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FERROELECTRIC LIQUID CRYSTAL POLYMERS

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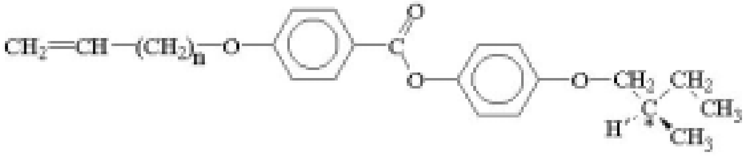
Abstract

The ferroelectricity of liquid crystal polymers can be utilized in electro-optic display devices. Liquid crystal polymers (LCP's) unite the properties of liquid crystals and of polymers, where the mesophase can be frozen in the polymer glass. The mesophase responsible for ferroelectricity is the chiral smectic C* phase (SmC*), which can be generated by mesogen side groups bearing chiral carbon atoms. This also means that ferroelectric liquid crystal polymers are side chain polymers with the mesogen groups in the side chain. According to the main chain, polysiloxanes, polyacrylates, polyethers and polyvinylethers are the most important groups of FLCP's.

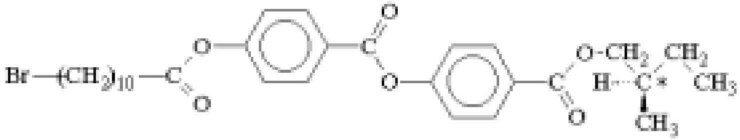
Our work can be divided into two main parts: One is the synthesis and characterization of the mesogen side groups, the other is the preparation of the corresponding polymer via polymerization or polymeranalog reaction. As the polymer main chain, polysiloxanes and polyacrylates were selected for the syntheses. For polysiloxanes the following mesogen groups were synthesized:



n = 8 (S)-4'-(2-methyl-butyloxy)-phenyl-4(9-decenyloxy)-benzoate
n = 9 (S)-4'-(2-methyl-butyloxy)-phenyl-4-(10-undecenyloxy)-benzoate

The polymer can be prepared by the addition of poly(methyl-hydrogen-siloxane) to the double bond of the mesogen monomer:

For polyacrylates the following mesogen side group was prepared:



S)-4'-(2-methyl-butyloxycarbonyl)-phenyl-4-[11-bromo-undecanoyloxy]-benzoate

The mesogen side group can be transferred to the polymer acrylate via a polymeranalog reaction. The synthesis of the mesogen side group for polysiloxanes is described in detail.

Keywords: FLCP, synthesis, mesogen monometers for polysiloxanes.

1. Introduction

The research of thermotropic liquid crystal polymers has grown into a field of science. Polymeric liquid crystals exhibit the anisotropy in liquid state and the advantageous properties of polymers permit new applications, which are not possible with low molecular liquid crystals.

1.1. Liquid Crystal Mesophases

The mesophases of thermotropic liquid crystals may be divided into three main groups; nematic, cholesteric and smectic phases [1]. The nematic phase, where the rod-like molecules are ordered in the direction of the molecular long axis (directory; d in *Figs. 1–3*), although the mass centers of the molecules are not ordered (*Fig. 1a*).

If a liquid crystal, capable of forming a nematic phase, contains a chiral carbon atom, a helical structure of the nematic phase will form. It is called cholesteric phase (*Fig. 1b*).

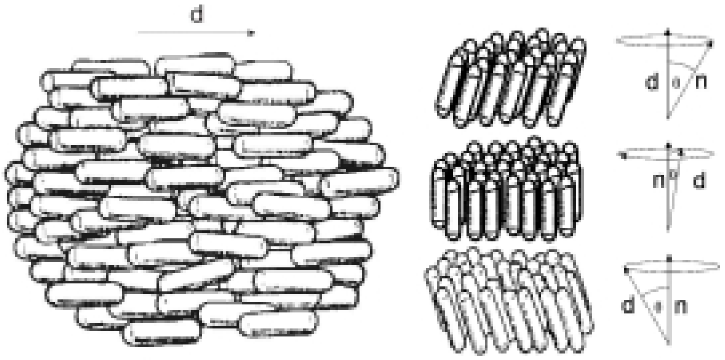


Fig. 1. Structure of the nematic phase (a) and the cholesteric phase (b)

In the smectic phases the molecules are ordered in layers. Different smectic phases are known. They are designated by capital letters A, B and C in chronological order of discovery. In the following, the most important smectic phases are shown, in logical order (*Figs. 2–3*). In the smectic A (SmA) phase the long axes of the rod-like molecules are oriented parallel to the layer normal '*n*'. The mass centers of the molecules within a layer, however, are disordered (*Fig. 2a*).

In the smectic C (SmC) phase the direction of the long axes of the molecules (d) is not parallel to the layer normal, the angle between d and n is called the tilt angle (θ). Similarly to the smectic A phase, the mass centers of the molecules are disordered (*Fig. 2b*).

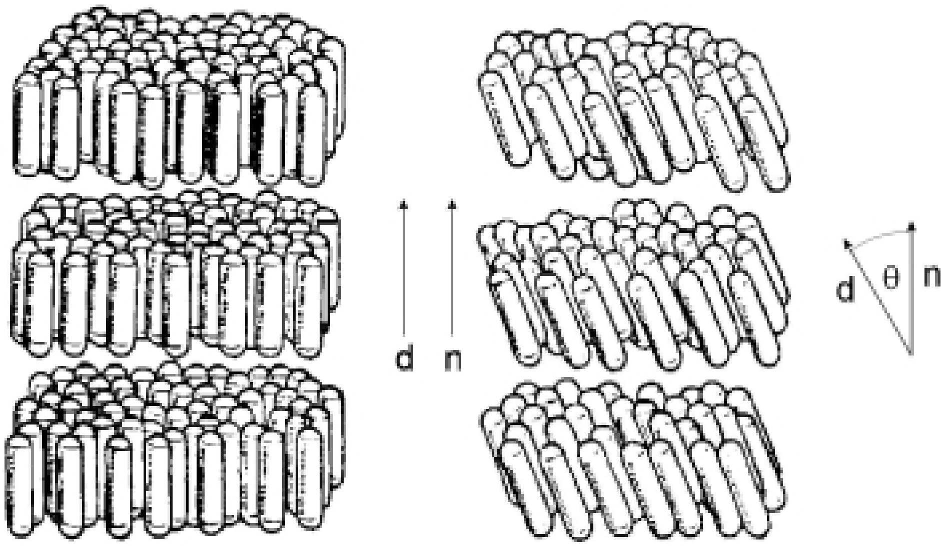


Fig. 2. Structure of the smectic A (SmA) phase (a) and the smectic C (SmC) phase (b)

The smectic B (SmB) phase is similar to the SmA phase. The difference is in the order of the mass centers of the molecules within the layers. The mass centers of the molecules are in hexagonal order in the SmB phase (*Fig. 3a*).

Any of the above mentioned smectic phases may be built up from molecules containing a chiral carbon atom. If molecules containing chiral carbon atoms build up a tilted smectic phase, the director of the molecular long axis (*d*) turns in each layer along a helix. In the case of a smectic C phase a chiral smectic C (SmC^*) will form (*Fig. 3b*).

1.2. Symmetry Classes and Electroactive Properties of Crystals

Electrical properties such as piezoelectricity, pyroelectricity, and ferroelectricity are closely associated with the chemical and crystalline structures of the materials [2]. Of the 32 different crystal point groups into which all crystalline materials have been classified, 11 possess a center of symmetry and are called centrosymmetric. The 21 which do not have a center of symmetry are noncentrosymmetric. Of the 21 noncentrosymmetric classes, 20 exhibit piezoelectricity, because the cubic class 432, although noncentrosymmetric, has other symmetry elements that combine to exclude the piezoelectric activity. A piezoelectric material exhibits polarization (electrical charge) on application of mechanical stress, such as pressure, or, in an external electric field a piezoelectric material exhibits expansion or contraction. Out of the above mentioned 20 piezoelectric classes only 10 permit the existence of pyroelectricity [2]. Since they possess a unique polar axis, these polar crystals

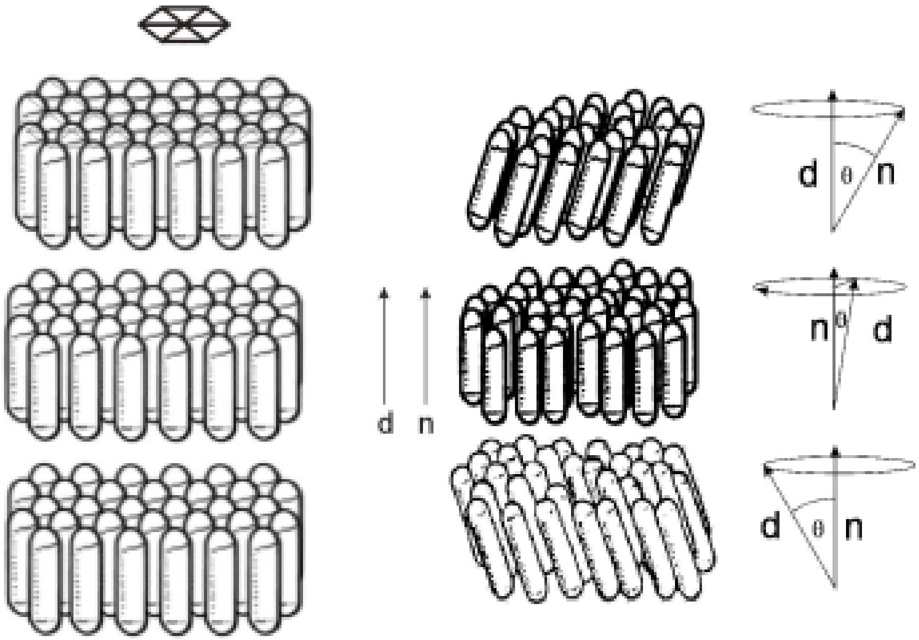


Fig. 3. Structure of the smectic B (Sm B) phase (a) and the chiral smectic C (SmC*) phase (b)

are spontaneously polarized along the polar axis. The magnitude of spontaneous polarization changes and also electrical changes occur as the temperature changes (pyroelectric effect) [3]. In pyroelectrics known as ferroelectrics, an externally applied electric field can reverse the direction of spontaneous polarization. Thus, all ferroelectrics are pyroelectric, but not all pyroelectrics are ferroelectric. *Fig. 4* represents the relation between symmetry classes and electroactive properties [4].

2. Ferroelectric Materials

2.1. Definition

A ferroelectric material is a pyroelectric material in which the application of an electric field reverses the direction of spontaneous polarization. Important features of a ferroelectric material include [4]:

- an electric hysteresis loop
- generally a very high dielectric constant
- the presence of spontaneous polarization without an external electric field

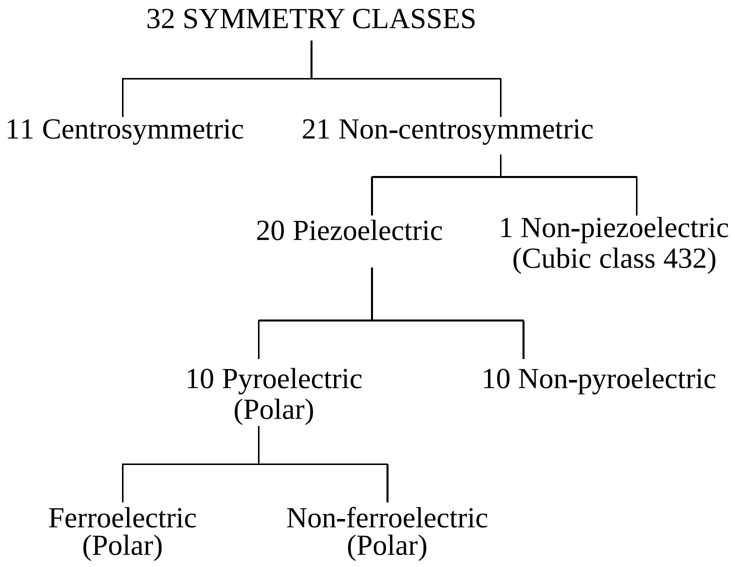


Fig. 4. Symmetry classes and electroactive properties of crystals

- temperature dependence of the dielectric parameters
- polar and domain structures.

Ferroelectricity can be observed only below the transition (Curie) temperature, above which the crystals show normal dielectric behaviour [2]. In some ferroelectrics the temperature dependence of the dielectric constant above the transition temperature can be described by the Curie–Weiss law:

$$\varepsilon = \varepsilon_0 + \frac{C}{T - T_0},$$

where ε is the dielectric constant at temperature T, ε_0 is the temperature independent part of the dielectric constant, T_0 is the Curie–Weiss temperature. In the vicinity of the Curie–Weiss temperature the dielectric constant becomes very large, and the relationship between dielectric constant (ε) and susceptibility (k) can be approximated by:

$$\frac{\varepsilon}{4\pi} \cong k.$$

A ferroelectric transition is generally the transition from a polar into a non-polar phase. The ferroelectric transition may be of second order or of first order. In case of a second order transition the Curie–Weiss temperature T_0 coincides with the Curie temperature T_C, however, in case of a first order transition it does not [2].

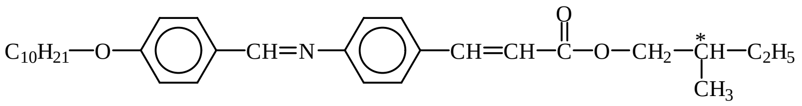
2.2. Development

The dielectric phenomenon known as ferroelectricity was discovered in 1921 on Rochelle salt, i.e. sodium potassium tartrate tetrahydrate ($NaKC_4H_4O_6 \times 4\ H_2O$) [2]. Ferroelectric properties of inorganic materials such as titanates ($BaTiO_3$, $PbTiO_3$, $SrTiO_3$ and $CdTiO_3$), zirconates ($PbZrO_3$), niobates, tantalates and vanadates had been utilized until the electroactive properties of polymeric materials were discovered [2].

Research efforts in the field of electroactive polymers began in earnest with the discovery of poly(vinylidene fluoride) (PVDF) in 1969 and electrically conducting polyacetylene in 1977 [4]. The ferroelectricity in PVDF was first reported in 1971 by Bergman et al. [5] and Wada et al. [6]. Although the highly conjugated organic polymer of acetylene was first reported by Zeigler in 1955 [7] and later by Natta in 1958 [8], polyacetylene as a free standing film was synthesized first by Shirakawa and coworkers in 1974 [9]. On the basis of their electronic properties organic polymers can be separated into three main classes, which determine their electroactive properties and practical application. These classes are [4]:

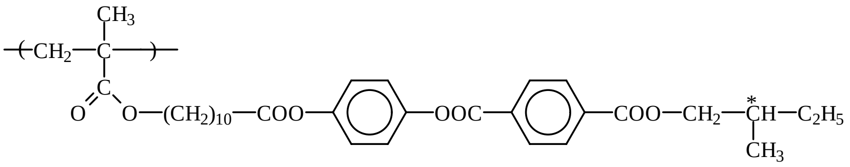
- dielectric-ferroelectrics
- nonlinear optical polymers
- conductive polymers.

Ferroelectricity of materials can be utilized in electro-optic display devices. For this purpose, however, extremely fast switching times are required. This could be attained by the application of thermotropic low molecular ferroelectric liquid crystals (FLCs) exhibiting the chiral smectic C (SmC^*) phase which is responsible for a non vanishing spontaneous polarization. Ferroelectricity in liquid crystals was investigated first by Meyer et al. in 1975 [10]. The first low molecular weight liquid crystal on which ferroelectricity has been discovered was p-decyloxybenzylidene-p'-amino-2-methylbutylcinnamate (DOBAMBC):



p-decyloxybenzylidene-p'-amino-2-methylbutylcinnamate (DOBAMBC)
C 76 °C (SmB 63 °C) SmC^* 92 °C SmA 117 °C I

The first side chain LCP exhibiting SmC^* mesophase was a polymethacrylate synthesized by Shibaev and coworkers [11–12]:



G 20-30 SmC* 73-75 SmA 83-85 I

Reversal of polarization in ferroelectric side chain liquid crystal polymers (SCFLCPs) was first detected by USHIDA and coworkers in 1988 [13]. Since polymers offer many advantages over low molecular materials, such as higher strength, toughness, flexibility, durability, environmental stability, and processability, the center of research turned toward a new class of polymers, i.e. ferroelectric liquid crystal polymers, in which the alignment can be frozen into the glassy state.

3. Low Molecular Ferroelectric Liquid Crystals (FLC's)

In the case of liquid crystals, ferroelectricity can be established in a material that satisfies the following three conditions [14]:

1. at least one asymmetric carbon must be included in the compound (chiral compound);
2. the component of the dipole moment perpendicular to the long axis of the molecules is inherent in its structure;
3. the material must show a smectic phase with a nonzero tilt angle (such as smectic C and smectic H phases, etc.). Therefore these materials are also called chiral smectic liquid crystals and are identified as SmC* or SmH*.

From practical points of view ferroelectric liquid crystals must possess various characteristics depending on their use:

1. large spontaneous polarization Ps
2. appropriate dielectric constant (ε and its anisotropy ($\delta\varepsilon$)) depending on the particular application
3. appropriate tilt angle θ (22.5° in SSFLC (surface stabilized ferroelectric liquid crystal) cell, or 45° in a guest-host (GH) cell
4. appropriate anisotropy of refractive indices (δn)
5. small viscosity (η) for the rotational motion of the molecules around the normal of the smectic layer with a constant tilt angle (reorientational viscosity)
6. wide temperature range of the ferroelectric phase
7. appropriate interaction strength between ferroelectric liquid crystal molecules and the substrate

8. appropriate high-temperature phase above the Curie temperature (phase transition temperature between the chiral smectic C* phase and the higher-temperature phase) (Tc), so that the alignment of ferroelectric liquid crystal molecules becomes easy

9. good stability against temperature, ionic current, and light irradiation.

Recently molecular design of ferroelectric liquid crystal materials has started. Although dielectric properties and spontaneous polarization as a function of molecular structure have been investigated so far for a great number of compounds, there exist many unresolved new phenomena in new types of ferroelectric liquid crystals.

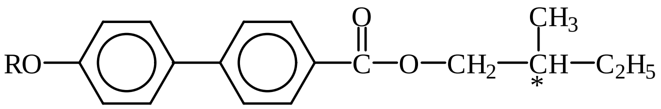
According to chemical constitution low molecular weight ferroelectric liquid crystals can be grouped in three main classes, i.e. the Schiff's base series of FLCs, the azo and azoxy series of FLCs, and the biphenyl and aromatic ester series of FLCs [14]. The first class of FLCs has been developed first, because ferroelectricity of a liquid crystal has been discovered on a Schiff's base LC (DOBAMBC). In spite of the many results concerning the relation between molecular structure and ferroelectric properties, Schiff's base LC's did not attain practical use because of their easy degradability by hydrolysis. Similarly, azo and azoxy compounds are not stable, they easily undergo degradation and coloration. Therefore the center of attention turned to the third class of LCs, i.e. biphenyl and aromatic ester series of FLCs. The most important representatives of the biphenyl and aromatic ester series of FLCs are the alkyl 4-n-alkoxybiphenyl-4'-carboxylate series of compounds and the 4'-(2-methylbutyl)phenyl 4-n-alkoxybenzoate series of compounds. They are prepared by introducing an optically active 2-methylbutanol into the well-known phenyl ester series of liquid crystals which exhibit smectic C phases. The chemical formula and the phase transitions of these FLCs are represented in *Tables 1–2*.

The series of chiral 2-methylbutyl 4-p-acyloxybiphenylcarboxylates were also synthesized and investigated. The phase transition temperatures are illustrated in *Table 3*. The ferroelectric phases of these compounds appear around room temperature.

4. Chiral Smectic C Liquid Crystal Side Chain Polymers

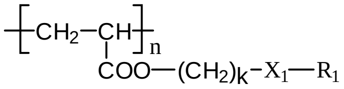
There are many aspects to be considered in designing the structure of an FLCP related to the backbone structure, copolymer composition and the structure of the mesogenic side group bearing the asymmetric carbon atom. According to the nature of the polymer backbone polyacrylates, α-substituted polyacrylates, polysiloxanes, polyethers and polyesters have been synthesized with the following structure [18]:

Table 1. Phase transition temperatures (°C) of the alkyl 4-n-alkoxybiphenyl-4'-carboxylate series of ferroelectric liquid crystals [15]



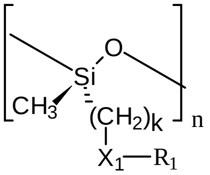
R	Crystalline	°C	SmC*	SmA	°C	Isotropic
CH_3	•	57.0	–	–		•
C_4H_9	•	55.5	–	•	73.8	•
C_5H_{11}	•	57.5	–	•	65.3	•
C_6H_{13}	•	48	–	•	66	•
C_7H_{15}	•	41.5	• 43	•	64.2	•
C_8H_{17}	•	48.5	(• 44)	•	65.5	•
C_9H_{19}	•	60.0	(• 38)	•	64.4	•
$C_{10}H_{21}$	•	48.5	(• 42)	•	64.9	•
$C_{12}H_{25}$	•	53.2	(• 39)	•	63.8	•
$C_{12}H_{25}$	•	61.1	–	•	61.7	•
$C_{18}H_{37}$	•	71.2	–	–		•

Polyacrylates

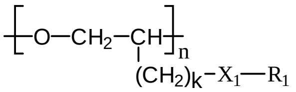


$$-\left[CH_2-\underset{\substack{|\\ COO-(CH_2)_k-X_1-R_1}}{CH}\right]_n-$$

Polysiloxanes

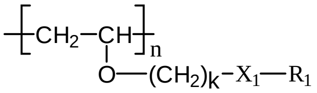


Polyethers



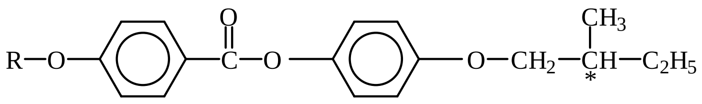
$$-\left[O-CH_2-\underset{\substack{|\\ (CH_2)_k-X_1-R_1}}{CH}\right]_n-$$

Polyvinylethers



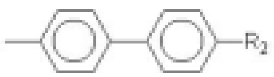
$$-\left[CH_2-\underset{\substack{|\\ O-(CH_2)_k-X_1-R_1}}{CH}\right]_n-$$

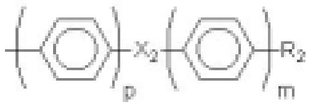
Table 2. Phase transition temperatures (°C) of the 4’-(2-methylbutyloxy)phenyl-4-n-alkoxybenzoate series of ferroelectric liquid crystals [16]



R	Crystalline	°C	SmC* °C	SmA °C	Cholesteric °C	Isotropic
C_4H_9	●	77	–	–	(● 40)	●
C_6H_{13}	●	63	–	(● 45.5)	(● 53.5)	●
C_7H_{15}	●	53	–	(● 48)	(● 52)	●
C_8H_{17}	●	40.5	● 42	● 53	(● 55)	●
C_9H_{19}	●	45	● 47	● 59	–	●
$C_{10}H_{21}$	●	45.5	● 50	● 63	–	●
$C_{11}H_{23}$	●	48	● 50	● 63	–	●
$C_{12}H_{25}$	●	47	(● 46)	● 65	–	●
$C_{13}H_{27}$	●	59	(● 50)	● 66	–	●
$C_{14}H_{29}$	●	60	–	● 65	–	●

where n is an integer
$k = 1 - 30$, possibly $k > 6$ for mesogenic behavior
$X_1 = -\mathrm{COO}-; -\mathrm{O}-$
R_1 is the mesogenic core





where $p, m = 1, 2$ (independently),
$X_2 = -\mathrm{COO}-, -\mathrm{OCO}-$
$R_2 = -\mathrm{COOR}_3, -\mathrm{OCOR}_3, -\mathrm{OR}_3, -\mathrm{R}_3$
R_3 terminal group bearing chirality

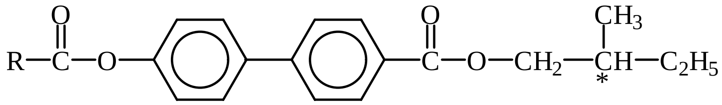
The possible synthetic routes to ferroelectric liquid crystal polymers are represented in *Fig. 5*.

5. Experimental

5.1. Objective

The final goal of our work is the synthesis and characterization of ferroelectric liquid crystal polysiloxanes and polyacrylates, in order to reveal the relation between polymer properties, such as molecular mass and copolymer composition, and mesophase behavior. For the synthesis of the appropriate polymers the structure of the mesogen side groups had to be selected. For this the relation between the chemical structure, mesophase transition, and ferroelectric behavior of low molecular ferroelectric liquid crystals was studied. The first stage of the experiments includes the synthesis and characterization of the mesogenic compounds. The second stage will include the synthesis of FLC polysiloxanes via hydrosilylation of the double bond as end group containing mesogen molecules. The third stage will comprise the preparation of FLC polyacrylates via polymerization of the mesogen molecules, as well as by polymeranalog reaction. This paper describes the structure and synthesis of the mesogen molecules selected for hydrosilylation and for synthesis of polyacrylates

Table 3. Phase transition temperatures (°C) of the (S)-2-methylbutyl-4'-n-alkanoyloxy-(1,1')-biphenyl-4-carboxylate series of ferroelectric liquid crystals [17]

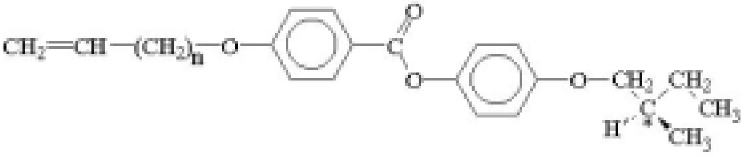


R	Crystalline	°C	SmC*	°C	SmA	°C	Isotropic
C_7H_{15}	•			35	•	58	•
	•	17	•	33	•	58	•
C_8H_{17}	•			23	•	49	•
	•	10	•	17	•	49	•
C_9H_{19}	•	38.4	•	46.2	•	61.5	•
	•	21	•	46.6	•	61.1	•
$C_{10}H_{21}$	•	44.5	•	47	•	62	•
	•	29	•	47	•	62	•
$C_{11}H_{23}$	•	40	•	50	•	63	•
	•	34	•	50	•	63	•
$C_{12}H_{25}$	•	46	•	48	•	62	•
	•	35	•	48.5	•	62	•
$C_{13}H_{27}$	•			50	•	64	•
	•	46	•	51	•	64	•

via polymeranalog reaction.

5.2. *Synthesis of Mesogen Groups for Polysiloxanes*

For hydrosilylation the following mesogen molecules have been selected:



n = 8 (S)-4'-(2-methyl-butyloxy)-phenyl-4(9-decenyloxy)-benzoate
n = 9 (S)-4'-(2-methyl-butyloxy)-phenyl-4-(10-undecenyloxy)-benzoate

The syntheses of the racemic compounds are described in detail in [19]. The reaction steps of the mesogen synthesis are as follows:

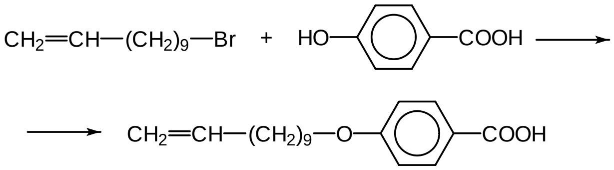
Preparation of 11-bromo-1-undecene

$$CH_2 = CH - (CH_2)_9 - OH + PBr_3 \longrightarrow CH_2 = CH - (CH_2)_9 - Br$$

10-undecenyl alcohol

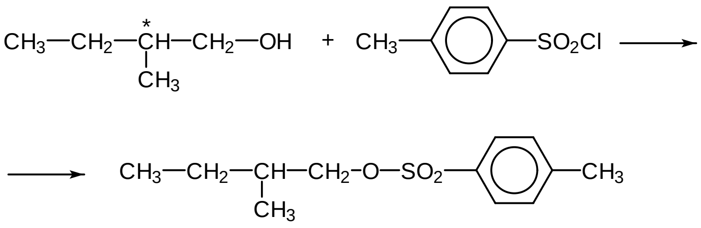
The resulted 11-bromo-1-undecene boils at 102 °C (0.2 Hgmm). The yield was 59%.

Preparation of (10-undecenyloxy)-benzoic acid:



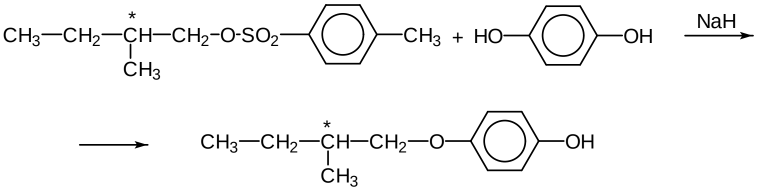
The resulted (10-undecenyloxy)-benzoic acid is a liquid crystal. The phase transitions are as follows: Heating: C-SmC 82–83 °C; SmC-N 121–122 °C; N-I 132–133 °C. Cooling: I-N 132 °C; N-SmC 120 °C; SmC-C 58 °C. The yield of this reaction was 57%, the overall yeald from the beginning was 34%.

Preparation of (S)-(-)-2-methyl-1-butyl-tozylate



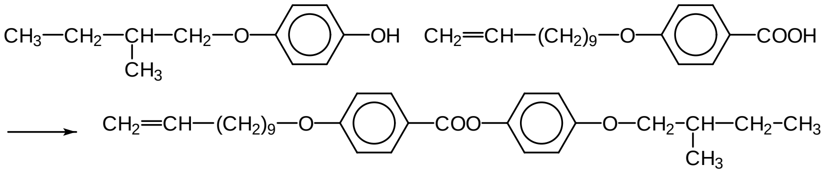
The yield of this reaction step was 76%.

Preparation of (4)-(S)-(-)-2-methyl-butyloxy-phenol



The resulted mixture was purified by flash chromatography. Melting point 172 °C, yield of this reaction step was 15%. Overall yield was 11%.

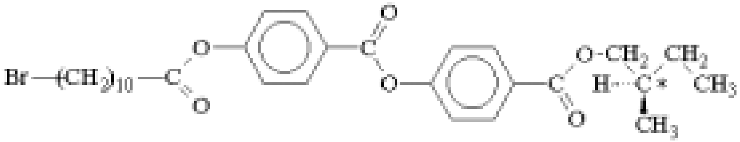
Preparation of (S)-(-)-4’-(2-methyl-butyloxy)-phenyl-4-(10-undecenyloxy)-benzoate



For the esterification dicyclohexyl-carbo-diimide (DCC) and catalytic p-dimethyl-amino-pyridine were used. The resulted material was purified via preparative (column) chromatography. For characterization further purification is necessary. The yield of this reaction was 13.0%, the overall yield 1.5%.

5.3. Synthesis of Mesogen Group for Polyacrylates

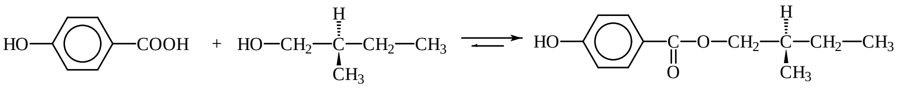
For polymeranalog reaction the following mesogen compound was selected:



(S)-4'-(2-methyl-butyloxycarbonyl)-phenyl-4-[11-bromo-undecanoyloxy]-benzoate

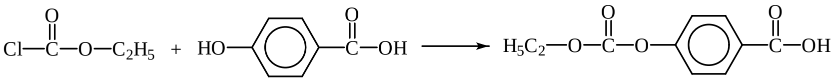
The reaction steps of the mesogen synthesis are as follows:

Preparation of (S)-4-hydroxy-2-methylbutylbenzoate



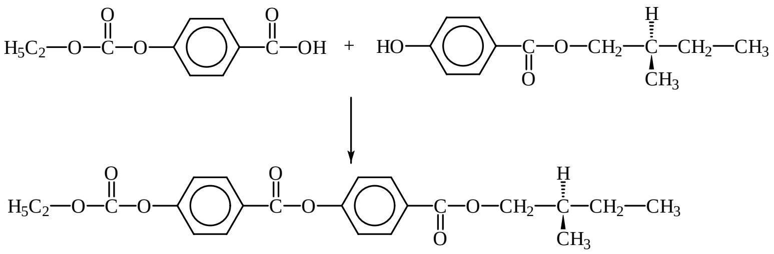
The resulted (S)-4-hydroxy-2-methylbutylbenzoate boils at 136° C (2 Hgmm).

Preparation of 4-(ethoxycarbonyloxy)-benzoic acid



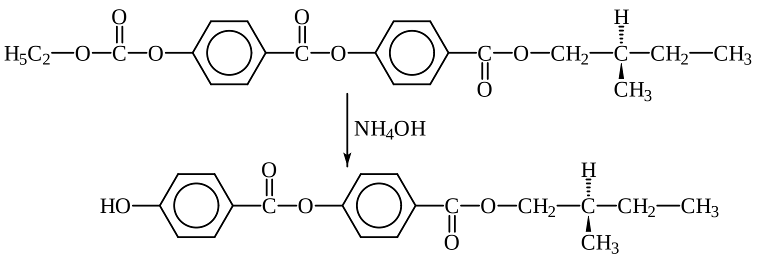
The resulted 4-(ethoxycarbonyloxy)-benzoic acid melts at 157°C.

Preparation of (S)-4[4’-ethoxycarbonyloxy-benzoyloxy]-2-methylbutyl-benzoate



For the esterification dicyclohexyl-carbo-diimide (DCC) and catalytic p-dimethyl-amino-pyridine were used. The resulted material was purified via preparative (column) chromatography. Melting point 62 °C.

Preparation of (S)-4-hydroxy-[4’-(2-methylbutyloxy)phenyl]-benzoate



The resulted intermediate products melts at 87 °C.

Preparation of (S)-4’-(2-methyl-butyloxycarbonyl)-phenyl-4-[11-bromo-undecanoyloxy]- benzoate

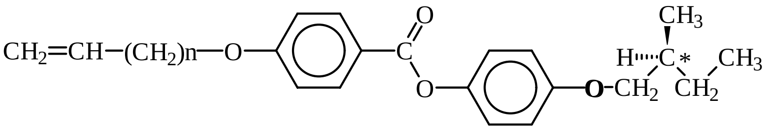
(S)-4-hydroxy-[4’-(2-methylbutyloxy)phenyl]-benzoate is esterified with ω-bromo-undecanoic acid in the presence of dicyclohexyl-carbo-diimide (DCC) and catalytic p-dimethyl-amino-pyridine.

For the characterization of the final product further purification is necessary.

6. Summary

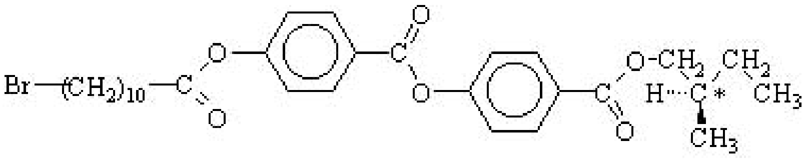
Ferroelectricity of liquid crystal polymers can be utilized in electro-optic display devices. Liquid crystal polymers (LCP's) unite the properties of liquid crystals and of polymers, where the mesophase can be frozen in the polymer glass. The mesophase responsible for ferroelectricity is the chiral smectic C (SmC*) phase, which can be generated by the mesogen side groups bearing chiral carbon atoms. This means that ferroelectric liquid crystal polymers are side chain polymers with the mesogen groups in the side chain. According to the main chain, polysiloxanes, polyacrylates, polyethers, and polyvinylethers are the most important groups of FLCP's.

Our work can be divided into two main parts. One is the synthesis and characterization of the mesogen side groups, the other is the preparation of the corresponding polymer via polymerization or polymeranalog reaction. As the polymer backbone, polysiloxanes and polyacrylates were selected for the syntheses. The structure of mesogen for hydrosilylation is as follows:



(I)

For polyacrylates the following mesogen side group was prepared:



(II)

The synthesis of (S)-4'-(2-methyl-butyloxy)-phenyl-4-(10-undecenyloxy)-benzoate (I) and of (S)-4'-(2-methyl-butyloxycarbonyl)-phenyl-4-[11-bromo- undecanoyloxy]-benzoate (II) is described.

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