Journal of Fluorine Chemistry, *47* (1990) 459–466

Received. May 20, 1989, accepted. January 30, 1990

SYNTHESIS OF FERROELECTRIC LIQUID CRYSTAL POLYMERS POSSESSING THE TRIFLUOROMETHYL GROUP

Tomoya KITAZUME* and Takeshi OHNOGI

Department of Bioengineering, Tokyo Institute of Technology,
Ookayama, Meguro-ku, Tokyo 152 (Japan)

SUMMARY

The preparation and polymerization of trifluoromethylated ferroelectric liquid crystal monomers of the acrylic type have been undertaken. Furthermore, the physical properties of the corresponding polymers have been described.

INTRODUCTION

Recently, we have reported that the real cause of stabilization of the third state and the possibility of the tristable switching in the surface stabilized ferroelectric liquid crystal displays device were based on the character of fluoroalkyl group on the chiral center [1].

In this paper, we describe the synthesis and properties of ferroelectric liquid crystal polymers involving a trifluoromethylated ferroelectric crystal unit. These materials have a quick response time for switching and possibilities exist of using ferroelectric liquid crystal polymers as functional materials, particularly for displays.

0022-1139/90/$3.50

RESULTS AND DISCUSSION

Preparation of the ferroelectric liquid crystal monomers (2 and 3)

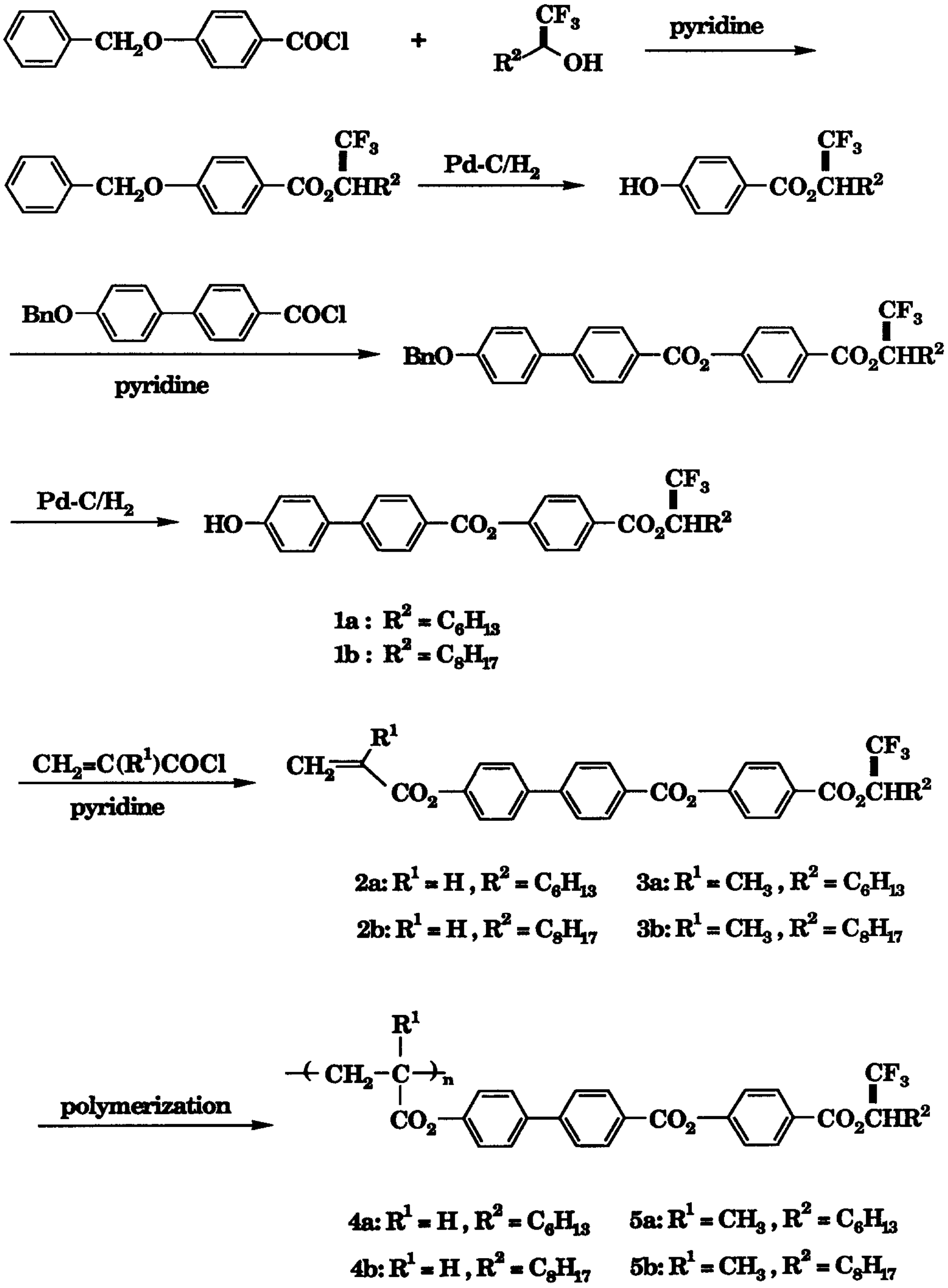
Synthetic methods for the construction of ferroelectric liquid crystal units have been widely investigated [2-5]; some work has involved trifluoromethylated compounds [1,6,7]. To establish practical routes to ferroelectric liquid crystal monomers, we examined extensions to these synthetic strategies. In the Scheme below is shown an outline of the route employed.

The ferroelectric liquid crystal units (1) [1,6,7] were reacted with acrylic acid chlorides, to give the title materials (2 and 3). The properties and nmr spectra of the ferroelectric liquid crystal monomers synthesised are reported in Table 1.

Polymerization reaction

The polymerization was carried out in the n-butyl lithium -tetrahydrofuran system [8] or in the azoisobutyronitrile (AIBN) benzene system [8] with ferroelectric liquid crystal monomers. The products were purified by flash column chromatography on silica gel. The samples were subjected to gel permeation chromatography (GPC) in tetrahydrofuran at 50℃. The results of the polymerizations are shown in Table 2.

All the synthesized compounds have the phase sequence of g ⟷ S_mC^* ⟷ S_mA ⟷ Iso ; the temperature range of the ordinary S_mC^* phase is rather narrow. However, the response time for the switching (m sec) shown in Table 2 is quick.



1a : $R^2 = C_6H_{13}$
1b : $R^2 = C_8H_{17}$

2a: $R^1 = H, R^2 = C_6H_{13}$
2b: $R^1 = H, R^2 = C_8H_{17}$
3a: $R^1 = CH_3, R^2 = C_6H_{13}$
3b: $R^1 = CH_3, R^2 = C_8H_{17}$

4a: $R^1 = H, R^2 = C_6H_{13}$
4b: $R^1 = H, R^2 = C_8H_{17}$
5a: $R^1 = CH_3, R^2 = C_6H_{13}$
5b: $R^1 = CH_3, R^2 = C_8H_{17}$

Scheme.

TABLE 1

Physical properties of ferroelectric liquid crystal monomers

Compound No	Yield (%)	Mp (℃)	$[\alpha]_D$/toluene	NMR $^{19}F^{a)}$	NMR ^1H
(2a) (nc)	76	61-62	+14.1 (c 1.14)	-1.5 (d, $J_{CF\underline{3}-H}$=6.0 Hz)	0.94-2.10 (13xH), 5.74 (C=CH), 6.18 (CH, m), 6.26, 6.35 (C=CH_2), 7.30 (Ar-H)
(2b) (nc)	59	74-75	+15.4 (c 1.07)	-1.0 (d, $J_{CF\underline{3}-H}$=6.0 Hz)	0.91-2.23 (17xH), 5.71 (C=CH), 6.23 (CH, m), 6.27, 6.38 (C=CH_2), 7.38 (Ar-H)
(3a) (nc)	68	71-73	+10.3 (c 1.01)	-1.7 (d, $J_{CF\underline{3}-H}$=6.5 Hz)	0.89-2.15 (16xH), 6.21 (CH, m), 6.24, 6.39 (C=CH_2), 7.05-7.35 (Ar-H)
(3b) (nc)	71	80-81	+9.60 (c 0.97)	-1.6 (d, $J_{CF\underline{3}-H}$=6.0 Hz)	0.88-2.16 (20xH), 6.20 (CH, m), 6.24 6.36 (C=CH_2), 7.07-7.41 (Ar-H)

[a] δ ppm from external CF_3CO_2H in $CDCl_3$.

TABLE 2

Physical properties of ferroelectric liquid crystal polymers

Compound No	Initiator	Polymer dispersity[a] M_w	M_n	$D=M_w/M_n$	Phase sequence[b]	Response time (m sec)
(4a) (nc)	n-BuLi	51500	39600	1.30	$g \underset{16^\circ C}{\overset{20^\circ C}{\longleftrightarrow}} S_mC^* \underset{47^\circ C}{\overset{58^\circ C}{\longleftrightarrow}} S_mA \underset{116^\circ C}{\overset{127^\circ C}{\longleftrightarrow}} Iso$	9.1
	AIBN	89900	53200	1.69	$g \underset{18^\circ C}{\overset{23^\circ C}{\longleftrightarrow}} S_mC^* \underset{57^\circ C}{\overset{67^\circ C}{\longleftrightarrow}} S_mA \underset{125^\circ C}{\overset{129^\circ C}{\longleftrightarrow}} Iso$	9.4
(4b) (nc)	n-BuLi	63400	49800	1.27	$g \underset{19^\circ C}{\overset{27^\circ C}{\longleftrightarrow}} S_mC^* \underset{52^\circ C}{\overset{64^\circ C}{\longleftrightarrow}} S_mA \underset{134^\circ C}{\overset{151^\circ C}{\longleftrightarrow}} Iso$	7.5
	AIBN	79600	46700	1.70	$g \underset{23^\circ C}{\overset{31^\circ C}{\longleftrightarrow}} S_mC^* \underset{58^\circ C}{\overset{71^\circ C}{\longleftrightarrow}} S_mA \underset{133^\circ C}{\overset{149^\circ C}{\longleftrightarrow}} Iso$	6.5
(5a) (nc)	n-BuLi	56700	46800	1.21	$g \underset{16^\circ C}{\overset{21^\circ C}{\longleftrightarrow}} S_mC^* \underset{54^\circ C}{\overset{67^\circ C}{\longleftrightarrow}} S_mA \underset{126^\circ C}{\overset{139^\circ C}{\longleftrightarrow}} Iso$	7.0
	AIBN	86100	52400	1.64	$g \underset{17^\circ C}{\overset{25^\circ C}{\longleftrightarrow}} S_mC^* \underset{49^\circ C}{\overset{58^\circ C}{\longleftrightarrow}} S_mA \underset{134^\circ C}{\overset{147^\circ C}{\longleftrightarrow}} Iso$	9.0
(5b) (nc)	n-BuLi	55700	41100	1.36	$g \underset{14^\circ C}{\overset{26^\circ C}{\longleftrightarrow}} S_mC^* \underset{35^\circ C}{\overset{49^\circ C}{\longleftrightarrow}} S_mA \underset{141^\circ C}{\overset{156^\circ C}{\longleftrightarrow}} Iso$	9.5
	AIBN	94100	67600	1.39	$g \underset{18^\circ C}{\overset{31^\circ C}{\longleftrightarrow}} S_mC^* \underset{52^\circ C}{\overset{67^\circ C}{\longleftrightarrow}} S_mA \underset{126^\circ C}{\overset{139^\circ C}{\longleftrightarrow}} Iso$	8.0

[a] The samples were subjected to gel permeation chromatography (GPC) in tetrahydrofuran at 50 ℃. The analysis was done with a Shimadzu LC-5A high performance liquid chromatograph using a Shodex GPC KF-803 column equipped a refractive index detector Shodex RI. The flow rate was 1.5 ml/min.

[b] g; glass state: S_mC^*; chiral smectic C liquid crystal: S_mA; smectic A liquid crystal: Iso; isotopic liquid.

EXPERIMENTAL

Ferroelectric liquid crystal monomer (2a; R^1=H, R^2=C_6H_{13}) (nc)

A suspension of ferroelectric liquid crystal unit (1a; R^2=C_6H_{13}) (5.5 g, 10 mmol), acryloyl chloride (4.55 g, 50 mmol) and pyridine (2 ml) in methylene chloride (50 ml) was stirred at room temperature. After 24h of stirring, the mixture was washed with saturated $NaHCO_3$ aq. and dried over magnesium sulfate. After evaporation of the solvent, the resulting crude products were chromatographed on silica gel (5:1, hexane/ethyl acetate) to give the monomer (2a; R^1=H, R^2=C_6H_{13}) (7.6 mmol, 76 %) as an oil, after evaporation of the solvent.

Analysis. Found : C, 67.35 ; H, 5.48 %
Calcd for $C_{31}H_{29}O_6F_3$: C, 67.14 ; H, 5.27 %

Ferroelectric liquid crystal monomer (2b; R^1=H, R^2=C_8H_{17}) (nc)

A suspension of ferroelectric liquid crystal unit (1b; R^2=C_8H_{17}) (6.0 g, 10 mmol), acryloyl chloride (4.55 g, 50 mmol) and pyridine (2 ml) in methylene chloride (50 ml) gave monomer (2b; 6.3 mmol, 63 %) as an oil, after evaporation of the solvent.

Analysis. Found : C, 67.88 ; H, 5.96 %
Calcd for $C_{33}H_{33}O_6F_3$: C, 68.03 ; H, 5.71 %

Ferroelectric liquid crystal monomer (3a; R^1=Me, R^2=C_6H_{13}) (nc)

A suspension of ferroelectric liquid crystal unit (1a; R^2=C_6H_{13}) (5.5 g, 10 mmol), methacryloyl chloride (4.70 g, 50 mmol) and pyridine (2 ml) in methylene chloride (50 ml) gave monomer (3a; 6.8 mmol, 68 %) as an oil, after evaporation of the solvent.

Analysis. Found : C, 67.29 ; H, 5.81 %
Calcd for $C_{32}H_{31}O_6F_3$: C, 67.60 ; H, 5.50 %

Ferroelectric liquid crystal monomer (3b;R^1=Me,R^2=C_8H_{17}) (nc)

A suspension of ferroelectric liquid crystal unit (1b; R^2=C_8H_{17}) (6.0 g, 10 mmol), methacryloyl chloride (4.55 g, 50 mmol) and pyridine (2 ml) in methylene chloride (50 ml) gave monomer (3b; 7.1 mmol, 71 %) as an oil, after evaporation of the solvent.

Analysis. Found : C, 68.74 ; H, 5.65 %
Calcd for $C_{34}H_{35}O_6F_3$: C, 68.45 ; H, 5.91 %

Conversion to ferroelectric liquid crystal polymers

a) By ionic polymerization

Into a solution of a ferroelectric liquid crystal monomer (2a;R^1=H, R^2=C_6H_{13}) (2.0 g, 3.6 mmol) in tetrahydrofuran (20 ml), n-butyl lithium (0.1 ml, 0.16 mmol) in hexane was added with a syringe under an atmosphere of nitrogen at -78℃. After 24h of stirring at that temperature, the mixture was quenched with saturated NH_4Cl solution, and then precipitates were collected. The crude product was purified by column chromatography on silica gel to give a ferroelectric liquid crystal polymer (4a) in a 57 % yield (2.05 g).

b) By free radical polymerization

A solution of a ferroelectric liquid crystal monomer (2a; R^1=H, R^2=C_6H_{13}) (2.0 g, 3.6 mmol) and azobisisobutyronitrile (0.2 g) in benzene (20 ml) was de-gassed under vacuum, and then heated at 100 ℃. After 24h of heating the glass-amplyfied vessel at that temperature, the solvent was removed. The crude product was purified by column chromatography on silica gel to give the ferroelectric liquid crystal polymer (4a) in a 69 % yield (2.48 g).

Other polymerization reactions were carried out on the same scale and in the same manners, to give the products described in Table 2.

REFERENCES

1 K. Yoshino, M. Ozaki, H. Taniguchi, M. Ito, K. Satoh, N. Yamasaki and T. Kitazume, Jpn. J. Appl. Phys., 26 (1987) L77.

2 R.B. Meyer, L Liebert, L. Strzelecki and P. Keller, J. Phys. (France), 36 (1975) L69.

3 N.A. Clark, M.A. Handschy and S.T. Lagerwall, Mol. Cryst. Liq. Cryst., 94 (1983) 213.

4 K. Ishikawa, Y. Ouchi, T. Uemura, T. Tsuchiya, H. Takezoe and A. Fukuda, Mol. Cryst. Liq. Cryst., 122 (1985) 175.

5 A.D.L. Chandani, Y. Ouchi, H. Takezoe and A. Fukuda, Jpn. J. Appl. Phys., 27 (1988) L276.

6 K. Yoshino, M. Ozaki, H. Taniguchi, M. Ito, K. Satoh, N. Yamasaki and T. Kitazume, Chemistry Express, 2 (1987) 53.

7 Y. Suzuki, T. Hagiwara, I. Kawamura, N. Okamura, T. Kitazume, M. Kakimoto, Y. Imai, Y. Ouchi, H. Takezoe and A. Fukuda, Liq. Cryst., 6 (1989) 167.

8 Y. Okamoto, K. Suzuki, K. Ohta, K. Hatada and K. Yuki, J. Am. Chem. Soc., 101 (1979) 4763.