Novel Ferroelectric Liquid Crystals Derived from Trifluoromethylated Pyranoses Showing Very Large Spontaneous Polarization

Keizou Itoh,* Mitsunori Takeda, Masaaki Namekawa, Shinichi Nayuki, Yoshinobu Murayama,
Takashi Yamazaki,† and Tomoya Kitazume†
R&D Dept., Kashima Oil Co., Ltd., 4 Towada, Kamisu, Kashima, Ibaraki 314-02
†*Department of Bioengineering, Tokyo Institute of Technology, 4259 Nagatsuta-cho, Midori-ku, Yokohama 227*

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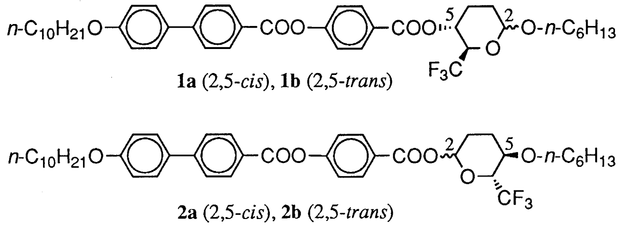
Novel ferroelectric liquid crystals with a trifluoromethylated pyranose were synthesized and their mesomorphic properties were investigated. These compounds exhibited a chiral smectic C phase and showed very large spontaneous polarization over 700 $nC\cdot cm^{-2}$. Relationships between molecular structures and physical properties were discussed.

A lot of new ferroelectric liquid crystals (FLCs) have been synthesized over the past decade because of their very useful properties such as quick response and bistability.[1] Recently, some compounds fixing a polar group in the chiral ring structure have attracted a great amount of attention due to their very large spontaneous polarization (Ps).[2-4] The reason for the large Ps may be that the polar group is fixed in the bulky ring structure so that the free rotation of the lateral dipole moment around the long axis must be hindered. In this respect, we have synthesized chiral pyranose derivatives with a trifluoromethyl group and showed they are excellent chiral dopants for FLCs.[5-6]

In this paper, we would like to report the synthesis and mesomorphic properties of the novel pyranose compounds **1** and **2** which have three-ring structures in the core part as shown in Figure 1.

As shown in Scheme 1, compound **1a** was synthesized from a chiral pyranose derivative *cis*-**3** which was prepared according to a method previously reported.[6-8] In the first step, *cis*-**3** was esterified with 4-benzyloxybenzoylchloride to give *cis*-**4** followed by the hydrogenation over palladium-carbon afforded *cis*-**5**. Then *cis*-**5** was esterified with 4'-decyloxybiphenyl-4-carboxylic acid chloride to give the target compound **1a**. Compound **1b** was obtained in the same way by using *trans* isomer of *cis*-**3** as a starting material. Compound **2a** and **2b** were synthesized from a chiral pyranose derivative **6**[5] in a similar manner and separated by column chromatography.

The mesomorphic properties of the synthesized compounds are listed in Table1. The phase sequence and phase transition temperatures were determined by using a polarized optical microscope and a differential scanning calorimeter. All compounds exhibit ferroelectric chiral smectic C phase (SmC*).



1a (2,5-*cis*), **1b** (2,5-*trans*)

2a (2,5-*cis*), **2b** (2,5-*trans*)

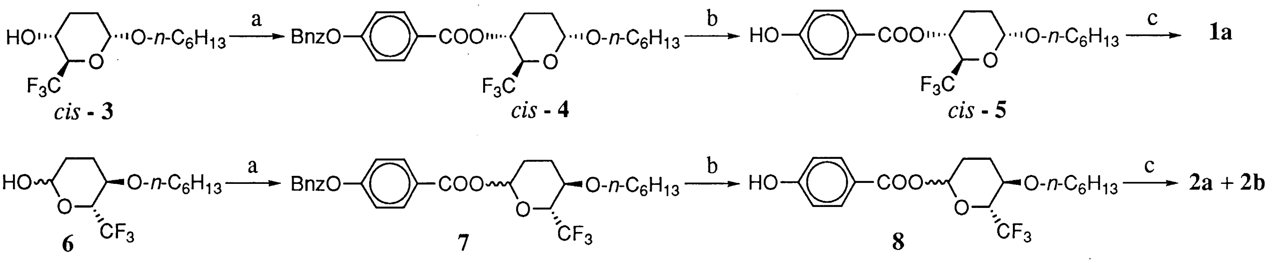
Figure 1. Chemical structures of the synthesized Pyranose compounds.

Compounds **1a** and **2a** show direct phase transition from isotropic phase (Iso) to SmC* phase and exhibit a fairly low clearing point compared with *trans* ones(**1b** and **2b**). This is probably due to the bent structure of the *cis* compounds. On the other hand, *trans* compounds have a much wider temperature range of the mesophase. Compounds **1b** and **2b** exhibit Iso-SmA-SmC* and Iso-N*-SmA-SmC* phase sequences, respectively.

The spontaneous polarization of the compounds **1a**, **1b** and **2b** was measured[9] by the triangular wave method and illustrated in Figure 2. Compound **1a** show fairly large Ps just below the transition temperature and increases gradually as the temperature decreases. On the contrary, compounds **1b** and **2b**, having very similar temperature dependence of Ps, show relatively small Ps just below the transition temperature and increase much larger than the *cis* one(**1a**). These differences may be caused by the differences of their phase sequences.

These compounds exhibit a quite large Ps of 700~800 $nC\cdot cm^{-2}$, which is larger than those of γ-lactone and δ-valerolactone derivatives[2,3] having similar chiral ring structure (590 and 310 $nC\cdot cm^{-2}$ respectively). Although compounds having a larger Ps over 1000 $nC\cdot cm^{-2}$ have already been reported,[4,10] pyranose derivatives count among a few compounds which exhibit a larger Ps over 500 $nC\cdot cm^{-2}$.

The reason for the large Ps of the pyranose compounds is considered to be that the dipole moments of an ether oxygen and



cis - **3**

cis - **4**

cis - **5**

6

7

8

Scheme 1. (a) 4-Benzyloxybenzoylchloride, Py; (b) H2, Pd/C, EtOH; (c) 4'-Decyloxybiphenyl-4-carboxylic acid chloride, Py.

Table 1. Mesomorphic properties of the synthesized pyranose compounds

Compounds	Phase Transition Temperature[a] / °C								
	Cry		SmC*		SmA		N*		Iso
1a (2,5-*cis*)	•	59	•			100			•
1b (2,5-*trans*)	•	91	•	156	•	175			•
2a (2,5-*cis*)	•	98	•			112			•
2b (2,5-*trans*)	•	71	•	140	•	155	•	160	•

[a] Iso: isotropic phase; N*: chiral nematic phase; SmA: smectic A phase; SmC*: chiral smectic C phase; Cry: crystal phase.

a trifluoromethyl group are fixed in a ring structure and cooperate effectively. Moreover, a bulky ring structure of the trifluoromethylated pyranose hinders the free rotation of the lateral dipole moment along the long axis, resulting in a very large Ps.

Temperature dependence of the optical tilt angle of the compounds **1b** and **2b** is illustrated in Figure 3. These compounds exhibit a large tilt angle of about 40 degrees. Those of *cis* compounds could not be measured because of their multi-domain alignment. Compounds **1b** and **2b** also have a similar temperature dependence of the tilt angle as well as the Ps. From these observation, it seems that the difference of *cis* and *trans* configuration influences the physical properties much more than the difference of the esterified position of the chiral pyranose ring.

As regards the SmC* of the compound **1a**, there is a possibility of another type of chiral smectic phase, such as antiferroelectric chiral smectic C phase (SmC_A*) or ferrielectric chiral smectic C phase ($SmC\gamma$*) as discovered in MHPOBC.[11] Because there observed one large peak and another small peak in the switching current signal of the compound **1a** when applying a triangular voltage wave.

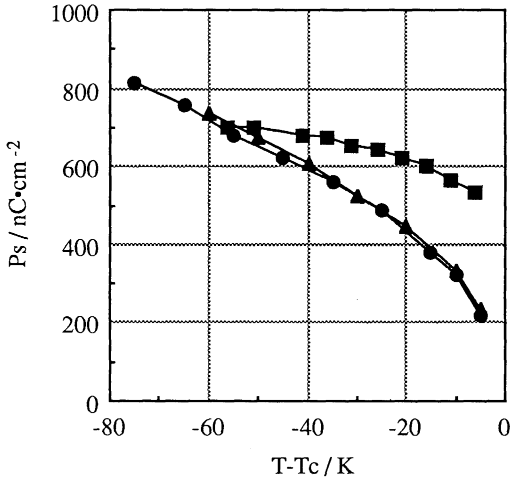


Figure 2. Temperature dependence of the spontaneous polarization for the compounds: 1a(■); 1b(▲); 2b(●).

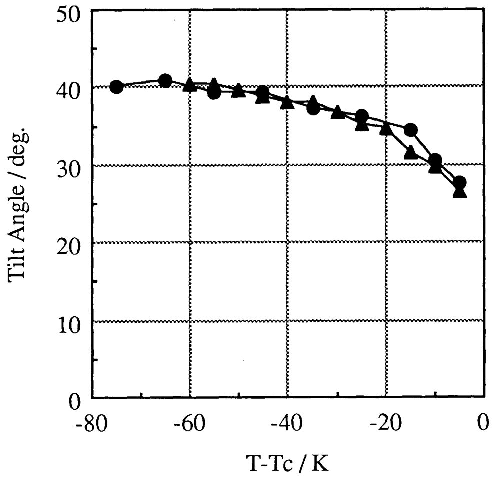


Figure 3. Temperature dependence of the tilt angle for the compounds: 1b(▲); 2b(●).

We examined the physical properties of the newly synthesized pyranose derivatives and found that they had very large spontaneous polarization. This may be attributed to the unique structure of the pyranose compounds. Further investigation is now in progress.

References and Notes

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