending to low frequencies. SD is seen at intermediate frequencies 1 - 20 MHz and reorientations dominate up to 50 MHz. Here SD contribution to total relaxation rate (40%) is comparable to $\Delta T_{IN} = 1^\circ$C (44%). Here also molecular reorientations are fast in the experimental range of study (Fig. 4.22).

Just below the isotropic-nematic transition, the relaxation due to nematic order parameter fluctuation (OPF) is caused by the fluctuation in the magnitude of the long-range orientational order. This long-range orientational order is the order parameter of the isotropic-nematic transition, which is of weakly first order nature. From the Table 4.3 it is clear that the correlation times ($\tau_o$) associated with the OPF are sharply increasing for a change of 0.5°C in temperature. The constant $A_o$ has also shown strong temperature variation. The increase in correlation time or equivalently the corresponding correlation length as the temperature decreases, in turn indicates the progressive onset of nematic order parameter. This slowing down of the correlation time as the nematic phase stabilizes, was observed earlier in other systems 4PCH (Pusiol and Chavez 1999) and in 8OCB (Phanikumar 2003). The smaller correlation time associated with nematic order parameter fluctuation near to $T_{IN}$ is attributed to the thermal effects, which randomize nematic order. The relaxation mechanism due to OPF modes is similar to that of short-range nematic clusters that exist just above $T_{IN}$ (Dong 1994).
4.4. PMRD Investigations of 4O.m Liquid Crystals Just Below $T_{IN}$

Figure 4.21: PMRD profile of 4O.2 and 4O.4 mixture at $\Delta T = 1^\circ C$

Figure 4.22: PMRD profile of 4O.2 and 4O.4 mixture at $\Delta T = 1.5^\circ C$
4.5 Conclusions

These studies show that PMRD study in nematic liquid crystals, together with temperature dependence studies provides an insight into the molecular motions in liquid crystals. Present investigations show that in 4O.2 and 4O.3 contributions from director fluctuations spread to considerably high frequencies which, in support of earlier results, seems to be a common feature of liquid crystals of low viscous, or nematics without underlying smectic phases. On the other hand similar effects from 4O.4 and the mixture are limited to low frequencies consistent with the results on high viscous liquid crystals. It is observed that translational self-diffusion contribution is increasing as the end chain length increases. In low viscous liquid crystals self-diffusion process is fast and hence their contribution to the relaxation is small within the experimental frequency range. The binary mixture of 4O.2 and 4O.4 in appropriate ratio could be expected to behave like 4O.3 as the result of odd-even effects. But the dynamics observed in 1:1 mixture are more similar to 4O.4. One could perhaps further study this mixture to verify this conjunction by varying the ratio of the composition. Just below $T_{NI}$ the nematic order parameter fluctuations are the dominant relaxation mechanism. The time scales of nematic order fluctuations and their slowing down are observed. Present PMRD studies in an unique way give an insight into how the molecular processes evolve with change in the end chain length in 4O.m homologous series. It also provides an opportunity to compare these results with earlier studies on high and low viscous samples.

Table 4.3: Parameters extracted from the fits of proton spin-lattice relaxation dispersions at just below $T_{NI}$ in 4O.3 and the mixture of 4O.2 and 4O.4. Data were fitted to equation 2.10 considering relaxation rate contributions from OPF, SD and R. Uncertainties in the parameters are enclosed in the parathesis.

<table>
<thead>
<tr>
<th>nO.m</th>
<th>T °C</th>
<th>$A_o$ $10^2$s$^{-1}$</th>
<th>$\tau_o$ $10^{-8}$s</th>
<th>B $10^8$s$^{-2}$</th>
<th>D $10^{-12}$m$^2$s$^{-1}$</th>
<th>C’</th>
</tr>
</thead>
<tbody>
<tr>
<td>4O.3</td>
<td>81</td>
<td>62.39 (0.89)</td>
<td>8211 (649)</td>
<td>3.31 (0.31)</td>
<td>18.98 (1.59)</td>
<td>0.63</td>
</tr>
<tr>
<td></td>
<td>81.5</td>
<td>66.5 (1.13)</td>
<td>2058 (80)</td>
<td>7.75 (0.13)</td>
<td>34.16 (0.98)</td>
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</tr>
<tr>
<td>4O.2</td>
<td>70</td>
<td>69.72 (5.43)</td>
<td>1316 (117)</td>
<td>1.979 (0.07)</td>
<td>4.8 (0.27)</td>
<td>2.34</td>
</tr>
<tr>
<td>+</td>
<td></td>
<td>(17.5) (18.5)</td>
<td>(0.16)</td>
<td>(0.32)</td>
<td>(0.1)</td>
<td></td>
</tr>
<tr>
<td>4O.4</td>
<td>70.5</td>
<td>113.53 (117)</td>
<td>255.3 (80)</td>
<td>2.01 (0.13)</td>
<td>5.2 (0.27)</td>
<td>2.17</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(17.5) (18.5)</td>
<td>(0.16)</td>
<td>(0.32)</td>
<td>(0.1)</td>
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</table>