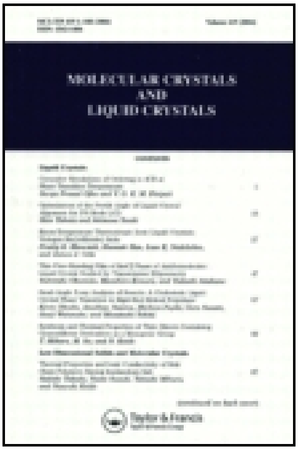

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Peculiar Molecular Dynamics Behaviour in the Isotropic Phase of Some Liquid Crystalline Systems

D. Filip [a] [b] , C. Cruz [a] [c] , P. J. Sebastião [a] [c] , A. C. Ribeiro [a] [c] , T. Meyer [d] & G. H. Mehl [d]

[a] Centro de Física da Matéria Condensada da Universidade de Lisboa Av, Prof. Gama Pinto 2, Lisboa, Portugal

[b] "Petru Poni" Institute of Macromolecular Chemistry, Iasi, Romania

[c] IST-UTL, Av. Rovisco Pais, Lisboa, Portugal

[d] Department of Chemistry, The University of Hull Cottingham Road, Hull, United Kingdom

Version of record first published: 31 Aug 2006

To cite this article: D. Filip, C. Cruz, P. J. Sebastião, A. C. Ribeiro, T. Meyer & G. H. Mehl (2005): Peculiar Molecular Dynamics Behaviour in the Isotropic Phase of Some Liquid Crystalline Systems, Molecular Crystals and Liquid Crystals, 436:1, 17/[971]-28/[982]

To link to this article: http://dx.doi.org/10.1080/15421400590955235

Mol. Cryst. Liq. Cryst., Vol. 436, pp. 17/[971]–28/[982], 2005
Copyright © Taylor & Francis Inc.
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400590955235

Peculiar Molecular Dynamics Behaviour in the Isotropic Phase of Some Liquid Crystalline Systems

D. Filip
Centro de Física da Matéria Condensada da Universidade de Lisboa Av. Prof. Gama Pinto 2, Lisboa, Portugal and
"Petru Poni" Institute of Macromolecular Chemistry, Iasi, Romania

C. Cruz
P. J. Sebastião
A. C. Ribeiro
Centro de Física da Matéria Condensada da Universidade de Lisboa Av. Prof. Gama Pinto 2, Lisboa, Portugal and IST-UTL, Av. Rovisco Pais, Lisboa, Portugal

T. Meyer
G. H. Mehl
Department of Chemistry, The University of Hull Cottingham Road, Hull, United Kingdom

NMR proton spin-lattice relaxation constitutes an important tool for the characterization of the molecular dynamics in liquid crystals (LC). For LCs, in general, the main difference between the proton relaxation dispersion in mesophases and in the isotropic phase appears in the low frequency regime: typically a plateau is observed in the isotropic phase and specific frequency dependences, due to collective movements, are found in the LC phases. In more complex systems, peculiar frequency dependencies, in the low frequency regime may be found in the isotropic phase. The results presented in this paper reveal the presence of particular slow motional mechanisms related to the specific characteristics of the investigated systems.

Keywords: isotropic phase; liquid crystals; molecular dynamics; proton NMR relaxation; tetrapodes

This work was partially supported by the Portuguese Science Foundation (FCT) – Project POCTI/34453/CTM/2000 and by the EU through project HPRN-CT-2000-0016.

Address correspondence to D. Filip, Centro de Física da Matéria Condensada da Universidade de Lisboa Av. Prof. Gama Pinto 2, 1649-003 Lisboa, Portugal. E-mail: dare67ro@yahoo.com

1. INTRODUCTION

Different types of molecular motions in liquid crystalline systems can be studied by NMR proton relaxation, particularly when standard and fast field-cycling NMR techniques are combined [1]. When a broad enough domain of Larmor frequencies is explored different molecular movements with different time scales can display their characteristic signatures in the proton relaxation dispersion profiles.

In general, the movements observed in liquid crystalline phases for the frequencies associated with this kind of NMR experiments are mainly of three types: local molecular rotations/reorientations (ROT) (effective at high frequencies $\sim$10–100 MHz), molecular self-diffusion (SD) (effective at intermediate frequencies 1–10 MHz) and collective movements (CM) (effective at low frequencies 0–1 MHz).

The main difference between the isotropic and LC phases, is the presence, of the long-range orientational order in the LC phases, which leads to characteristic relaxation mechanisms, due to the collective movements. This slow motional process usually produces a particular dependence of the spin-lattice relaxation time on the Larmor frequency, typically a square root law $T_1(\nu^{1/2})$ for the nematic phase and linear frequency dependence law $T_1(\nu^1)$ for the smectic phase. In the isotropic phase, only two mechanisms (self-diffusion and local molecular rotations/reorientations) with short characteristic times τ were generally found to contribute to the relaxation rate [2]. In this case, no frequency dispersion is observed when $\nu\tau \ll 1$.

Local molecular rotations are basically determined by the molecular characteristics; molecular translational self-diffusion is conditioned by short range molecular arrangements and is determined by the phase structure at local level, whilst the collective movements specific to liquid crystalline phases depend on the existence of long range molecular ordered domains.

In the past years many proton relaxation studies have been carried out in different types of mesophases exhibited by calamitic [3–5], disc-like [6] and polycatenar molecules [7]. These studies dealt with various relaxation models contributing to the structural characterization of different mesophases. Also the experimental results in the isotropic phase were analysed, mainly in order to differentiate the molecular movements in the LC and isotropic phases. The most basic result was that the low-frequency T_1 dispersion, corresponding to the collective movements completely vanishes above LC-isotropic transition temperature, whereas the dispersion in the high frequency region is almost similar in the two types of phases. Many other studies dealt with the liquid crystal molecular dynamics slightly above the clearing temperature when, locally, molecules are still parallel to each other, and therefore form "pseudo-nematic domains" [8]. The relaxation mechanism associated with this short-range order fluctuations in the isotropic phase was considered as a possible explanation of the T_1 experimental results in the isotropic phase of the discotic LC compound studied in [9].

In this paper, we focus on the peculiar molecular dynamics in the isotropic phase of more complex LC systems comparing their behaviour with the one exhibited by more conventional low molecular weight LCs. New proton NMR relaxation results obtained with new LC compounds, namely organosiloxane tetrapodes (oligomers), precursors for LC dendrimers are presented.

2. A COMPARATIVE SHORT OVERVIEW OF THE MOLECULAR DYNAMICS IN LC SYSTEMS

Molecular motions in liquid crystal polymers (LCPs) have been in general analysed in terms of the models developed for low molecular weight LCs. Naturally, due to the large molecular dimensions, the dynamics in polymers is more complex than for small molecules. Consequently, the contributing motional modes in the LCPs could be merely distinguishable. It was shown by NMR relaxometry studies [10] that in the case of LCPs, collective order fluctuations are also effective in the low frequency regime whilst the MHz range is dominated by molecular reorientations. The same square root law was observed also for nematic polymers and dimers, as in the case of monomers. With isotropisation, the collective modes associated with order director fluctuations should normally vanish. The interest in liquid crystal dimers and oligomers, which are composed of molecules containing two or more mesogenic groups linked through flexible spacers, stems not only from their ability to act as model compounds for semiflexible main-chain liquid crystal polymers but also from their quite different properties compared to low molecular weight LCs [11]. It was found [12] that the motional correlation times corresponding to the model compounds are similar to those of monomeric liquid crystals whereas the dynamics of the polymers is much slower.

Another complex LC systems in which the contributing motional mechanisms seem to be not so clear are lyotropic LCs and biological membranes [13,14]. For instance, the proton relaxation dispersion results in the case of lyotropic potassium laurate-D_2O mixtures [15] are somewhat similar to the ones corresponding to low molecular weight thermotropics: in the low frequency range, for the isotropic phases (cubic, micellar), the results show a plateau, whereas for both anisotropic phases (lamellar and hexagonal phases) the experimental results show a linear frequency law corresponding to a smectic order fluctuations in the lamellar system. Also in the case of dimyristoylglycerophosphocholine-water membrane [3,16] the linear profile found in the LC phase becomes completely absent in isotropic phase. A different result was presented for the potassium laurate/6.24% 1-decanol/ 68.6% D_2O lyotropic mixture [13]. The T_1 dispersion curves for this amphiphilic system exhibit no differences in isotropic and LC phases. This peculiar behaviour was supposed to arise as a consequence of the slow internal motions associated with individual molecular aggregates.

The LC systems presented in this paper (see Fig. 1), namely two organosiloxane tetrapodes (T_a and T_b), precursors to LC dendrimers, show molecular dynamics features in line with those presented for LC polymers and lyotropics revealing their complexity, due to the presence of additional slow motional processes acting in the low frequency regime. The compound T_a (molecular mass 3597.96 $\mathrm{g\,mol^{-1}}$) has three aromatic groups in the mesogens and alkyl chains formed by eight and eleven methylene groups. The flexible spacer which links the mesogenic core to the siloxane core is formed by five methylene groups and tetramethyldisiloxane groups. The tetrapode T_b (molecular mass 2071.9 g/mol) has cyanobiphenyls as mesogenic groups linked to

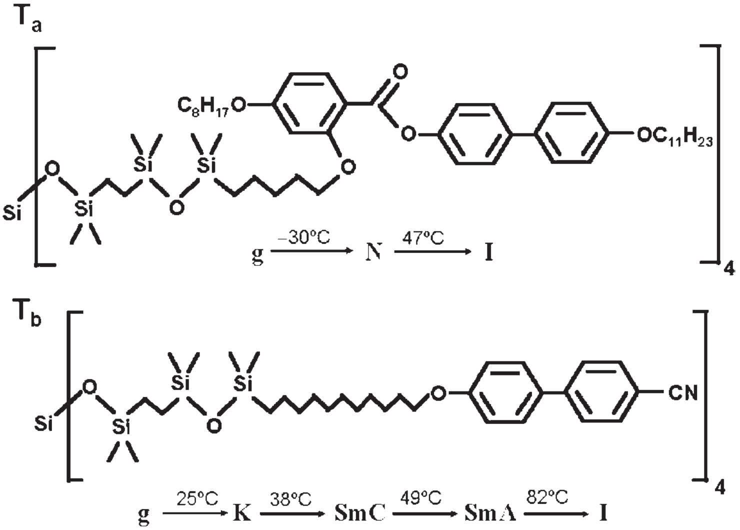

FIGURE 1 Chemical structures and phase sequences of the T_a and T_b tetrapodes.

the siloxane core by much longer flexible spacers formed by eleven methylene groups and tetramethyldisiloxane groups. They were synthesized as described in [17]. Their chemical structures and phase sequences are presented in Figure 1.

3. NMR RELAXATION RESULTS OBTAINED FOR THE LC ORGANOSILOXANE TETRAPODES

3.1. Experimental

Different experimental NMR techniques and spectrometers were used for performing T_1 measurements over a broad frequency range, from 10 kHz to 300 MHz. The T_1 data for Larmor frequencies between 10 kHz and 1 MHz were obtained using a home build fast field-cycling spectrometer [18] with a polarisation and detection field of 0.215 T (corresponding to a Larmor frequency of 9.1 MHz) and switching times of 2–3 ms. The T_1 results between 4 and 100 MHz were obtained with a conventional pulsed NMR spectrometer BRUKER SXP 4-100 using the inversion-recovery RF pulse sequence with phase cycling $((\pi)_x - (\pi/2)_{x,-x})$ for suppression of the DC bias. Finally, a Bruker MSL 300 was used for the measurements at 300 MHz. The samples consisted of a few hundred milligrams of the LC material sealed under moderate vacuum ($<10^{-4}$ Torr) in NMR glass tubes. With the aim of orienting the LC molecules in the magnetic field in the mesophases, all the measurements were carried out after slowly cooling the sample (<1°C/min) in the presence of the external magnetic field, from the isotropic phase to the desired temperature. The temperature was controlled within ±0.5°C.

3.2. Results and Discussion

The T_1 dispersion experimental results in the isotropic and LC phases at different temperatures of the T_a and T_b tetrapodes are presented in Figures 2 and 3, respectively.

The random error limits are estimated to be ±10%. Comparing the T_1 dispersion results in all the phases for these two compounds the following observations can be done:

a) Above 20 MHz a similar behaviour (regular monotonic increase) of T_1 (ν) is detected in all the phases. Usually, in this frequency regime, the most important relaxation mechanisms are molecular rotations/reorientations or fast conformational changes within the molecule, modulating the intra-molecular dipolar interactions,

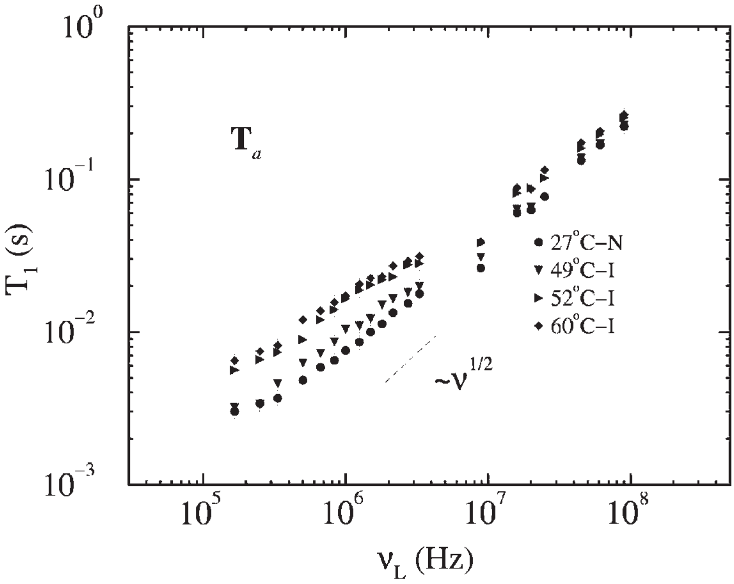

FIGURE 2 T_1 dispersion experimental results in the isotropic and LC phases at different temperatures of the T_a compound.

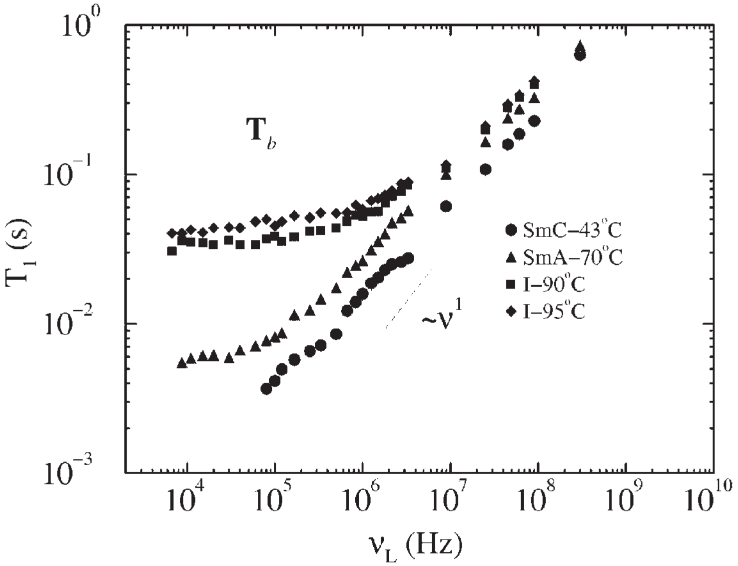

FIGURE 3 T_1 dispersion experimental results in the isotropic and LC phases at different temperatures of the T_b compound.

and translational self-diffusion modulating the inter-molecular interactions.

b) At lower frequencies, differences between the relaxation behaviour of the two tetrapodes in the isotropic and LC phase can be noticed. For T_a an almost similar dispersion profile is detected both in the isotropic and nematic phases, which is unusual. In both phases T_1 decreases with decreasing frequency. In nematic phase the typical square root law is revealed by the experimental results. Interestingly, the dispersion results of T_a are somewhat similar to the one referred for lyotropic mixture discussed in [13]. As to the T_b tetrapode, the T_1 experimental curves show a behaviour similar to that of the low molecular weight liquid crystals and the lyotropic system studied in [15]. No frequency dependence is obtained in the isotropic phase whilst the liquid crystalline phases, in particular SmA and SmC phases are characterized by a linear law typical for these two lamellar systems. This behaviour may be related to the long flexible spacer, which assures a strong decoupling of the movements of the mesogenic units from the siloxane cores. The terminal mesogenic groups have more freedom to develop ordered structures and the behaviour of the system becomes similar to the one of the low molecular weight LCs. Also this long flexible aliphatic chain promotes a high degree of microsegregation in this polyphilic system which may also favour the usual linear dependence in smectic phases of liquid-like layers.

The T_1^{-1} dispersion results at different temperatures were fitted with theoretical expressions corresponding to the relaxation models found in the literature [1]. These models depend on several parameters related to physical properties of the phases and of the compounds, namely: the spins density, n; and geometric factors, A^k, that account for the average intramolecular distance and orientation of proton spin pairs. In this preliminary analysis averaged values $\sim 6 \times 10^{28}$ spins·m^{-3}(calculated from a specific density of $\cong 1$ gcm^{-3} and taking into account the number of proton spins present in each molecule) and $\sim 10^{58}$ m^{-6} (obtained by simulation considering an average of a sample of possible molecular conformations) where considered for these parameters, respectively. In addition, correlation times for the different molecular movements considered were used as fitting parameters.

In the isotropic phase, the rotations/reorientations contribution was interpreted in terms of an extension of the Woessner model [19], whereas for molecular self-diffusion the Torrey model [20] was used.

As an hypothesis, the monomeric mesogenic arms were considered as the relevant structural elements for the relaxation process in view of the decoupling of these units from the siloxane core, expected due to the flexibility of the spacers. This hypothesis is subjected to verification through the fitting of the theoretical curves to the experimental results as described below.

a) **T_a**

The best fit obtained for the isotropic phase (60°C) for the organosi loxane tetrapode T_a is presented in Figure 4.

The fitting parameters are presented in Table 1.

As can be seen in Figure 4 the T_1 dispersion curve was coherently fitted taking into account two possible relaxation mechanisms:

i) local reorientations of the mesogenic arms effective at high frequencies
ii) a contribution proportional to $\nu^{1/2}$ at intermediate and low frequencies.

Like in the case of polymers, molecular self-diffusion was found to be negligible and not to contribute to the relaxation rate. Moreover, the peculiar relaxation behaviour in isotropic phase almost identical to that in nematic phase is quite unusual. A possible explanation to these

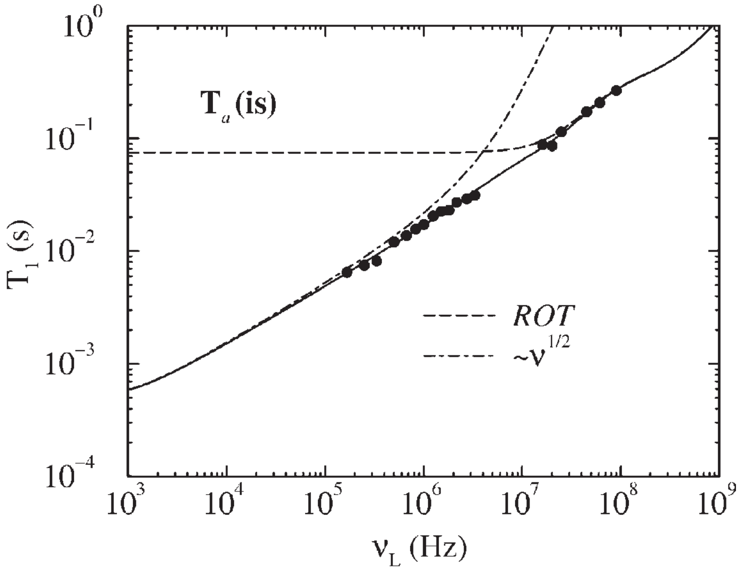

FIGURE 4 Best fit obtained in the isotropic phase (60°C) for the T_a compound.

TABLE 1 Model Fitting Parameters Obtained from the Fits in Isotropic Phase for the T_a and T_b Compounds: τ_S – Correlation Time for Reorientational Movements Around the Short Axis of the Mesogenic Unit. τ_L – Correlation Time for Reorientational Movements Around the Long axis of the Mesogenic Unit. τ_D – Mean Time between Translational Displacements. A – Strength of the $\nu^{1/2}$ Contribution

Phase (T°C)	I(95)	I(90)	I(60)	I(52)	I(49)
T_a					
$\tau_S \times 10^9$(s)	–	–	3.8	4.5	4.7
$A \times 10^{-4}(s^{-3/2})$	–	–	6.8	8.0	8.8
T_b					
$\tau_D \times 10^9$(s)	6.4	7.9	–	–	–
$\tau_S \times 10^{10}$(s)	2.9	3.8	–	–	–
$\tau_L \times 10^{12}$(s)	2.9	3.8	–	–	–

results could be the interdigitated structure typical to low generation dendrimers and found for this compound [21]. The interdigitation of the interconnected mesogenic units which determines a local restriction to molecular movements of the laterally attached mesogenic units could be an explanation for the frequency dispersion and for the absence of the molecular self-diffusion in the isotropic phase of this compound. Locally the molecules adopt a preferred orientation like in nematic cybotactic groups and the fluctuations around it could be a possible relaxation mechanism characterized by this square root frequency law.

As can be noticed from Table 1 the correlation times for rotations/reorientations around short molecular axis, τ_S shows values around 10^{-9} s similar to other more conventional LC compounds [1]. These results constitute an indication of the validity of the starting hypothesis of the decoupled motion of mesogenic arms. These parameters reveal a tendency to increase with decreasing temperature which is typical for thermally activated mechanisms. The values of the strength of the square root mechanism (A) show the same tendency as a function of temperature, which can be related to the temperature dependence of the viscosity. The correlation times for rotations/reorientations around long molecular axis, τ_L could not be precisely determined due to insufficient data at high Larmor frequencies.

b) **T_b**

The best fit obtained in the isotropic phase (90°C) for the organosi loxane tetrapode T_b is presented in Figure 5.

The fitting parameters are presented in Table 1.

As can be observed in Figure 5 a behaviour similar to more conventional low molecular weight liquid crystals in the isotropic phase is obtained:

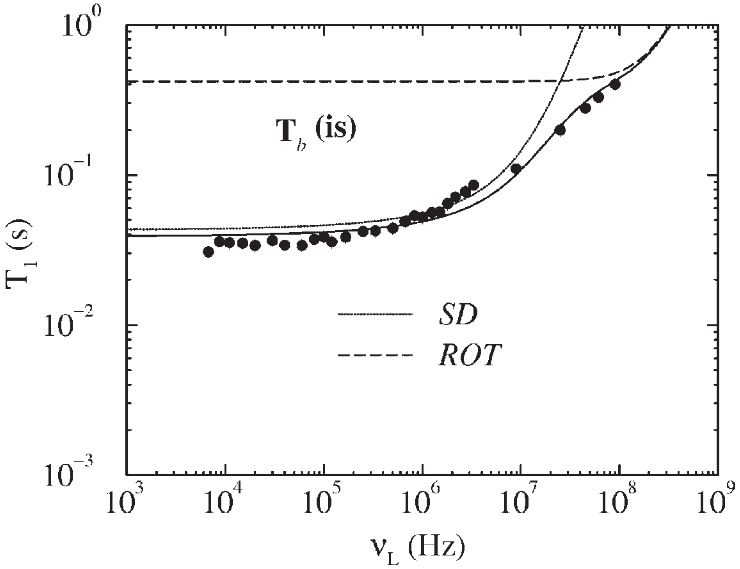

FIGURE 5 Best fit obtained in the isotropic phase (90°C) for the T_b compound.

only two relaxation mechanisms (self-diffusion at low and intermediate frequencies and local molecular rotations/reorientations at higher frequencies) were found to contribute. The typical absence of frequency dispersion at low frequencies is observed. The main explanation for the different behaviour of this system when comparing to the previous one (Ta) may be related to the longer and terminally attached flexible spacer which allows for a stronger decoupling of the movements of the mesogenic units, (see Fig. 1). From Table 1 it can be noticed that the values of the correlation times for self-diffusion (τ_D) and molecular rotations/reorientations (τ_S) are of about 10^{-9} and 10^{-10} s similar with those found for low molecular weight liquid crystals. For τ_L, values of about 10^{-12} s were obtained. These values are merely indicative, since the model used to account for the translational displacements in isotopic liquids [20] should be modified in order to better describe the more complex movements of this type of compounds.

4. CONCLUSIONS

The presented NMR relaxation results for liquid crystalline oligomeric organosiloxane tetrapodes show molecular dynamics features akin to more complex systems like liquid crystalline polymers and lyotropics. One of the tetrapode exhibits the same unusual behaviour both in liquid crystalline and isotropic phases. The peculiar relaxation profile in the isotropic phase may be explained by an interdigitated structure typical of low generation dendrimers. The other tetrapode characterized by a stronger decoupling of the mesogenic units and a higher degree of microsegregation, contrary shows a similar behaviour to low molecular weight liquid crystals. Further work will be done in order to clarify the nature of the differences detected between the T1 dispersion in the isotropic phases of the two studied compounds. However, there is enough evidence from the presented results showing that the length and linking position of the flexible spacers and the degree of interdigitation of the mesogens have a strong influence on molecular dynamics in oligomeric (tetrapode) LC systems.

REFERENCES

[1] Dong, R. Y. (1997). *Nuclear Magnetic Resonance of Liquid Crystals*, 2nd ed., Springer Verlag: New York; Ribeiro, A. C., Sebastião, P. J., & Cruz, C. (2001). *Mol. Cryst. Liq. Cryst.*, *362*, 289.

[2] Abragam, A. (1961). *The Principles of Nuclear Magnetism*, Clarendon Press: Oxford.

[3] Noack, F., Notter, M., & Weiss, W. (1988). *Liq. Cryst.*, *3*, 907.

[4] Pusiol, D. & Noack, F. (1989). *Liq. Cryst.*, *5*, 377.

[5] Sebastião, P. J., Ribeiro, A. C., Nguyen, H. T., & Noack, F. (1995). *J. Physique II*, *5*, 1707; Figueirinhas, J. L., Ferraz, A., Ribeiro, A. C., Nguyen, H. T., & Noack, F. (1997). *J. Phys. II France*, *7*, 79.

[6] Cruz, C., Sebastião, P. J., Figueirinhas, J. L., Ribeiro, A. C., Nguyen, H. T., Destrade, C., & Noack, F. (1998). *Z. Naturforsch.*, *53a*, 823; Žumer, S. & Vilfan, M. (1981). *Mol. Cryst. Liq. Cryst.*, *70*, 1317.

[7] Cruz, C., Figueirinhas, J. L., Sebastião, P. J., Ribeiro, A. C., Noack, F., Nguyen, H. T., Heinrich, B., & Guillon, D. (1996). *Z. Naturforsch.*, *51a*, 155.

[8] De Gennes, P. G. & Prost, J. (1993). *The Physics of Liquid Crystals*, Clarendon Press: Oxford; Gottke, S. D., Brace, David, D., Cang, H., Bagchi, B., & Fayer, M. D. (2002). *J. Chem. Phys.*, *116*, 360.

[9] Vilfan, M., Lahajnar, G., Rutar, V., Blinc, R., Topič, B., Zann, A., & Dubois, J. C., (1981). *J. Chem. Phys.*, *75*, 5250.

[10] Zeuner, U., Dippel, T., Noack, F., Müller, K., Mayer, C., Heaton, N., & Kothe, G. (1992). *J. Chem. Phys.*, *97*, 3794; Kimmich, R., Stapf, S., Möller, M., Out, R., & Seitter, R.-O. (1994). *Macromolecules*, *27*, 1505; Heaton, N. J. & Kothe, G. (1998). *J. Chem. Phys.*, *108*, 8199.

[11] Imrie, C. T. & Henderson, P. A. (2002). *Curr. Opin. Colloid In.*, *7*, 298; Gogoi, B., Alapati, P. R., & Verma, A. L. (2002). *Cryst. Res. Technol.*, *37*, 1331; Yelamaggad, C. V., Nagamani, S. A., Hiremath, U. S., Rao, D. S. S., & Prasad, S. K. (2003). *Mol. Cryst. Liq. Cryst.*, *397*, 507.

[12] Kohlhammer, K., Müller, K., & Kothe, G. (1989). *Liq. Cryst.*, *5*, 1525.

[13] Grinberg, F., Kimmich, R., Seitter, R.-O., & Pusiol, D. (1998). *J. Magn. Reson.*, *135*, 54.

[14] Žumer, S. & Vilfan, M. (1985). *J. Physique.*, *46*, 1763; Marqusee, J. A., Warner, M., & Dill, K. A. (1984). *J. Chem. Phys.*, *81*, 6404.

[15] Kühner, W., Rommel, E., Noack, F., & Meier, P. (1987). *Z. Naturforsch.*, *42a*, 127.

[16] Rommel, E., Noack, F., Meier, P., & Kothe, G. (1988). *J. Phys. Chem.*, *92*, 2981.

[17] Mehl, G. H., Thornton, A. J., & Goodby, J. W. (1999). *Mol. Cryst. Liq. Cryst. A*, *332*, 2965; Diez, S., Dunmur, D., De La Fuente, M. R., Karahaliou, P., Mehl, G., Meyer, T., Perez Jubindo, M. A., & Photinos, D. (2003) *Liq. Cryst.*, *30*, 1021; Elsasser, R., Mehl, G. H., Goodby, J. W., & Photinos, D. J. (2000). *Chem. Commun.*, 851.

[18] Sousa, D. M., Fernandes, P. A. L., Marques, G. D., Ribeiro, A. C., & Sebastião, P. J. (2004). *Solid State Nucl. Magn. Reson.*, *25*, 160; Sousa, D. M., Marques, G. D., Sebastião, P. J., & Ribeiro, A. C. (2003). *Rev. Sci. Instrum.*, *74*, 4521.

[19] Woessner, D. E. (1962). *J. Chem. Phys.*, *36*, 1; Woessner, D. E. (1962). *J. Chem. Phys.*, *37*, 647.

[20] Torrey, H. C. (1953). *Phys. Rev.*, *92*, 962.

[21] Filip, D., Meyer, T., Cruz, C., Sebastião, P. J., Ribeiro, A. C., & Mehl, G. H. (Sept. 2003). *Phase Structure and Molecular Dynamics in Liquid Crystal Organo-Siloxane Tetrapodes*, Euroconference on Dendrimer Soft Self-Assembly Systems, “Densom”, York, UK, 7–11.