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# Synthesis and Pyroelectric Properties of Novel Ferroelectric Organosiloxane Liquid Crystalline Materials

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Novel ferroelectric liquid crystal materials with large pyroelectric coefficients (exceeding 100 nC/cm<sup>2</sup>·K even under zero applied bias field) as compared to those reported so far have been synthesized. The materials described show a low melting point (<−10 °C) and low SmC\*–SmA phase transition temperatures suitable for practical devices. Combined with the fact that the real part of the dielectric constant is also low as compared to that of ferroelectric ceramic materials used in pyroelectric devices, these new materials have significant potential for application in uncooled infrared sensing devices.

## Introduction

Ferroelectric liquid crystals (FLCs) are materials of great interest because of their enormous potential for industrial applications.<sup>1–3</sup> A liquid crystal material can exhibit ferroelectricity if the following conditions are satisfied: the molecules are chiral, the molecules have a dipole moment in the direction perpendicular to the long molecular axis, and the molecules are tilted with respect to the smectic layer normal. Because of the molecular chirality, there is no symmetry mirror plane in the liquid crystal structure, and the material will have a spontaneous polarization ( $P_s$ ) in the plane of the smectic layer. The demonstration of pyroelectricity in the chiral smectic C (SmC\*) phase of liquid crystalline materials<sup>4–12</sup> has sparked substantial interest in these

systems for uncooled IR ferroelectric sensors. The reason for this is that current uncooled IR detectors, on the basis of ceramic materials, use a device configuration wherein the active pixel is thermally isolated from the substrate (e.g., silicon) using polyimide. This polymer cannot withstand the high temperatures (nearly 600 °C) required for annealing the pyroelectric ceramic sensing element. Liquid crystals, on the other hand, can be processed at or close to room temperature and therefore are attractive from a process point of view as well.

Pyroelectricity is a fundamental property of ferroelectric materials and is due to a change in the spontaneous polarization with temperature. The spontaneous polarization of ferroelectric inorganic material typically varies rapidly with temperature particularly at the ferroelectric phase transition temperature  $T_c$  (Curie transition) and therefore gives rise to a large pyroelectric coefficient  $p$  ( $p = dP_s/dT$ ). However, in the majority of ferroelectrics (so-called proper ferroelectrics), the dielectric constant ( $\epsilon'$ ) and dielectric loss ( $\tan \delta$ ) also increase near  $T_c$  with the result that there is little improvement in the figure of merit (the figure of merit is directly proportional to  $p$  but inversely proportional to both  $\epsilon$  and  $\tan \delta$  of merit of the materials).

FLC materials, on the other hand, are “improper” ferroelectrics wherein the spontaneous polarization is derived from molecular tilt.<sup>13</sup> Consequently, these materials do not exhibit this divergent dielectric behavior

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near the transition SmC\*–SmA; therefore, while the pyroelectric coefficient increases near the transition, the dielectric constant remains low. This makes FLCs attractive for pyroelectric detection. Despite this, FLC materials have not been considered in the past since none have shown  $p$  values comparable to that of inorganic ferroelectrics.

In this paper, we report our studies on a newly synthesized family of liquid crystals that exhibit pyroelectric coefficients that are much higher than that of inorganic materials. We show that, by a careful manipulation of the organosiloxane groups attached to the chiral part of the molecule, high pyroelectric coefficients as well as low SmC\*–SmA transition temperatures can be achieved. We also report pyroelectric measurements on a homologous class of materials whose synthesis procedures and electroclinic properties have been published earlier.<sup>14</sup>

## Experimental Section

**General.** All reactions were performed under a positive pressure of nitrogen using standard manifold techniques unless otherwise stated. Analytical thin-layer chromatography was performed on glass silica plates (0.25 mm thick E. Merck silica gel 60-F254), using the solvent mixtures indicated. Preparative chromatographic purifications were performed by employing flash chromatography on E. Merck 40–63  $\mu$ m normal-phase silica gel.

Dry THF, dichloromethane, and toluene were used as received from Fluka, as were diethyl azodicarboxylate, triphenylphosphine, (*S*)(–)-methyloxirane, and bromobutene. Trimethylsilane and derivatives were obtained from Gelest.

300 MHz <sup>1</sup>H NMR spectra were recorded on a Bruker MSL300 spectrometer in CDCl<sub>3</sub> or DMSO solutions. Observations by optical microscopy were carried out using a Nikon polarizing microscope equipped with a mettler hot stage. The thermal transitions of the materials were determined by using a Perkin-Elmer DSC-7 differential scanning calorimeter (scan rate 5 °C min<sup>–1</sup>).

**Sample Cell Preparation.** The ferroelectric sample cell is fabricated as follows: One of the glass plates forming the liquid crystal cell is patterned with a thin layer of gold, and the second glass plate is patterned with transparent conducting indium tin oxide (ITO). A thin alignment layer (~100 Å) is obliquely deposited by a thermal evaporation process on the ITO-coated glass plate to align the FLC molecules. The two glass plates are spaced apart using glass bead spacers and bonded at the edges using an epoxy, and the cell thickness was measured to be 3.3  $\mu$ m. The cell filling is done in the high-temperature phase (isotropic) under vacuum. For alignment, the sample is heated into the isotropic phase, and an electric field of 5 V/ $\mu$ m is applied. The cell is then cooled in the presence of the field at a rate of 0.01 V/ $\mu$ m into the smectic phase. The alignment is verified under a polarizing microscope, and large aligned regions with very few defects are observed.

**Synthesis.** Typical preparations of the materials are described below.

**(*S*)-2-Heptenol 2.** A total of 2.8 g of magnesium in a 100-mL flask was dried overnight at 100 °C. After being cooled with a stream of nitrogen gas, a small amount of iodine was added to the magnesium. A solution of 1-bromobutene (8.19 g, 66 mmol) in 30 mL of dry THF was added slowly dropwise keeping the temperature of the mixture below the boiling point of THF. The reaction mixture was stirred an additional 1 h after the end of THF addition. The resulted dark color mixture was cooled in an ice-bath. Copper iodide (1.26 g) was added at once, and the mixture was stirred for 0.5 h at 0 °C. (*S*)-

Propylene oxide (3.12 g, 54 mmol) in 15 mL of THF was slowly added to the reaction mixture. The solution was stirred for 3 h at 0 °C, poured into saturated aqueous solution of NH<sub>4</sub>Cl, and stirred for 1 h. The crude product was extracted several times with ethyl ether. The combined organic extracts were washed with water and dried over MgSO<sub>4</sub>. Evaporation of the solvent yielded a yellowish liquid. Chromatography on silica gel eluting with 4:1 hexane/ethyl acetate produced 70% of pure alcohol **2** with the following physical properties:  $R_f$  0.4;  $[\alpha]_D^{25} = 10.74^\circ$  ( $c = 0.078$ , CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (CDCl<sub>3</sub>, TMS)  $\delta$  (ppm): 1.13 (t, 3H, –CH<sub>3</sub>); 1.42–1.60 (m, 2H, CH<sub>2</sub>–CH(OH)); 1.52 (m, 2H, –CH<sub>2</sub>–); 2.1 (m, 2H, –CH<sub>2</sub>–); 3.41 (d, 1H, OH); 3.76 (m, 1H, –CH); 4.98 (m, 2H, CH<sub>2</sub>=CH–); 5.82 (m, 1H, –CH=CH<sub>2</sub>). Anal. Calcd for C<sub>7</sub>H<sub>14</sub>O: C, 73.63; H, 12.36. Found: C, 73.55; H, 12.30.

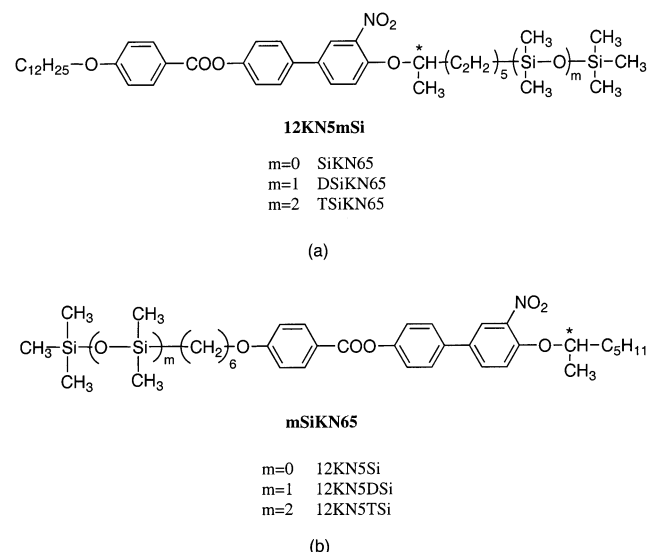
**4'-[[(1*R*)-1-Methyl-5-hexenyloxy]-3'-nitro[1,1'-biphenyl]-4-yl benzoate 4.** To a nitrogen-flushed flask containing a mixture of 2-heptenol **2** (1.02 g, 8.95 mmol), nitro phenol derivative<sup>14</sup> **3** (3 g, 8.95 mmol), and triphenylphosphine (2.38 g, 9.13 mmol) in 30 mL of dry THF, a solution of diethyl azodicarboxylate (1.5 mL, 9.53 mmol) in 10 mL of THF was added dropwise. The reaction mixture was stirred under nitrogen at room temperature overnight. After evaporation of the solvent, the residue was subjected to column chromatography on silica gel (eluent, hexane/ethyl acetate 4:1) to give **4** in 90% yield as a yellow liquid.  $R_f$  0.6 (hexane/ethyl acetate 4:1). <sup>1</sup>H NMR (CDCl<sub>3</sub>, TMS)  $\delta$  (ppm): 1.37 (d, 3H, CH<sub>3</sub>CH); 1.51 (m, 2H, –CH<sub>2</sub>–); 1.52–1.61 (m, 2H, CH<sub>2</sub>–CH(CH<sub>3</sub>)); 2.05 (m, 2H, –CH<sub>2</sub>–); 4.54 (m, 1H, –CH); 5.0 (m, 2H, CH<sub>2</sub>=CH–); 5.81 (m, 1H, –CH=CH<sub>2</sub>); 7.09 (d, 1H, ArH); 7.26 (d, 2H, ArH); 7.41–7.64 (m, 5H, ArH); 7.67 (dd, 1H, ArH); 8.02 (d, 1H, ArH); 8.19 (dd, 2H, ArH). Anal. Calcd for C<sub>26</sub>H<sub>25</sub>NO<sub>5</sub>: C, 72.37; H, 5.84; N, 3.25. Found: C, 72.31; H, 5.79; N, 3.20.

**4'-[[(1*R*)-1-Methyl-5-hexenyloxy]-3'-nitro[1,1'-biphenyl]-4-ol 5.** To a solution of nitro benzoate derivative **4** (3.7 g, 8.27 mmol) in 50 mL of methanol and 10 mL of water was added LiOH·H<sub>2</sub>O (1.3 g, 33.1 mmol). The reaction mixture was stirred overnight at room temperature. After evaporation of the solvent, the residue was neutralized by HCl ice solution, and the product was extracted several times with ethyl ether. The combined organic extracts were washed with sodium bicarbonate solution, dried over anhydrous MgSO<sub>4</sub>, and evaporated under reduced pressure. The final product was purified by column chromatography on silica gel (eluent, hexane/ethyl acetate 4:1) to give **5** in 85% yield as an orange oil.  $R_f$  0.4 (hexane/ethyl acetate 4:1). <sup>1</sup>H NMR (CDCl<sub>3</sub>, TMS)  $\delta$  (ppm): 1.37 (d, 3H, CH<sub>3</sub>CH); 1.51 (m, 2H, –CH<sub>2</sub>–); 1.52–1.61 (m, 2H, CH<sub>2</sub>–CH(CH<sub>3</sub>)); 2.04 (m, 2H, –CH<sub>2</sub>–); 4.54 (m, 1H, –CH); 5.0 (m, 2H, CH<sub>2</sub>=CH–); 5.81 (m, 1H, –CH=CH<sub>2</sub>); 6.4 (br s, 1H, OH); 6.95 (d, 2H, ArH); 7.17 (d, 1H, ArH); 7.39 (d, 2H, ArH); 7.64 (dd, 1H, ArH); 7.98 (d, 1H, ArH). Anal. Calcd for C<sub>19</sub>H<sub>21</sub>NO<sub>4</sub>: C, 69.71; H, 6.47; N, 4.28. Found: C, 69.68; H, 6.41; N, 4.25.

**4'-[[(1*R*)-1-Methyl-5-hexenyloxy]-3'-nitro[1,1'-biphenyl]-4-yl 4-(decyloxy)benzoate 6.** To a mixture of 4-(decyloxy)benzoic acid (0.32 g, 1.16 mmol), the phenol derivative **5** (0.4 g, 1.16 mmol), and dimethylamine pyridine (DMAP) (0.01 g, 0.079 mmol) in 20 mL of dichloromethane was added 1-(3-(dimethylamino)propyl)-3-ethylcarbodiimide methiodine (EDC·CH<sub>3</sub>I) (0.357 g, 1.2 mmol). The mixture was stirred for 24 h at room temperature. After dilution with dichloromethane, the organic phase was washed with water, a saturated solution of sodium bicarbonate, and brine and finally dried over sodium sulfate. The solvent was evaporated, and the residue was purified by column chromatography on silica gel (eluent, hexane/ethyl acetate 9:1) to give **6** as a yellow solid in 79% yield.  $R_f$  0.6 (hexane/ethyl acetate 9:1). <sup>1</sup>H NMR (CDCl<sub>3</sub>, TMS)  $\delta$  (ppm): 0.89 (t, 3H, CH<sub>3</sub>–CH<sub>2</sub>); 1.21–1.85 (m, 20H, –CH<sub>2</sub>–); 1.37 (d, 3H, CH<sub>3</sub>CH); 2.04 (m, 2H, –CH<sub>2</sub>–); 4.02 (t, 2H, –CH<sub>2</sub>OAr); 4.54 (m, 1H, –CH); 5.0 (m, 2H, CH<sub>2</sub>=CH–); 5.81 (m, 1H, –CH=CH<sub>2</sub>); 6.95 (d, 2H, ArH); 7.17 (d, 1H, ArH); 7.38 (dd, 2H, ArH); 7.62 (dd, 2H, ArH); 7.74 (d, 1H, ArH); 8.02 (d, 1H, ArH); 8.19 (dd, 2H, ArH). Anal. Calcd for C<sub>36</sub>H<sub>45</sub>NO<sub>6</sub>: C, 73.57; H, 7.72; N, 2.38. Found: C, 73.51; H, 7.68; N, 2.31.

**4'-[[(1*R*)-1-Methyl-6-(1,1,3,3,3-pentamethyldisiloxanyloxy)-3'-nitro[1,1'-biphenyl]-4-yl 4-(decyloxy)benzoate 12KN65DSi.**

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**Figure 1.** (a) Structure of ferroelectric organosiloxane liquid crystalline materials. (b) Structure of the homologous series.

The synthesis of the ferroelectric liquid crystalline material 12KN65DSi is given here as an example. The two other materials 12KN65Si and 12KN65TSi were made following the same procedure. To a solution of pentamethyldisiloxane (0.31 g, 2.2 mmol) and (0.8 g, 1.26 mmol) of **6**, dissolved in 20 mL of dry THF, was added 100  $\mu$ L of a solution (1 mg/mL) in  $\text{CH}_2\text{-Cl}_2$  of dicyclopentadienylplatinum (II) chloride catalyst. The reaction mixture was stirred at 60  $^\circ\text{C}$  under nitrogen for 24 h. The solvent was removed, and the crude product was purified by column chromatography on silica gel (eluent, hexane/ethyl acetate 9:1). The product was obtained as a jelly yellow material in 75% yield.  $R_f$  0.7 (hexane/ethyl acetate 9:1).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  (ppm): 0.06–0.8 (d, 15H,  $\text{Si}(\text{CH}_3)_5$ ); 0.5 (m, 2H,  $\text{Si-CH}_2$ ); 0.88 (t, 3H,  $-\text{CH}_2\text{-CH}_3$ ); 1.21–1.90 (m, 24H,  $-\text{CH}_2-$ ); 1.37 (d, 3H,  $\text{CH}_3\text{CH}$ ); 4.02 (t, 2H,  $-\text{CH}_2\text{OAr}$ ); 4.54 (m, 1H,  $-\text{CH}$ ); 6.95 (d, 2H, ArH); 7.17 (d, 1H, ArH); 7.38 (dd, 2H, ArH); 7.62 (dd, 2H, ArH); 7.74 (d, 1H, ArH); 8.02 (d, 1H, ArH); 8.19 (dd, 2H, ArH). Anal. Calcd for  $\text{C}_{41}\text{H}_{61}\text{NO}_7\text{Si}_2$ : C, 66.90; H, 8.35; N, 1.90. Found: C, 66.8; H, 8.27; N, 1.80.

## Results and Discussion

The structures of the new series of ferroelectric materials are presented in Figure 1a. Figure 1b shows the structure of the homologous series whose synthesis has been described earlier.<sup>14</sup>

**Synthesis.** The synthesis steps leading to the preparation of the chiral liquid crystalline compounds having siloxy end groups are illustrated in Schemes 1 and 2.

(*S*)-1-Hepten-6-ol was prepared by stereospecific opening of (*S*)-(-)-methyloxirane by the Grignard reagent **1** in the presence of copper(I) iodide catalysis.<sup>15</sup> The alcohol formed in the coupling is produced with overall retention of configuration. Nitrophenol derivative **3** was then coupled with alcohol **1** using the stereospecific Mitsunobu coupling procedure<sup>16</sup> to give **4**. This reaction proceeds with inversion of configuration of the chiral center. Deprotection of the phenol by hydrolysis of the benzoate ester with hydroxide ion then gave **5**. The vinylic derivative material **6** was obtained by esterification of 4-(decyloxy)benzoic acid with **5** in the presence of 1-(3-dimethylaminopropyl)-3-ethylcarbo-

**Table 1.** Transition Temperatures and Pyroelectric Coefficient Values for the Ferroelectric Organosiloxane Liquid Crystalline Series<sup>a</sup>

| compound | phase sequence ( $^\circ\text{C}$ ) <sup>b</sup>       | $\frac{p}{\text{nC/cm}^2\cdot\text{K}}$ zero bias <sup>c</sup> | $\frac{p}{\text{nC/cm}^2\cdot\text{K}}$ (1 V bias) |
|----------|--|--|--|
| 12KN5Si  | $K < -10 \text{ SmC}^* 47 \text{ SmA } 61 \text{ I}$   | 4  |  |
| 12KN5DSi | $K < -10 \text{ SmC}^* 40.5 \text{ SmA } 59 \text{ I}$ | 104  | 260  |
| 12KN5TSi | $K < -10 \text{ SmX } 46 \text{ SmA } 56 \text{ I}$    |  |  |
| SiKN65   | $K < -10 \text{ SmC}^* 48.2 \text{ SmA } 51 \text{ I}$ | 5  |  |
| DSiKN65  | $K < -10 \text{ SmC}^* 40.5 \text{ SmA } 55 \text{ I}$ | 20   | 140  |
| TSiKN65  | $K -10 \text{ SmC}^* 28 \text{ SmA } 55.5 \text{ I}$   | 45   | 95   |

<sup>a</sup> Values of the  $p$  coefficient in the presence of bias is also shown for those materials that have reasonably high  $p$  values for zero bias. <sup>b</sup> For all samples, the melting point is below  $-10 \text{ }^\circ\text{C}$ . <sup>c</sup>  $p$  values are quoted at temperatures corresponding to their maximum values. These are slightly offset with respect to the phase transition temperatures that were measured using DSC.

diimide methiodine (EDC- $\text{CH}_3\text{I}$ ) and (dimethylamino)-pyridine (DMAP) (Scheme 1). The corresponding organosiloxane liquid crystalline materials were obtained through the classical hydrosilylation reaction<sup>17</sup> between the vinyl mesogenic groups and the hydrosiloxane derivatives in the presence of a Pt catalyst (Scheme 2).

**Mesophase Behavior.** Phase identification was carried out by means of optical microscopy. Typical textures were observed for the chiral smectic C phases as broken fan-shaped texture with superimposed dechiralization lines and for smectic A as focal conic textures. The crystal to mesophase transition temperatures were determined by means of DSC (heating runs). The transition temperatures of the new organosiloxane materials are shown in Table 1.

The SmA isotropic transition of all materials remains practically the same, while the melting points are very low: DSC thermograms show no melting peaks above  $-10 \text{ }^\circ\text{C}$ . In fact, the samples were kept at room temperature for several months without showing any evidence of crystallinity. The lack of crystallinity seems to be associated with the flexibility of the siloxane chains as seen in other homologue materials.<sup>14,18,19</sup> Unlike typical FLC molecules that consist of a rigid core and hydrocarbon or fluorocarbon chains, the new organosiloxane series possess the unique feature of having a siloxane chain near the chiral center of the molecule. The partial substitution of alkyl chains by more flexible dimethylsiloxane groups is expected to enhance the thermal and mechanical stability and lower the phase transition temperatures of the LC materials. The bulky and high flexible siloxy tail causes a reduction of the interchain interaction and the degree of crystallinity of these materials.

As can be seen from Table 1, increasing the number of siloxy units in the chain stabilizes the smectic A and inhibits the formation of the chiral smectic C; the temperature range of SmC\* phase is reduced and shifted to lower temperature. Incorporation of more dimethylsiloxane units (12KN5TSi) in the chain does

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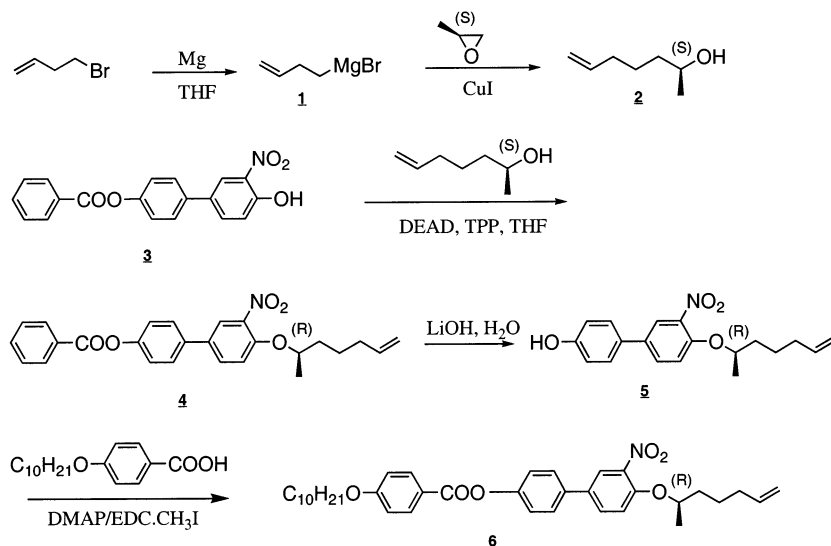
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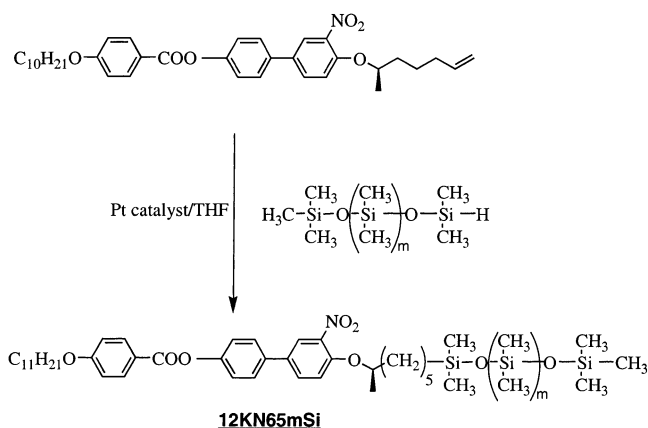
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Scheme 1



Scheme 2



not destroy the liquid crystallinity but instead generates a high ordered SmX mesophase below SmA phase.

**Material Properties.** The sensitivity of a pyroelectric device is dependent on the pyroelectric coefficient  $p$  of the material chosen as the sensing element in the device. An approach to improve the pyroelectric coefficient of a material is to ensure that the spontaneous polarization shows a large change close to the transition point. Since the pyroelectric coefficient is the derivative of the spontaneous polarization with respect to temperature, this translates into a large pyroelectric coefficient. In addition to this, it is desirable to have a reasonably constant value of the pyroelectric coefficient over a small temperature interval (nearly 0.2 °C) around the operating temperature of the device. This is because practical devices use temperature controllers that may have an uncertainty around the set point temperature of the order of 0.2 °C.

The pyroelectric coefficient has been measured in the past using various indirect techniques. For example, in the Chynoweth technique,<sup>12,20</sup> the pyroelectric coefficient is extracted from an integration procedure. This method is prone to errors because of the large inaccuracies that can arise from integration procedure, particularly close to the SmC\* to SmA phase transition temperature. To

overcome this problem, we have used a direct experimental method for measurement of  $p$ , called the Byer Roundy method.<sup>21</sup> The Byer Roundy method is based on the principle that the pyroelectric coefficient can be extracted from the following equation:

$$i = pA \frac{dT}{dt}$$

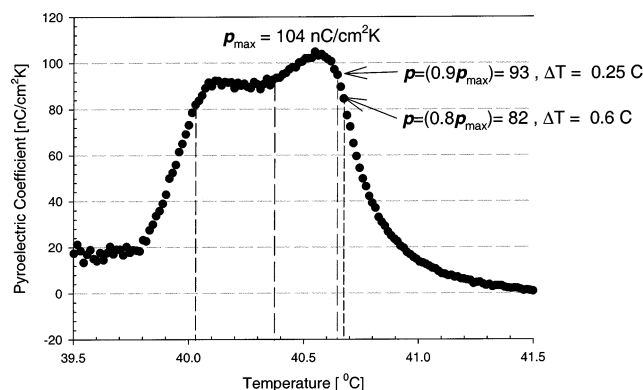
where  $i$  is the pyroelectric current generated due to the temperature change  $dT$  during a time interval  $dt$  and  $A$  represents the area of the overlapping patterned electrodes active (pixel). Thus, by ramping the temperature of the sample linearly and knowing the differential quantities involved, the pyroelectric coefficient can be estimated from the measured current. The temperatures are measured using a calibrated thermistor.

The pyroelectric coefficient values of the materials are given in Table 1. The first two materials, 12KN5Si and 12KN5DSi, clearly exhibit both ferroelectric smectic C\* and the electroclinic smectic A phases. 12KN5TSi on the other hand, shows a smectic A phase and at around 45 °C changes to another high-order smectic phase. This unknown phase did not exhibit any ferroelectric or optical switching behavior, which excludes it from being used as a pyroelectric sensing material. Of all the materials studied, 12KN5DSi is the most promising candidate for uncooled IR sensing applications on the basis of the fact that it has the highest  $p$  value for zero bias. The pyroelectric coefficient peak has a value of 104 nC/cm<sup>2</sup>·K, an order of magnitude larger than reported in the literature.<sup>4,5,9</sup> In addition, the pyroelectric coefficient is large over a relatively large range of temperature. As shown in Figure 2, the  $p$  value drops only to 93 nC/cm<sup>2</sup>·K over a temperature interval of 0.25 °C and to 82 nC/cm<sup>2</sup>·K over a temperature interval of 0.6 °C.

In a pyroelectric device, these temperature intervals represent the temperature excursion around the mean operating temperature that can be tolerated without losing significant performance. Also, the mean operating temperature of about 40 °C is reasonably close to room temperature, allowing the use of simple Peltier-type

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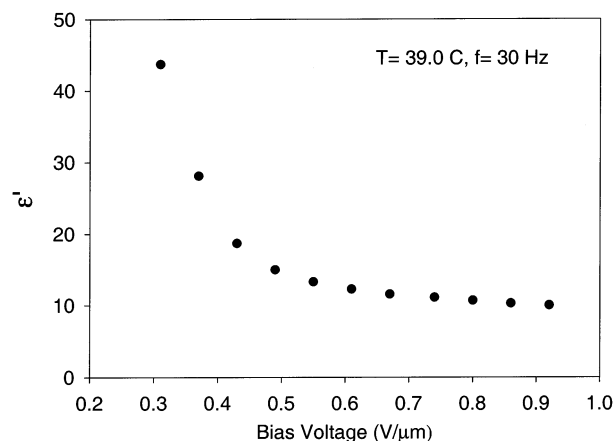
**Figure 2.** Plot of pyroelectric coefficient,  $p$ , for 12KN5DSi as a function of temperature. These values are measured using the direct Byer Roundy technique. Note that the  $p$  values remain high over a finite temperature interval (of the order of 0.6 deg). This is useful for a device held at its operating temperature using a typical peltier device.

temperature controllers to be used to hold the device at this value. It is also interesting to observe, in Figure 2, that there is a small shoulder in addition to the main peak in the  $p$  value. We believe this to be due to the presence of a subphase in addition to the main SmC\* to SmA phase transition. This is, however, yet to be confirmed.

Since device operation is typically performed under a small bias voltage, we used the Byer Roundy method to evaluate the pyroelectric coefficient with an applied bias field. In all cases, the applied bias field increased the  $p$  value significantly (Table 1). We chose to apply a bias field and to evaluate  $p$  values in those materials that had large  $p$  coefficients in the absence of a bias field (as these are the materials that would be chosen for a test device). The values with bias are shown for three of the materials (12KN5DSi, DSiKN65, and TSiKN65). Although the  $p$  value in the presence of the bias cannot be stated unambiguously (since there is also an unknown resistive component), we do infer that the  $p$  values with bias are higher than those without bias. Figure 2 shows the  $p$  value variation with temperature during an up-ramp for 12KN5DSi (with no bias field applied).

As seen from Table 1, the introduction of a siloxy chain on either side of the molecule has a dramatic effect on the pyroelectric coefficient. In the 12KSi series, where the siloxy chain is close to the chiral center, the pyroelectric coefficient increases (with the increase of the number of siloxy groups) from a value of 4 nC/cm<sup>2</sup>·K for 12KN5Si to 104 nC/cm<sup>2</sup>·K for 12KN5DSi. The same behavior is observed in the mSiKN65 series where the pyroelectric coefficient increases from 5 nC/cm<sup>2</sup>·K for SiKN65 to 45 nC/cm<sup>2</sup>·K for TSiKN65.

To understand the molecular basis for the variation in pyroelectric coefficient and to correlate the structure to the pyroelectric property is obviously not trivial. Measurements of the spontaneous polarization of 12KN5DSi, for example, show that these materials have high polarization values<sup>14,22</sup> (saturated value of the polarization close to the transition temperature is about 245 nC/cm<sup>2</sup>·K). High polarization values by themselves



**Figure 3.** Real part of the dielectric constant ( $\epsilon'$ ) of 12KN5DSi as a function of applied voltage. The dielectric constant drops significantly with applied bias. The measurement temperature and frequency is chosen to be device relevant.

are, however, not enough to achieve a high pyroelectric coefficient. The temperature derivative of the polarization close to the transition temperature should also be high. Clearly, the presence of the siloxane group, the number of such groups, and their position in the molecule relative to the chiral center all play an important role in dictating the value of the pyroelectric coefficient. Presumably, other parts of the molecule play a lesser role in determining the high  $p$  values.

For a high device figure of merit, not only should the pyroelectric coefficient be large but also the real part of the dielectric constant of the material ( $\epsilon'$ ) should be small. Hence, dielectric measurements were performed on the same sample cell used in the pyroelectric measurement. An HP 4192 A LCR bridge is used for this purpose. Corrections were made for stray capacitance in the experimental setup. Typical values of dielectric constant of 12KN5DSi were measured to be around 10 with application of bias field (Figure 3). Similar values were obtained for other materials with bias. As can be seen from Figure 3, the dielectric constant drops dramatically with applied bias voltage to about 10. This decrease in  $\epsilon'$  with increasing bias can be attributed to the suppression of the Goldstone mode obtained before in other materials.<sup>23</sup> This is far lower than typical values for ceramic materials for comparable thickness of the material.<sup>24</sup> The high pyroelectric coefficient coupled with the low value of the dielectric constant leads to a high figure of merit for the pyroelectric device. In addition to these parameters ( $p$  and  $\epsilon'$ ), it is important to reduce the ionic impurities since they reduce the signal to noise ratio in the device. We have recently demonstrated an approach to minimize such impurities (and therefore the dielectric loss of the material) through a temperature annealing procedure.<sup>25</sup> We are currently in the process of developing and testing a multi-pixel device for an uncooled IR sensor using the material of choice, 12KN5DSi. The perfor-

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mance parameters of such a device will be published elsewhere.

### **Summary**

We have developed novel ferroelectric liquid crystals containing siloxy chains that show low melting point and exhibit ferroelectricity over a large temperature range. The pyroelectric properties of these materials are very sensitive to the number of siloxy units attached to the hydrocarbon chain at the end of the molecule. One

of these materials exhibits an unusually large pyroelectric coefficient at subambient temperatures. The combination of a high  $p$  value and low  $\epsilon'$  of these materials and the possibility for a device to operate at or close to room temperature makes these materials attractive for use in uncooled IR detectors.

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