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Cone motion viscosity and optical second harmonic generation of ferroelectric liquid crystalline dendrimers

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We report second harmonic generation in a ferroelectric liquid crystalline trimer and ferroelectric liquid crystalline dendrimers of first, second and third generation. Thin cells were filled with the compounds by capillary forces at elevated temperature, and cooled from the surface stabilized ferroelectric state to below the glass transition temperature, while kept in an electric field. The cone motion viscosity and the threshold electric field for unwinding of the helix axis of the chiral tilted smectic mesophases were studied separately at elevated temperature, and these data were used to optimize the preparation of the films. The measured response time was between 0.3 and 3 ms, which corresponds to a cone motion viscosity between 0.5 and 50 Pa s. Second harmonic generation was studied both at elevated temperature with an electric field and at room temperature with and without electric field. The first generation dendrimer exhibited a strong increase in the second order non-linear optical response with time at room temperature. The d_{23} -coefficient of this dendrimer was approximately four times larger than for the other macromolecules and was 0.045 pm V^{-1} . The relatively large d -coefficient of the first generation dendrimer is ascribed to crystallization, which improved the orientation of the molecular dipoles.

1. Introduction

In the past decades, considerable effort has been directed towards the design, synthesis, and characterization of organic materials for second order nonlinear optics (NLO). The main advantages of using organic materials for second order NLO are their good processability, the possibility for integration with passive polymeric waveguides, and the potential for continuous improvement of the intrinsic molecular properties by synthesis, e.g. to increase the molecular hyperpolarizability [1, 2]. Important fields of application are frequency up-conversion, optical parametric power generation, and other frequency conversion schemes based on non-linear interaction of light waves [1, 2].

A severe constraint on the second order NLO material is that the crystal or polymer has to possess non-centrosymmetry. In a guest–host system, consisting of randomly distributed NLO dopants dissolved in a polymer matrix, non-centrosymmetry can be induced by a static electric field applied at a temperature where the dopants can orient along the electric field direction [3–6]. The polymer is then cooled with the field on (symmetry $C_{\infty v}$, Schoenflies notation). The density of the NLO dopants in these systems is restricted by their solubility in the polymer matrix. Polymers with incorporated, covalently bonded, NLO dyes have also been developed, resulting in a higher density of NLO active groups [7–10]. In order to increase the orientational order, side chain liquid crystalline polymers with a donor–acceptor group have been prepared [11, 12]. A different symmetry (C_2) is accomplished by the use of ferroelectric liquid crystals (FLCs) [13, 14]. The spontaneous polarization of this material makes it suitable

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for second order NLO [15], and synthesis with the specific purpose of increasing the second order non-linearity has been carried out [16,17]. Electro-optic effects in ferroelectric liquid crystalline polymers have also been reported [18–20].

Recently, a new class of materials, liquid crystalline dendrimers [21–23], has received considerable attention. The first paper on a dendritic liquid crystalline polymer with ferroelectric properties was a third generation dendrimer reported by our group [24]. Thereafter the first and second generation analogues of the same dendrimer have been synthesized and characterized [25]. This paper reports data on the second order NLO susceptibility of these recently synthesized FLC dendrimers of first, second, and third generation. We also report data on the ‘zeroth generation’ analogue, which is from hereon referred to as a FLC trimer. The second order NLO susceptibility was obtained by measurement of the second harmonic generation (SHG) response, and data were obtained both at elevated temperature in an electric field and at room temperature with and without applied electric field. We also report on the cone motion viscosity

and the threshold electric field of these materials. The viscosity is a critical parameter in the preparation of ‘frozen-in’ ferroelectric films, since the necessary polar order is obtained by aligning the molecular dipoles with a static electric field at a suitable temperature, and then cooling. In order to prevent ions causing the build-up of an inner reverse field during cooling, the temperature was kept as low as possible during the alignment of the molecular dipoles.

2. Experimental

The synthesis and phase characterization of the FLC dendrimers FerG#1, FerG#2, and FerG#3 have been reported elsewhere [24,25]. The dendritic scaffolds consist of first, second, and third generation aliphatic polyesters, which have been functionalized with six, twelve, and twentyfour ferroelectric mesogen-containing units, respectively (figure 1). We have also studied the trimer FerG#0 seen in figure 1. Information about the low molecular mass liquid crystal analogue of the ferroelectric mesogen-containing unit shown in figure 1 was reported by Inukai *et al.* [26] and Takato and Sakamoto [27].

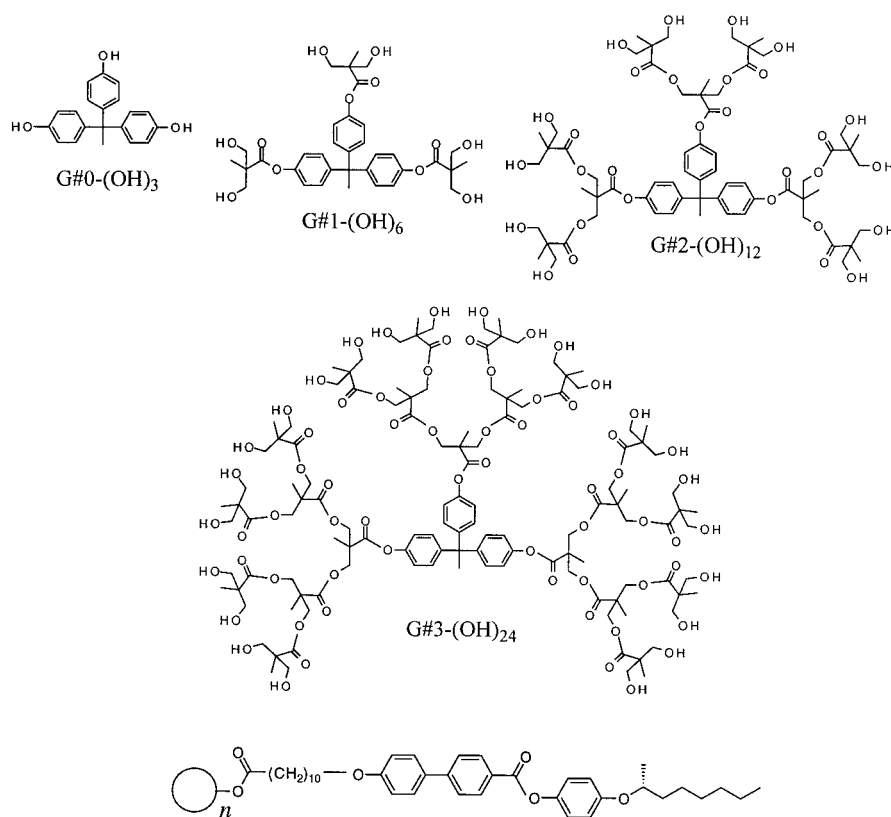


Figure 1. The trimer FerG#0 and the dendrimers FerG#1, FerG#2, and FerG#3. To each core, represented by the circle, n mesogen-containing units are covalently bonded.

- $n = 3$: FerG#0
- $n = 6$: FerG#1
- $n = 12$: FerG#2
- $n = 24$: FerG#3

Thermal transitions in the trimer FerG#0 and the dendrimers FerG#1, FerG#2, and FerG#3 were studied by differential scanning calorimetry (DSC) at heating and cooling rates of 10°C min⁻¹ in a Mettler-Toledo DSC 820.

Commercial 4 μm glass cells (EHC, Japan) were used for the film preparation of the compounds for viscosity and for optical SHG measurements. The compounds were heated to a temperature close to the isotropization temperature, and drawn into the glass cell by capillary forces. At lower temperatures the cells could not be filled, and at higher temperatures the wetting of the surfaces was poor, leaving large air bubbles in the films.

The cone motion viscosity, γ_φ , of the surface stabilized ferroelectric liquid crystal (SSFLC) [14] cell was estimated from the optical response time and the ferroelectric polarization. These quantities were measured by means of a standard electro-optic set-up [28, 29]. We define the response time as the time between 10% and 90% of the total change in light intensity as the SSFLC switches from one bistable state to the other. Surface forces did not accomplish a complete unwinding of the helix axis of the tilted chiral smectic phases, and at low electric fields a linear electro-optic response was observed. This linear electro-optic response originated from the optic axis motion related to deformation of the helix. Above a critical electric field, the threshold field, a sharp shift in birefringence colour occurred due to the helix unwinding process, and coincided with a change of the electro-optic response. Above the threshold field, the optic response was similar to the ordinary SSFLC switching behaviour. The threshold electric field was measured with a square wave at 5 Hz for all compounds.

Samples of FerG#0, FerG#1, FerG#2, and FerG#3 made for room temperature SHG measurements were exposed to a static electric field of 20 V μm⁻¹ at 70, 80, 100, and 110°C, respectively. The electric field was applied perpendicular to the planarly aligned mesogens. The heating was then turned off, and the cell left to cool to room temperature in the oven, with the electric field applied over the cell.

For the SHG set-up, a pulsed Nd:YAG laser with a wavelength of 1064 nm, at a pulse repetition frequency of 10 Hz and a pulse width of 5 ns, was used as the light source. Appropriate intensity (~48–50 μJ/pulse) and spectral and polarization purities were obtained by adjusting optical density filters, a cold mirror, and a Glan–Thompson polarizer. Part of the intensity was extracted by a beam splitter and detected with an InGaAs-pin diode as a reference. A 400 mm lens focused the pump beam onto the sample. The sample was placed in a holder, which could be rotated about two axes using two rotation stages controlled by a Microcontrole IP28/PP28 unit. An oven, Instec Hot Stage (HS1),

controlled by an Instec RTC1, was mounted onto the holder for measurements at elevated temperature. The power of the SHG light was, after first passing a second polarizer, a 45° hot mirror and a narrow band-width interference filter, recorded by a photomultiplier tube (Hamamatsu 5783-01). The recorded power was obtained as the peak to peak value of the average of sixteen pulses. The signals of the reference detector and the photomultiplier tube were detected with a Lecroy 9360 oscilloscope; 0.5 mm z-cut lithium niobate was used as a reference.

3. Calculations

In a first order dynamic description of a SSFLC, the viscous torque $\gamma_\varphi(d\varphi/dt)$ is in balance with the electric torque $PE \sin \varphi$, where φ is the angle between the ferroelectric polarization P and the electric field E . The angular momentum equation is then written:

$$\gamma_\varphi \frac{d\varphi}{dt} = PE \sin \varphi \quad (1)$$

where the dielectric and the elastic contributions have been neglected [28]. Equation (1) has the solution: $t/\tau = \ln[\tan(\varphi/2)/\tan(\varphi_0/2)]$ with $\tau = \gamma_\varphi/(PE)$. The correction factor arising from the measurement of transmitted light was set to 1.8 [30], which gives:

$$\gamma_\varphi \approx \tau PE/1.8. \quad (2)$$

For SHG calculations, the transmitted second harmonic power of light $P_{2\omega}$ is given by [1, 31, 32]:

$$P_{2\omega} = \frac{m}{n_{2\omega} n_\omega^2} \frac{d_{\text{eff}}^2 l^2}{\lambda^2} P_\omega^2 \text{sinc}^2(\Delta k l) \quad (3)$$

where P_ω is the incoming power of light, $n_{2\omega, \omega}$ is the refractive index at the specific frequency, l is the length of interaction given by $l = l_0/\cos \theta$ (where l_0 is the sample thickness), λ is the wavelength in vacuum of the incoming light, and m is a constant related to the experimental set-up, which was received from the reference material (lithium niobate). θ is related to the angle of incidence θ_{in} by Snell's law ($\sin \theta_{\text{in}} = n_\omega \sin \theta$) where the angular dependence of the refractive index was calculated from the refractive index indicatrix [33] with the extraordinary (e) and the ordinary (o) refractive indices set to $n_{\omega, \text{o}} = 1.53$, $n_{\omega, \text{e}} = 1.71$, $n_{2\omega, \text{o}} = 1.55$, $n_{1\omega, \text{e}} = 1.73$. The term $\text{sinc}(\Delta k l) = \sin(\Delta k l)/(\Delta k l)$ describes the conversion efficiency between the fundamental and the second harmonic lightwave where Δk is given by $\Delta k = 2\pi(n_{2\omega} - n_\omega)/\lambda$. For a small phase mismatch (small $\Delta k l$), the sinc-term is close to one. Under the conditions assumed here, the phase mismatch is small ($\text{sinc}(\Delta k l) \approx 0.96$) and it was possible to estimate the effective d -value (d_{eff}) with reasonable accuracy, although the dispersion in the refractive index of the compounds was not known. The

effective d -value is given by:

$$d_{\text{eff}} = \mathbf{e}_{2\omega} \mathbf{d} : \mathbf{e}_{\omega} \mathbf{e}_{\omega} \quad (4)$$

where $\mathbf{e}_{2\omega}$ and \mathbf{e}_{ω} are unit vectors describing the direction of linear fundamental and second harmonic polarization. In explicit terms equation (4) becomes:

$$d_{\text{eff}} = [e_{2\omega,1} \ e_{2\omega,2} \ e_{2\omega,3}] \mathbf{d} \\ \times [e_{\omega,1}^2 \ e_{\omega,2}^2 \ e_{\omega,3}^2 \ 2e_{\omega,2}e_{\omega,3} \ 2e_{\omega,3}e_{\omega,1} \ 2e_{\omega,1}e_{\omega,2}]^T \quad (5)$$

where the additional subscript denotes the column of the unit vector $e_{2\omega,\omega}$. The matrix \mathbf{d} of a material showing C_2 symmetry with the polar axis along y is given by [34]:

$$\mathbf{d} = \begin{bmatrix} 0 & 0 & 0 & d_{14} & 0 & d_{16} \\ d_{16} & d_{22} & d_{23} & 0 & d_{14} & 0 \\ 0 & 0 & 0 & d_{23} & 0 & d_{14} \end{bmatrix} \quad (6)$$

assuming Kleinman symmetry conditions [35].

The co-ordinate system (x, y, z) in figure 2 represents the dielectric axis of the film. To simplify the calculations we assume that the film is uniaxial, with the optical axis along the mesogen molecules. z is the optic axis (the axis of extraordinary refractive index), and x and z were assumed to lie in the plane of the film. y is the polar axis as mentioned above, and is normal to the surface. (X, Y, Z) is the laboratory co-ordinate system where Y and Z are the horizontal axes and X is the vertical axis. ϕ is the azimuthal angle (rotation around y) and ϕ_0 is the tilt angle. θ_{in} is the angle of incidence for rotation around X . p-p polarized light propagating along Y gives the following unit vector(s):

$$\mathbf{e}_{2\omega,\omega} \\ = [\cos \theta_{2\omega,\omega,0} \sin(\phi + \phi_0), \sin \theta_{2\omega,\omega,0}, \cos \theta_{2\omega,\omega,0} \cos(\phi + \phi_0)] \quad (7)$$

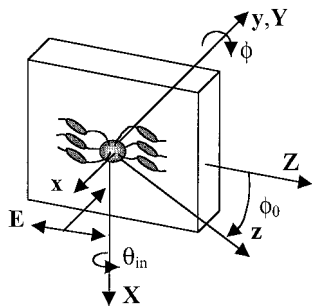


Figure 2. The laboratory coordinate system (X, Y, Z) and the dielectric axes (x, y, z) of the dendritic film in the SHG set-up.

which gives for $\phi + \phi_0 = 90^\circ$ (ooo-waves):

$$d_{\text{eff}} = d_{16}(\sin 2\theta_{\omega,0} \cos \theta_{2\omega,0} + \cos^2 \theta_{\omega,0} \sin \theta_{2\omega,0}) \\ + d_{22} \sin^2 \theta_{\omega,0} \sin \theta_{2\omega,0} \quad (8)$$

and for $\phi = -\phi_0$ (eee-waves):

$$d_{\text{eff}} = d_{23}(\sin 2\theta_{\omega,0} \cos \theta_{2\omega,e} + \cos^2 \theta_{\omega,e} \sin \theta_{2\omega,0}) \\ + d_{22} \sin^2 \theta_{\omega,0} \sin \theta_{2\omega,0}. \quad (9)$$

The SHG measurements were performed by recording the frequency-doubled light intensity during azimuthal rotation of the sample at a fixed angle of incidence. The azimuthal geometry of the axis of second order non-linear optical susceptibility was thereby revealed. By making SHG power measurements over a range $(-30^\circ$ to $+30^\circ)$ of angle of incidence at a suitably chosen and fixed azimuthal angle, the d -coefficients of the film were determined.

4. Results and discussion

The heating enthalpies, as measured by DSC, of the trimer FerG# and the dendrimers FerG#, FerG#, and FerG# per gram of material are shown in table 1. FerG# and FerG# exhibit four mesophases, where the highest temperature mesophase is the chiral smectic A phase (SmA*) [24], and the other three are tilted chiral smectic phases with small relative enthalpy differences. FerG# and FerG# exhibit only one mesophase; this is chiral and tilted (SmC*) [25], and thus ferroelectric. Moreover, FerG# and FerG# both exhibit recrystallization, FerG# exhibiting two melting peaks at a heating of rate $10^\circ\text{C min}^{-1}$, and FerG# exhibiting a relatively large crystallization peak, revealing a low energy molecular arrangement at low temperature. The

Table 1. Phase transition temperatures and the corresponding heating enthalpies of FerG# and the dendrimers FerG#, FerG#, and FerG#. Cr₁, Cr₂, Cr = crystal state, recr. = recrystallization, SmC* = chiral smectic C phase, SmX₁ = unknown tilted chiral smectic phase, SmX₂ = unknown tilted chiral smectic phase, SmA* = chiral smectic A phase, I = isotropic state.

Compound	Transition temperatures/ $^\circ\text{C}$, Heating enthalpy $\Delta H/\text{J g}^{-1}$					
FerG#	Cr ₁ 62	Cr ₂ 77	SmC* 135	I		
	2.0	3.2	11.8			
FerG#	recr. Cr	82	SmC* 124	I		
	-4.5	12.8	11.0			
FerG#	Cr 84	SmC* 91	SmX ₁ 121	SmX ₂ 127	SmA* 150	I
	5.5	0.5	0.034	0.074	7.6	
FerG#	Cr 84	SmC* 107	SmX ₁ 130	SmX ₂ 134	SmA* 151	I
	4.5	0.59	0.048	0.10	7.5	

compounds FerG#0, FerG#1, FerG#2, and FerG#3 contain up to 86, 85, 85 and 84 wt% of the mesogen-containing unit seen in figure 1, respectively. The number of mesogens per unit volume is therefore nearly the same for the four materials.

The response times, τ , of the trimer FerG#0 and the dendrimers FerG#1, FerG#2, and FerG#3 were in the range of 0.3 to 3 ms, and on applying between 30 and 200 V over the 4 μm cells, no deviation from the $1/E$ dependence of τ , predicted by equation (2), was detected (figure 3).

In order to study the influence of the dendritic generation number on the cone motion viscosity, the viscosity data are presented at the same reduced temperature T_{red} , defined as:

$$T_{\text{red}} = T - T_{\text{tr}} \quad (10)$$

where T_{red} is the transition temperature to the first tilted chiral phase (i.e. the first ferroelectric phase) on cooling. T_{tr} is 132, 120, 126 and 132°C for FerG#0, FerG#1, FerG#2 and FerG#3, respectively. The cone motion viscosity of the compounds, as calculated from equation (2), was in the range 0.5 to 50 Pa s, and was larger for the higher generation dendrimers at the same reduced temperature. The spontaneous polarization of the dendrimers, used for the calculation of the cone motion viscosity, has been reported elsewhere [25]. The spontaneous polarization of FerG#0 was slightly larger than that of the dendrimers, and was approximately 60 nC cm⁻² at $T_{\text{red}} = -30^\circ\text{C}$. Far below T_{tr} , the cone motion viscosity could be described by an Arrhenius-type equation:

$$\gamma_\phi(T) \propto \exp[E_a/(RT)] \quad (11)$$

where E_a is the activation energy and R is the gas constant. The Arrhenius plots and the values of the activation energy for the cone motion viscosity are seen in figure 4. The activation energy is lowest for the trimer, and increases with increasing dendritic generation number.

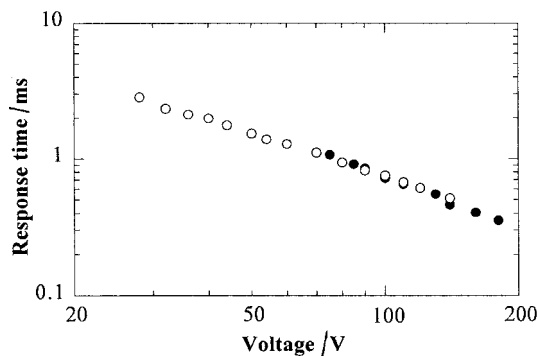


Figure 3. Response time measurements on FerG#0 at 112°C (filled circles) and FerG#1 at 110°C (open circles).

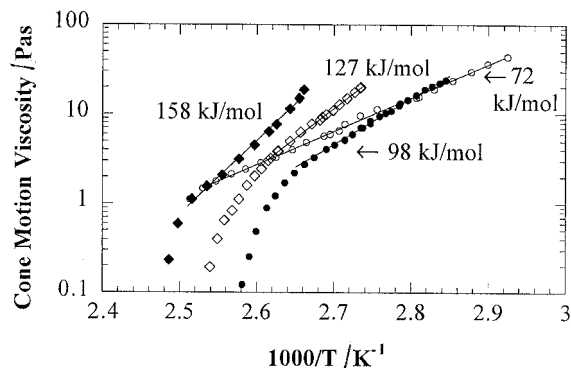


Figure 4. Arrhenius plots for the cone motion viscosity of FerG#0 (open circles), FerG#1 (filled circles), FerG#2 (open squares) and FerG#3 (filled squares). The values of the activation energy are shown.

The threshold electric fields of the trimer FerG#0 and the dendrimers FerG#1, FerG#2, and FerG#3 are seen in figure 5. The higher generation dendrimers exhibited a larger threshold field at the same reduced temperature T_{red} .

The samples made for room temperature SHG measurements were studied in a polarized light microscope, while cooling with an electric field applied over the cell. The birefringence of the films increased during the cooling for all the compounds. The birefringence colour of the films at room temperature was not influenced by the removal of the electric field, and a birefringence of 0.16 to 0.18 was estimated by means of a Michel-Levy chart. The tilt angle of the ferroelectric liquid crystalline dendrimers (FerG#1, FerG#2, and FerG#3) was found to be between 25° and 30°, where FerG#2 and FerG#3 exhibited good extinction of transmitted light in the polarized light microscope. The tilt angle of the trimer FerG#0, as well as FerG#1, was difficult to estimate due to poor sample alignment, which deteriorated the extinction of the polarized light.

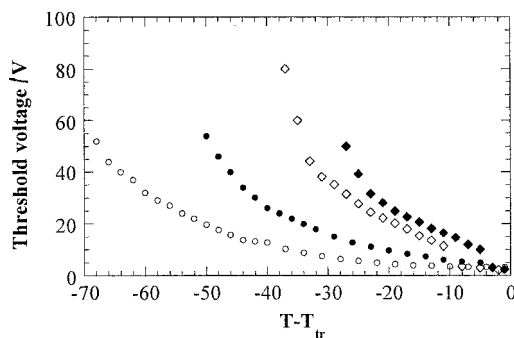


Figure 5. Threshold voltage in a 4 μm film of FerG#0 (open circles), FerG#1 (filled circles), FerG#2 (open squares) and FerG#3 (filled squares).

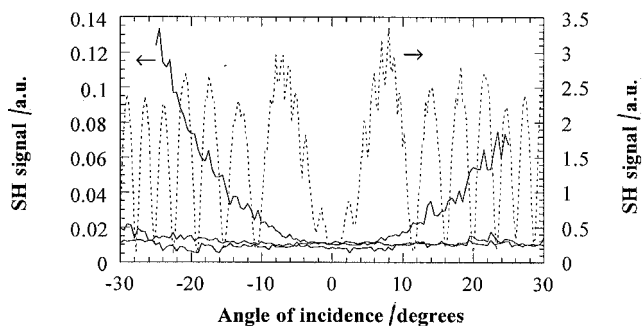


Figure 6. Typical SHG response of FerG#A, FerG#B, and FerG#C drawn with filled curves (left axis), and the reference lithium niobate drawn with a dotted curve (right axis), as a function of angle of incidence. The films made from the dendrimers were placed in the eee-polarization mode without electric field applied and SHG was recorded after > 1 h at room temperature. The large signal (filled curve) is recorded from FerG#A. The four curves are directly comparable.

SHG was recorded on the dendrimers FerG#A, FerG#B, and FerG#C at room temperature in the p-p polarization mode without an external electric field (figure 6). The p-s polarization set-up did not give a second harmonic response that could be distinguished from the background noise. The weak dependence of d_{eff} on d_{22} at the geometry used made the assessment of d_{22} less accurate—see equations (8), (9). However, the shape of the SHG response as a function of angle of incidence made it possible to estimate d_{23} and d_{16} , where the contribution from d_{22} gives an inaccuracy which we approximate to < 20%. The inaccuracy of d_{23} and d_{16} was estimated from fitting the three aforementioned d -values with different internal relations to experimental data. The accuracy is furthermore decreased by the lack of information on the dispersion relation of the refractive index (inaccuracy estimated to < 10%). However, from the measurements and the analysis accounted for here, we present in table 2 the d -coefficients of FerG#A, FerG#B, and FerG#C measured at room temperature without external electric fields. The limit of resolution corresponds to a d -coefficient of < 0.004 pm V^{-1} , and d_{16} of FerG#A, FerG#B, and FerG#C and d_{23} of FerG#A were below this value. d_{14} was very small for all four compounds and could not be detected (p-s polarization mode).

Table 2. SHG d -coefficients for FerG#A, FerG#B, and FerG#C.

Compound	$d_{23}/\text{pm V}^{-1}$	$d_{16}/\text{pm V}^{-1}$
FerG#A	0.045	0.006
FerG#B	0.012	—
FerG#C	0.011	—

The relatively large d -coefficients of FerG#A prompted further studies and SHG was subsequently run on FerG#A and FerG#B at elevated temperatures with an applied electric field of $15 \text{ V } \mu\text{m}^{-1}$. On measuring SHG with an applied electric field, a third order non-linear optical effect was included; in order to distinguish the pure second order effects from the combined second and third order effects, a prime is added to the notation in the latter case in the following context. d'_{23} of FerG#B was measured to be: 0.011 (SmA*), 0.018, 0.019, 0.021 pm V^{-1} at 140, 128, 115, and 93°C , respectively. On cooling to room temperature, d'_{23} remained at approximately 0.02 pm V^{-1} , and decreased as the electric field was removed ($d_{23} = 0.011 \text{ pm V}^{-1}$). The described behaviour of FerG#B is in agreement with studies on other materials reported earlier [36]. The same type of experiment performed on FerG#A, yielded d'_{23} values of 0.005 and 0.015 pm V^{-1} at 105 and 85°C , respectively. On cooling the sample in the turned-off oven, the SHG signal increased approximately three to four times before reaching room temperature. At room temperature, the SHG response increased another three to four times during the first hour. Furthermore, the SHG response was independent of the applied electric field up to $\pm 15 \text{ V } \mu\text{m}^{-1}$ at room temperature, and we obtained for this run $d_{23} = 0.041 \text{ pm V}^{-1}$.

The SHG signal is dependent on the number density of molecules with second order hyperpolarizability, the strength of this hyperpolarizability, and their average orientation in space [1]. We may exclude the two former factors in explaining the relatively large d_{23} -coefficient of FerG#A, for the following reasons: (1) the number of polar groups per unit volume is essentially the same for all four materials studied; (2) ferroelectric measurements gave similar spontaneous polarization at the same reduced temperature for all three dendrimers [25]; (3) the SHG response at elevated temperatures was of the same order of magnitude for FerG#A and FerG#B. Keeping in mind the large crystallization peak of FerG#A as measured by DSC, we conclude that FerG#A crystallizes on cooling to a structure of low relative energy, in which the molecular dipoles align and cause the strong increase in SHG. In the ferroelectric state, alignment of the molecular dipoles is energetically favoured, although counteracted by thermally stimulated rotations of these dipoles. On crystallizing, the gain in energy is large enough to suppress the rotations, and the alignment of the dipoles increases. The behaviour of FerG#A as measured by SHG is in agreement with measurements by Sprunt *et al.* [37, 38] on a molecular crystal formed from the chiral smectic C mesophase. The SHG response increased with time as the crystal formed, and the SHG power was unaffected on applying external electric fields.

5. Conclusions

We report data on the cone motion viscosity and the second order non-linear optical (NLO) susceptibility of three recently synthesized ferroelectric liquid crystalline dendrimers of first, second, and third generation. We also report data on the 'zeroth generation' analogue, a ferroelectric liquid crystalline trimer. The measured response time for ferroelectric switching of the four compounds was between 0.3 and 3 ms, which corresponds to a cone motion viscosity between 0.5 and 50 Pa s. The second order NLO susceptibility was obtained by measurement of the second harmonic generation (SHG) response, and data were obtained both at elevated temperatures with an electric field and at room temperature with and without electric field. Without electric field and at room temperature the d_{23} -coefficient of FerG#1, FerG#2, and FerG#3 was 0.045, 0.012 and 0.011 pm V⁻¹, respectively, and the d_{16} -coefficient of FerG#1 was 0.06 pm V⁻¹. The behaviour of FerG#1 differed from the other compounds not only in the value of d -coefficients: on cooling FerG#1 from the liquid crystalline phase, the SHG power increased several orders of magnitude, and the SHG power of FerG#1 was unchanged on applying external electric fields up to ± 15 V μm^{-1} at room temperature. We attribute the relatively large d -coefficients of the first generation dendrimer FerG#1 to crystallization effects that increase the orientation of the molecular dipoles.

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