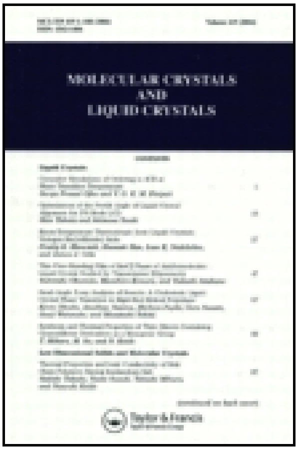

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NMR Relaxation Study of Molecular Dynamics in the Smectic A Phase of PAMAM Liquid Crystalline Dendrimers of Generation 1 and 3

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We present a comparative study of the molecular dynamics in the smectic A phase (SmA) of two poly-(amidoamine) (PAMAM) liquid crystalline dendrimers of generation 1 and 3, respectively, using proton (^1H) spin-lattice relaxation time dispersion. The dispersions are interpreted using two main relaxation mechanisms associated with collective motions and fast reorientational movements of the dendritic segments in the low and high frequency ranges, respectively. Our results can be interpreted on the basis of a decrease in the size of the coherent smectic domains that experience layer undulations compared to what is found in low molar mass liquid crystals,as a consequence of disorder induced by the dendritic core. At high frequency, the relaxation results reveal that the reorientational motions of the mesogenic units are conditioned by their covalent links with the dendritic core.

Keywords: molecular dynamics; nuclear magnetic resonance; smectic A phase

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1. INTRODUCTION

The most common molecular structure of liquid crystalline dendrimers consists of a central core of dendritic architecture [1] with mesogenic units attached peripherically. In this kind of systems two opposite tendencies compete: as the flexible central dendritic architecture tends to adopt a pseudo-spherical morphology, the rigid terminal mesogenic units by interacting with each other tend to arrange parallely to one another. The existence of mesophases in liquid crystal (LC) dendrimers and the type of mesophases observed depend on the balance between these two tendencies and result mainly from the formation of layer-block structure driven by microphase separation [2,3]. LC dendrimers are quasi-monodispersed and have in general lower viscosities than those of polymeric LCs and higher than that of low molar mass (LM_m) LCs.

Nuclear Magnetic Resonance (NMR) is an important tool for the study of molecular dynamics. In LM_m LCs, the dispersion of the spin-lattice relaxation time (T_1) with the Larmor frequency — from generally 10 kHz up to hundreds of MHz — has permitted to identify several kinds of motions, from collective motions at low frequency to local reorientations in the high frequency regime, while self-diffusion of mesogens is generally observed in the medium frequency range [4,5]. In liquid crystalline dendrimers beside the study of their structural and macroscopic properties, a coming challenge is to understand how the increasing molecular complexity will affect or be reflected by the molecular dynamics.

We report here ^{1}H NMR measurements carried on poly-(amidoamine) (PAMAM) LC dendrimer of generation 1 and 3 that exhibit SmA mesophase [2b,3]. The compound of generation 3 exhibits also a Col_r mesophase at lower temperatures; the molecular dynamics of which was studied and reported elsewhere [6]. The T_1 dispersion was obtained for Larmor frequencies between 10 kHz and 300 MHz. As a primary analysis of the data, we used existing spin-lattice relaxation models developed for LM_m LCs of liquid-like layered structures. We compare the results with earlier measurements in low M_m LCs and discuss the influence of the topological constraints imposed by the dendritic core.

2. EXPERIMENTAL

2.1. PAMAM Liquid Crystalline Dendrimers of Generation 1 and 3

The compounds were synthesized as described in [2b,3]. $PAMAM(L_1)_8$ homo-dendrimer of generation 1 consists of a PAMAM core of generation 1 ($G = 1$) with a single kind of terminal promesogenic units

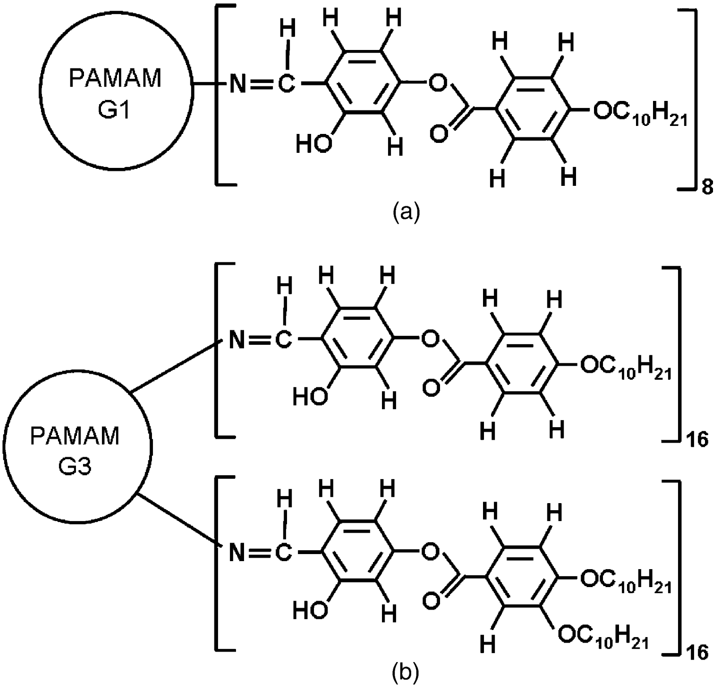

FIGURE 1 Structure of PAMAM LC dendrimers of generation 1 (a) and 3 (b).

derived from salilcylalmide bearing one terminal decyloxy chain (Fig. 1a). PAMAM$(L_1)_{16}(L_2)_{16}$ is a co-dendrimer of generation 3 ($G = 3$) with 32 promesogenic units of two types: 16 of those bear one terminal aliphatic chain, the remaining ones bearing two aliphatic chains (Fig. 1b). The compounds exhibit the following phase sequences:

$G = 1$: g – 80°C → SmA → 139°C → I
$G = 3$: g – 35.5°C → $\mathrm{Col_r}$ → 108.2°C → SmA → 171°C → I

It has been found that in the smectic phase of these two systems the supermolecules adopt a cylindrical arrangement [2]: the dendritic core, the aromatic moieties and the aliphatic chains micro-seggregate and form distinct smectic sub-layers due to the amphiphilic effect.

2.2. NMR Relaxometry Technique

The ^{1}H T_1 was measured for Larmor frequencies between 6 kHz and 300 MHz. Below 8 MHz a home-built fast field cycling relaxometer, with a polarisation-detection field of 0.215 T and a switching time smaller than 3 ms, was used [7]. Between 8 MHz and 100 MHz the data were obtained using a conventional pulsed NMR spectrometer (Bruker SXP-4-100) by means of an inversion-recovery sequence, The T_1 at 300 Hz were obtained on a Bruker MSL 300 spectrometer. The samples consist in a few hundred milligrams of compound sealed under moderate vacuum in a 8 mm NMR glass tube.

3. FUNDAMENTAL BACKGROUND

As it is detailed in [6], we assume that the softness of the dendritic core at its periphery allows for some uncorrelated local motions of the mesogenic units. Moreover, the chemical nature of the terminal units is similar to that of LM_m LCs. Although the T_1 dispersions correspond to the relaxation of the whole ^1H population, we used the relaxation models developed for LM_m LCs and discuss, in the light of the parameter values obtained, the effects of the dendritic core on the mesogens' dynamics.

In LM_m LCs, three frequency ranges are generally considered. In each one a specific spin-lattice relaxation mechanism dominates. In smectics, three main relaxation mechanisms are usually considered [4]: *i*) at low frequencies, collective motions usually associated with layer undulations (LU) [5a,5c], *ii*) at intermediate frequencies self-diffusion (SD) of the mesogens, and *iii*) at high frequency local molecular reorientations (ROT) of the mesogens.

Assuming that these different motions are decoupled, as it is usually the case for LCs, the global relaxation rate observed is the sum of the relaxation rates coming from the different contributions.

The covalent links between the mesogenic units and the dendritic arms should result in strong topological constraints clearly affecting the mesogens' motions, the mesogenic units not being able to diffuse as freely as they are in LM_m LCs. Also self-diffusion of a whole supermolecule at the time scales investigated is unlikely due to the size of the supermolecule and the existence of entanglements and/or interdigitation at the dendrimer's periphery. Moreover, it was verified that self-diffusion is not an effective relaxation mechanism in the mesophases of some liquid crystalline organosiloxane tetrapodes [13] (generation 0 dendrimers). Therefore self-diffusion is not taken into account in the present case and the global relaxation time may be written as

$$\frac{1}{T_1} = \left(\frac{1}{T_1}\right)_{LU} + \left(\frac{1}{T_1}\right)_{ROT}$$

This hypothesis will be validated by the fitting of this expression to the experimental data.

The details of the contributions to the relaxation rate that are considered to be operative in our systems are given in section 3.1 and 3.2. The spin-lattice relaxation of the protons being induced by proton-proton dipolar coupling, a general expression for $1/T_1$ as a function of the spectral densities $J^{(k)}(\omega)$ $(k = 0, 1, 2)$ is [8]:

$$\frac{1}{T_1(\omega)} = \frac{9}{8}\left(\frac{\mu_0}{4\pi}\right)^2 \gamma^4 \hbar^2 [J^{(1)}(\omega) + J^{(2)}(2\omega)]$$

where ω is the Larmor frequency, γ is the ^{1}H gyromagnetic ratio, and μ_0 is the magnetic permeability of vacuum.

3.1. Layer Undulations

In the low frequency range the spin-lattice relaxation rate for layer undulations varies with ω^{-1}. The collective fluctuation modes are limited by a low ω_{low} and a high ω_{high} cut-off frequency. The spectral densities are [9]

$$[J^{(k)}(\omega)]_{LU} = \frac{A}{\omega}\delta_{k1}\left[\frac{2}{\pi}\arctan\left(\frac{\omega_{high}}{\omega}\right) - \frac{2}{\pi}\arctan\left(\frac{\omega_{low}}{\omega}\right)\right]$$

with

$$\omega_{low} = \frac{2\pi}{\xi_\perp^2}\frac{K_1}{\eta}$$

$$\omega_{high} = \frac{2\pi}{d^2}\frac{K_1}{\eta}$$

A is related to viscoelastic properties of the material, K_1 is the splay elastic constant, η is an effective viscosity, and $\xi_\perp$ is the coherence length normal to the director. d is the shortest wavelength of the oscillations and in calamitic LM_m LCs is taken equal to the lateral distance between neighbouring molecules.

3.2. Local Molecular Reorientations

In order to interpret the high frequency data, we used a local reorientational model. For both compounds we noted that 30% of the protons are located in the dendritic core, therefore their contribution to the spin-lattice relaxation cannot be ignored. Because of the covalent links between the dendritic arms and the mesogens, the motions of the latter may be constrained and the relaxation models developed for the local reorientations of mesogens in LM_m LCs should be carefully considered in the present case. Indeed, the contribution of the molecular reorientations may involve mesogenic units, core segments and/or a combination of the two. We chose a two time scales Bloembergen, Purcell and Pound (BPP) model implying two correlation times, τ_f and τ_s, characterizing a fast and a slow motion, respectively. The corresponding spectral densities are [10]:

$$[J^{(1)}(\omega)]_{ROT} = \frac{4}{15\langle r\rangle^6}\sum_{l=s,f} A_l\left(\frac{\tau_l}{1+(\omega\tau_l)^2}\right)$$

$$[J^{(2)}(2\omega)]_{ROT} = \frac{4}{15\langle r\rangle^6}\sum_{l=s,f} A_l\left(\frac{4\tau_l}{1+(2\omega\tau_l)^2}\right)$$

where $\langle r\rangle$ is an average intra-molecular inter-proton distance and A_l are amplitude factors.

4. RESULTS AND DISCUSSION

^{1}H spin-lattice relaxation time dispersions were obtained at 100°C for the PAMAM homo-dendrimer of generation 1 and at 120°C for the PAMAM co-dendrimer of generation 3. The corresponding curves are displayed on Figure 2. In each case, the isotropic phase was not reached due to potential thermal degradation close to the clearing point. The samples were heated from room temperature to the desired one at a rate of $+1^{\circ}\mathrm{C}\cdot\mathrm{min}^{-1}$, in the presence of the magnetic field. No angular dependence in the ^{1}H NMR line shape or in the T_1 values was found. Therefore the samples were treated as polydomain powders.

The two dispersion curves of Figure 2 show a similar behaviour at high frequency whilst below 4 MHz the T_1 evolution depends on the dendrimer generation. The dispersion of the generation 3 LC dendrimer shows a decrease in the spin-lattice relaxation time values around 2.50 MHz. We attribute it to a cross-relaxation process between ^{1}H and ^{14}N spin systems: this was observed in the Col_r phase of the compound too and discussed elsewhere [6]. We then used an additional relaxation mechanism in order to fit the data obtained for the PAMAM LC of generation 3, the so-called "quadrupole dip" with a Lorentzian form characterized by a resonant frequency ω_{CR}, an amplitude factor D, and a correlation time τ_{CR} related to the half-height width [11]:

$$\left(\frac{1}{T_1(\omega)}\right)_{CR} = D\frac{\tau_{CR}}{1+(\omega_{CR}-\omega)^2\tau_{CR}^2}$$

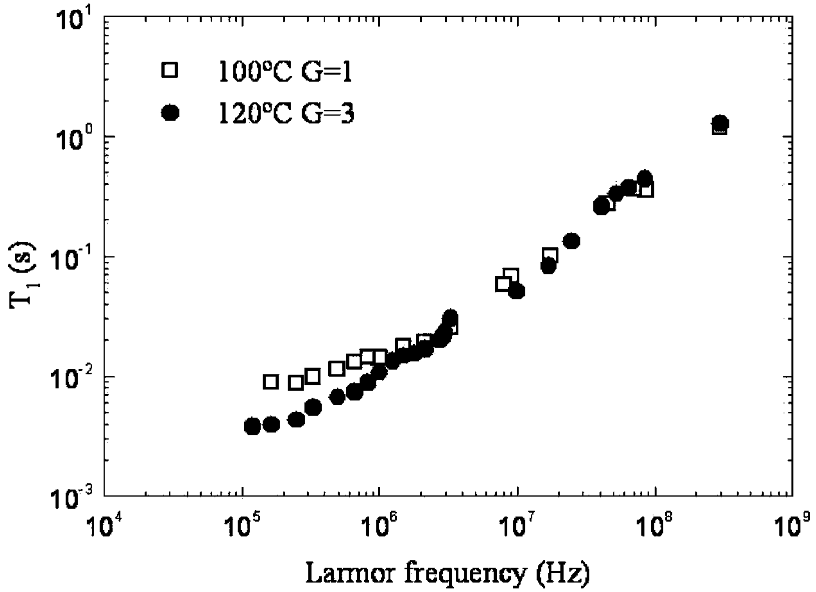

FIGURE 2 ^1H T_1 dispersion data obtained in the SmA phase at 100°C for generation 1 and at 120°C for generation 3. Note for the latter the local decrease of the T_1 values around 2.50 MHz.

The sharpness of the ^1H and ^{14}N energy level overlapping that cause a decrease of the T_1 values at certain frequencies makes the quadrupole dip difficult to detect experimentally and might explain the absence of quadrupole dip in the T_1 dispersion of the compound of generation 1.

Layer undulations' and BPP models were used to fit the experimental data by means of a non linear least square minimization algorithm. The parameters of the quadrupole dip were determined from the T_1 dispersions in the columnar phase [6] where the dip was better defined than in the SmA phase. X-ray diffraction studies have shown that the mesogenic units are arranged parallel to one another in the SmA phase of both compounds [2a], therefore the shortest wavelength of the layer oscillations, *d*, is set to 5 Å, the average lateral distance between mesogenic units of the supermolecules. Table 1 summarizes the values obtained for the free parameters and Figures 3a and 3b show the global curve fits; for the sake of clarity, the contribution from each individual relaxation mechanism is plotted as well.

TABLE 1 Free Fitting Parameters Determined from the T_1 Dispersion for the Two Generations. The Notations are Explained in the Text

Relaxation mechanism	Generation	1	3
LU	$\omega_{low}/2\pi$ (Hz)	1.3×10^6	2.2×10^5
	$\omega_{high}/2\pi$ (Hz)	3.6×10^8	2.0×10^9
ROT	τ_S (s)	7.0×10^{-9}	6.7×10^{-9}
	τ_f (s)	3.6×10^{-10}	1.1×10^{-10}

4.1. Low Frequency Regime

No relevant information could be extracted from the high cut-off frequency values, ω_{high}, the fits not being sufficiently sensitive to this parameter. A low cut-off frequency ω_{low} was found for generation 1 around 1.3×10^6 Hz and 2.2×10^5 Hz for generation 3. These values are two and one orders of magnitude, respectively, greater than those for LM_m LCs [5b,12] and still higher than those found in LC organosiloxane tetrapodes [13]. Since ω_{low} varies with the inverse of the coherence length perpendicular to the director, $\xi_\perp$, this high value for the two generations might be interpreted as a decrease in the size of the smectic domains that move coherently as layer undulations occur. This size limitation of such domains could be a consequence of defects in the layers induced by the disordered dendritic cores or by their entanglement. Assuming as a first approximation that K_1/η does not vary significantly from generation 1 to 3, the ratio of the coherence length for the two generations $(\xi_\perp)_3/(\xi_\perp)_1$ can be estimated. From X-ray data, the average diameter of the cylinders, Φ_1 and Φ_3, that schematically represent the ideal molecular shape of the LC dendrimers may be computed [2a]. We found that Φ_3/Φ_1 is about 2.2 which is roughly equal to the ratio of the coherence lengths. In other words, within the frame of the approximations made we find an average number of supermolecules moving coherently as layer undulations occur on the same order for the two generations.

4.2. High Frequency Motions

The fit of the BPP model to the experimental data leads to two correlation time values as introduced in section 3.2. However, the determination of these correlation times is somehow complicated because layer undulations and molecular reorientations assume a similar behavior above 100 MHz and therefore are difficult to distinguish. Thus the values of τ_s and τ_f are considered in their order of magnitude.

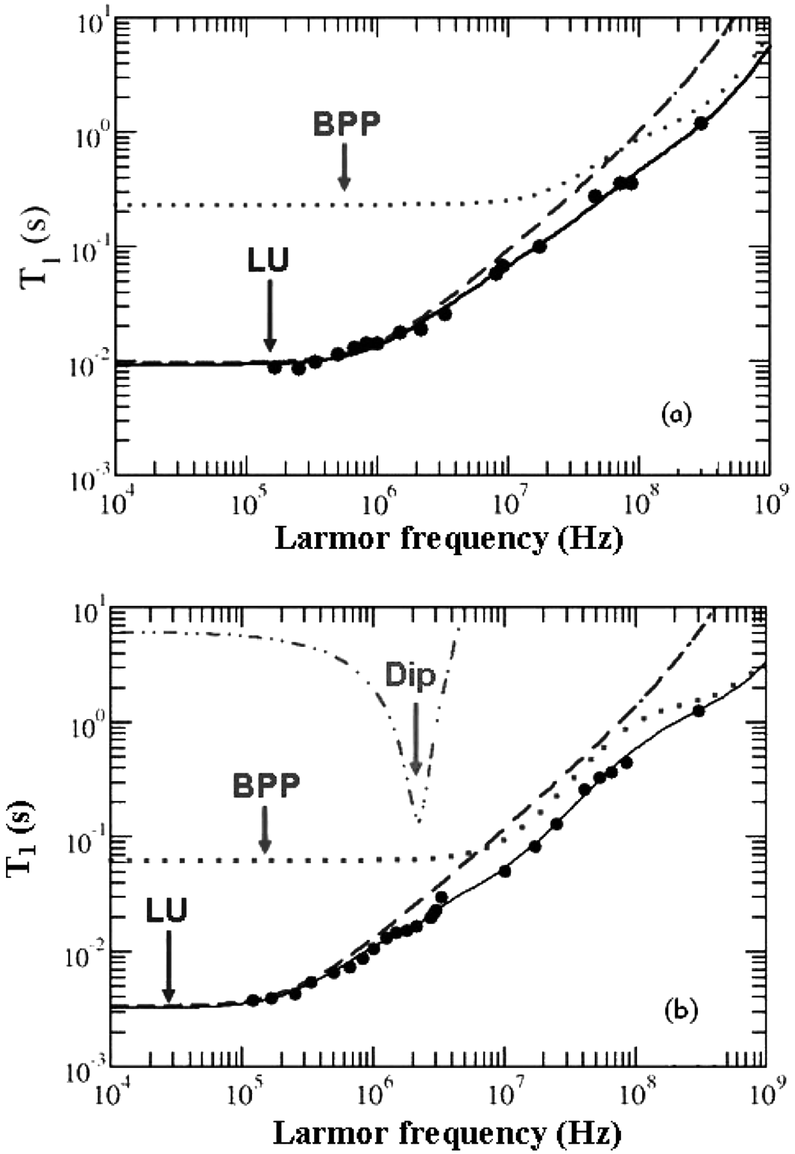

FIGURE 3 Best fits obtained using LU and BPP models for generation 1 (a) and 3 (b). For PAMAM of generation 3, an additional relaxation model ("Dip") was added centred at $\omega_{CR} = 2.3\,\mathrm{MHz}$ (see text for detail). On each figure, the solid line corresponds to the global fit.

Whatever the generation, τ_s is on the nanosecond scale while τ_f is about one hundred of picoseconds. In the scope of some relaxation models used for LM_m LCs, the ratio of these two correlation times reflects the size of the mesogens what cannot be realistically envisioned in the present case since the mesogenic units are attached to the core. The value found for τ_f is on the same order of magnitude than the correlation time for reorientation of LM_m mesogens along their long molecular axis [5b,14] and it is reasonable to attribute τ_f to the same type of motion. The value obtained for τ_s is slightly greater than what is found in the smectic phase of biforked molecules for the reorientation around the short molecular axis [5b]. Assigning τ_s to the same kind of motions, this slowing down in the local reorientations can be ascribed to spatial restrictions as the result of the covalent links to the core. τ_s could also characterize slow conformational changes of the dendritic core.

5. CONCLUSIONS

The molecular dynamics in the SmA phase of PAMAM liquid crystalline dendrimers of generation 1 and 3 was investigated by means of ^1H T_1 relaxation dispersion. The results show that the motions of the mesogens are affected by their covalent links to the dendritic core, both in the low and high frequency ranges. At low frequency, the layer undulations seem to involve small smectic domains, the size of which depending on the dendrimer generation. This decrease in the smectic domain size (compared to what is generally found in LM_m LCs) can be attributed to disorder induced by the flexible core. Local reorientation movements – the dominant relaxation process at high frequency – are constrained due to the specific molecular structure of the dendrimers. In particular, the local reorientations of the mesogenic units are slowed down as an effect of their links to the dendritic arms.

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