Liquid Crystals

Chiral Liquid Crystalline Side Chain Polymers

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SUMMARY

      Optically active liquid crystalline side chain polymers with dif
ferent flexible spacer groups (n = 2–11) and different main chains (acry
lates, methacrylates and α chloroacrylates) are described. (+)-2-methyl
butyloxyphenyl esters of benzoic acid were chosen as the mesogenic group.

INTRODUCTION

      For many years, the study of thermotropic liquid crystalline (LC)
polymers with mesogenic side groups have been investigated intensively
for their theoritical and technological aspects (1,2,3). If mesogenic
groups are not directly fixed to the main chain, but decoupled by a fle
xible spacer, the motions of the main chain of the polymer do not affect
the anisotropic orientation of the mesogenic groups and the polymer is
expected to exhibit the liquid crystalline state. Until now, the synthe
sis and the identification of nematic, cholesteric and some smectic phases
such as S_A, S_B, S_C have already been reported (4,5,6). Parallel to the
research on LC polymers, low molecular weight liquid crystals with chiral
mesogenic groups exhibiting N^*, S_C^* and other tilted ordered phases have
been developed (7,8) and a recent work (9), on the synthesis of a chiral
smectic polymer, having ferroelectric properties has been published. Thus,
the synthesis of new polymers carrying chiral mesogenic group as a side
group or within the main chain of the polymer (chiral flexible spacer)
should be possible.

      The publication deals with preliminary results on chiral polyacry
lates (X = H), polymethacrylates (X = CH_3) and poly α chloroacrylates
(X = Cl) with different values for the spacer (n). The selection of such
materials will permit determination of the effect of each macromolecular
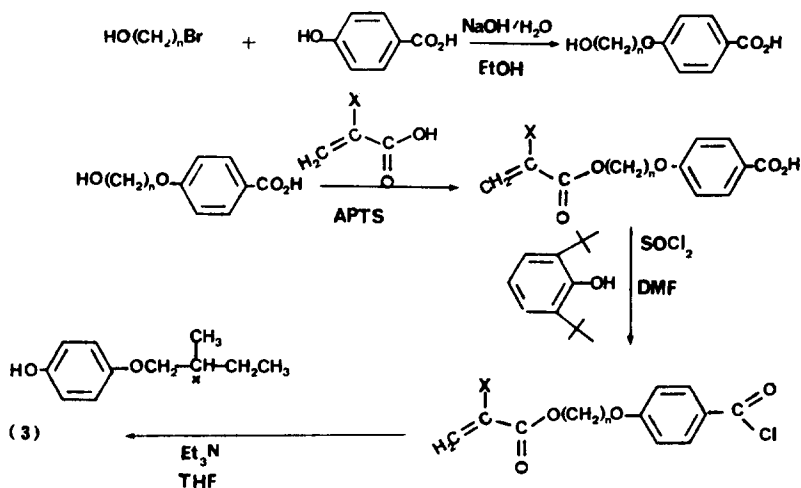unit n and X on the physico–chemical properties of the comblike polymers.

MAIN CHAIN

SPACER GROUP

CHIRAL MESOGENIC GROUP
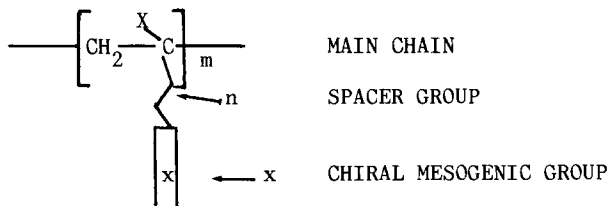
RESULTS AND DISCUSSION

Monomers have the following general structure : (3)


(3)

with X = H, CH_3, Cl

and n = 2, 6, 11
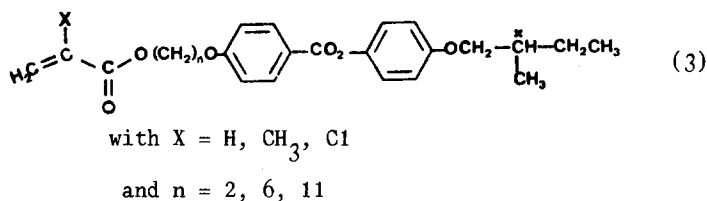
They were synthesized by standard methods (see experimental part) via the following scheme

In Tab. 1, the properties of monomers (3) are summarized. The phase transitions of monomers (3) and resulting polymers were determined by differential scanning calorimetry (DCS) (Perkin Elmer DSC4) and polarization microscopy (Leitz Orthoplan). The structures of the smectic phases were identified by their isomorphy with a know reference compound.

Only crystalline monomers are observed in the case of chloroacry loyloxy monomers and equally, when the spacer is equal to two. In the case of methacryloyloxy monomers with n = 6 and 11 monotropic smectic A phase can be observed. The last family (acryloyloxy monomers) illustrates the importance of the spacer and the influence of the group carried by the main chain on mesogenic properties. Monomer 3d exhibits a monotropic Smectic A phase, while monomer 3g shows an enantiotropic Smectic A phase and a mono tropic chiral Smectic F phase. Therefore, as the value of the spacer (n) is increased, the Smectic A phase can be stabilized and it is possible to place the various substituents in an order of increasing efficiency in giving rise to smectic behaviour :

$$H \quad > \quad CH_3 \quad > \quad Cl$$
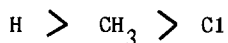
Tab.1 Phase transitions for monomers 3a) and phase transition enthalpies
ΔH

Compound	n	X	Phase Transitions in °C	ΔH cal/g
3a	2	H	k 66,3 i	18,8
3b	2	CH₃	k₁ 39 k₂ 62,5 i	18,5
3c	2	Cl	k 86,5 i	21
3d	6	H	k 21 [smA] 31 i	2{i→smA}
3e	6	CH₃	k 21 [smA] 24,5 i	1,6 {i→smA}
3f	6	Cl	k 43,4 i	20
3g	11	H	k -4 [smF* 24 smA 43 i	3{smA→i}
3h	11	CH₃	k 29 smA 36 i	2,7 {i→smA}
3i	11	Cl	k₁ 39 k₂ 45 k₃ 49 i	19

a) k = crystalline, i = isotropic, s = smectic, * = chiral
[ ] = monotropic phase.

The glass transition temperatures and phase transitions of the resulting polymers 4 (Tab.2) were at first determined by differential scanning calorimetry. But, the observation of the glass transition tempe rature was not possible for all the polymers, because some of them became partially crystalline, and because of that, the change of the specific heat at the glass transition decreased. This occurs for polyacrylates with high values for n (n = 11). Polymer 4g exhibits a perfect crystallisation. Fig. 1, shows as an example, thermogramms of two polymers. Polymer 4g (11, H) has a semi crystalline character, whereas Polymer 4d (6,H) has an amorphous behaviour.

So, in order to determine, the effect of n and X parameters on the glass transition temperature, these comb like polymers were studied by fre quence and temperature depent dielectric measurements (LCR Meter HP 4262 A : tempperature range : 70°C + 200 °C, frequency range : 100 Hz, 10 kHz). In the dielectric relaxation investigations, up to three different kinds of motion were found before the conductivity mechanism (fig.2).The relaxation is found in all polymers (T$_\beta$ (1 kHz) = 45°C and T$_\beta$ (10kHz) = 30°C) independently of the spacer length (n) and the polymer chain (X). It may be attributed to internal relaxations of the

mesogenic groups : the ester bridge (- C ⟍O⟋O).

Fig:1. DSC Curves of Polymer 4d and Polymer 4g

FSCL 132 COOL

WT: 19.30 mg

SCAN RATE: -20.00 deg/min

Polymer 4d

T/G FROM: -30.09
TO: 35.98
ONSET:
CAL/GDEG: -15.101
MIDPOINT: 19.53

PEAK FROM: 53.86
TO: 89.19
ONSET:
CAL/GRAM: -2.1

MIN: 77.38

MCAL/SEC

T(°C)

FSCL 87

WT: 9.60 mg

SCAN RATE: 20.00 deg/min

MAX: 55.01

PEAK FROM: 28.42
TO: 76.35
ONSET: 50.25
CAL/GRAM: 3.52

Polymer 4g

PEAK FROM: 76.34
TO: 122.25
ONSET: 93.43
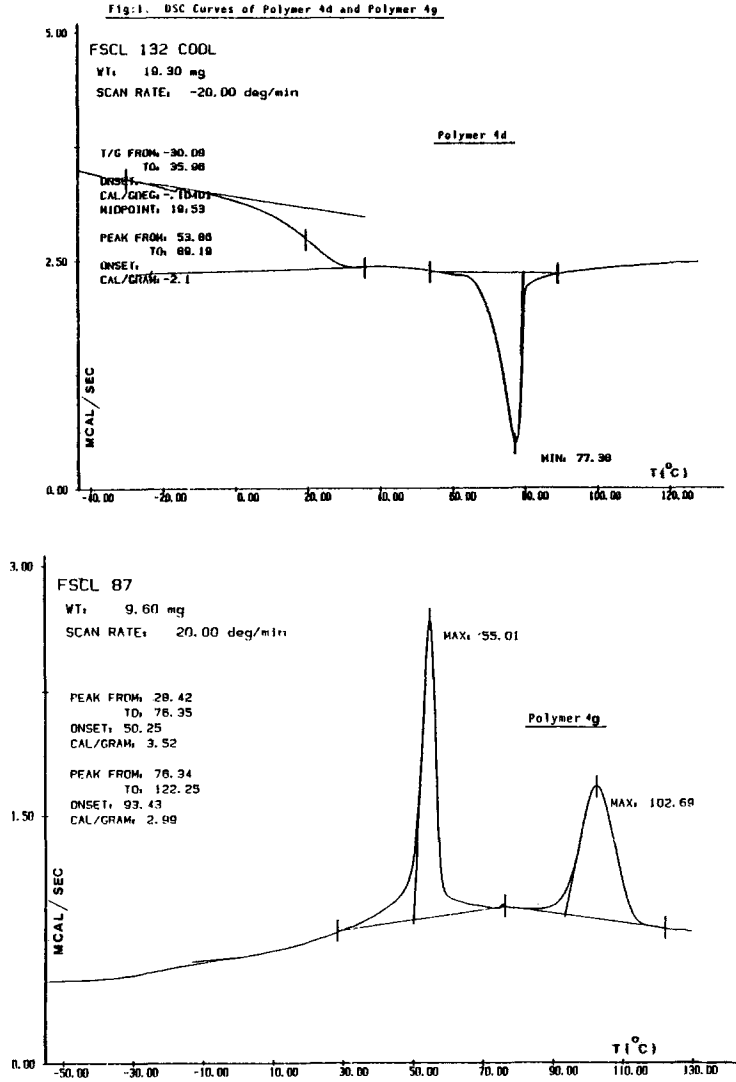CAL/GRAM: 2.99

MAX: 102.69

MCAL/SEC

T(°C)

Fig. 1: DSC curves of polymer 4d and polymer 4g

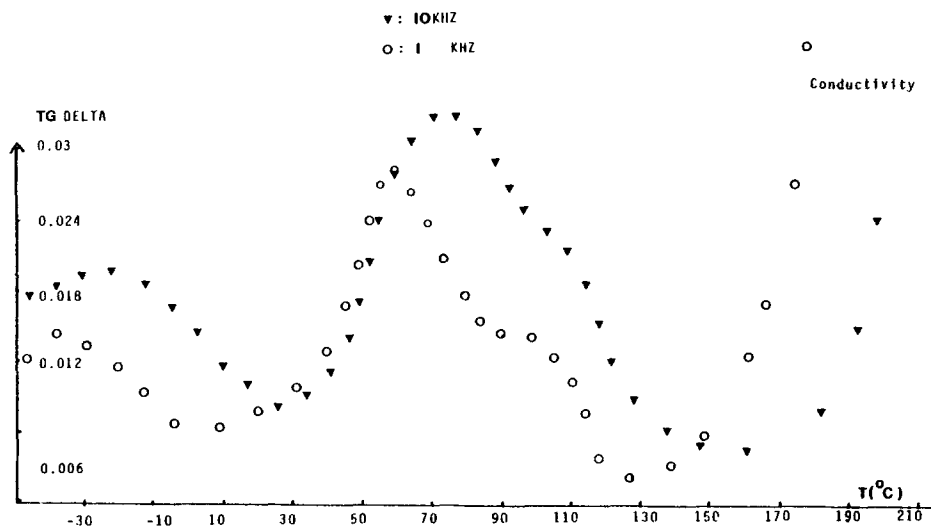Fig. 2 : <u>Dielectric Relaxation Spectrum for Polymer 4h</u>

Fig. 2: Dielectric Relaxation Spectrum for Polymer 4h

At the glass transition (αrelaxation), the polymer chain become mobile and dipole reorientations are possible. THis motion contribute to the αdielectric relaxation .

Sometimes (for instance polymer 4h), it is possible to observe a third peak near the conductivity domain in the dielectric spectum corres ponding to the clarification peak of the polymer (found with DSC). In Tab.2, the temperature of the α relaxation corresponding to the glass temperature transition (T_G) are summarized for the polymers 4 and we have plotted the dependence of log ν on 1/T in fig.3

What can be seen first, is the same relationship between the tempera ture glass transition and the spacer n in the case of both acrylic, methacry lic and chloroacrylic series ; this relationship points out the plastici zing effect, increasing with length of n, of the aliphatic chain between the main chain and the mesogenic core. Comparison of polyacrylates, poly methacrylatees and poly chloroacrylates with equal lengths of the methy lene link, shows that the glassy to mesophase transition is strongly shifted towards lower temperature with increasing flexibility of the poly mer backbone.

$$T_G \text{ (H)} \; \langle \; T_G \text{ (Cl)} \; \sim \; T_G \text{ (CH}_3)$$

The results of opticomicroscopic studies, X ray and EPR analysis and determination of structures will be published in further papers with "L. Monnerie, C. Noel, C. Friedrich and S. Lukovic Laboratoire de Physico Chimie Structurale et Macromoléculaire, ESPCI, 10, rue Vauquelin, 75231 PARIS CEDEX 05, France".
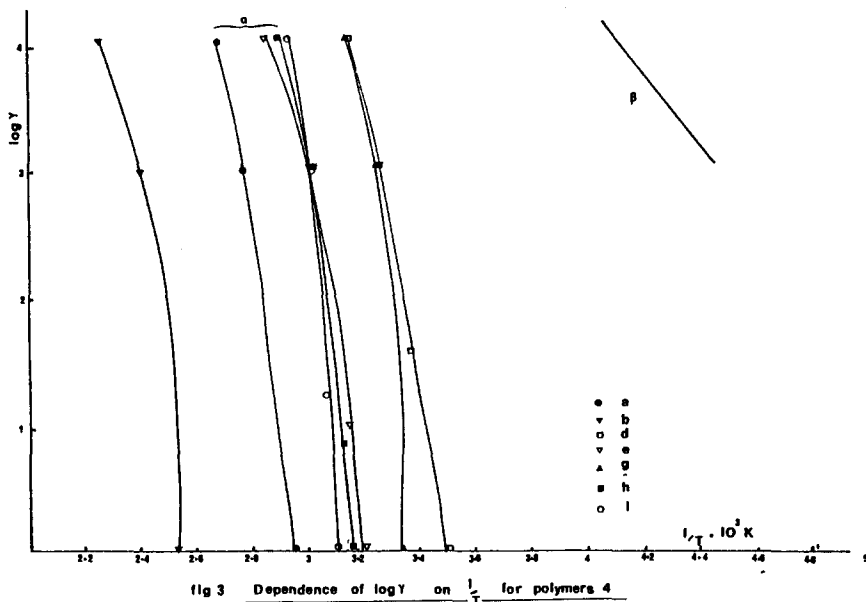
Fig. 3: Dependence of log ɣ on 1/T for polymers 4

EXPERIMENTAL PART

Preparation fo the monomers

4 (hydroxyalkyloxy) benzoic acids (1) : 0,36 mol of 4 hydroxy
benzoic acid is dissolved in a mixture of 130 ml of ethanol, 31 g of
NaOH in 56 ml of water. After heating the solution and adding a small
of KI, the bromoalkanol (0,28 mol) is added drop by drop and the mixture
refluxed for 20 h. Then, the solution is cooled, diluted with 20 ml of
water and acidified with HCl. The precipitate is filtered and recrystal
lized from ethanol.

4 (methacryloyloxy or chloroacryloyloxy or acryloyloxy) alkyloxy
benzoic acids (2) : 4 (hydroxyalkyloyloxy) benzoic acids (0,025 mol) are
esterified azeotropically in a Dean Stark apparatus with a 4 fold excess
of (methacrylic or chloroacrylic or acrylic) acid in 200 ml of benzene,
3g of ptoluenesulfonic acid and 1g of hydroquinone during 15 hours. The
solution is diluted with ether , washed several times with hot water. The
organic layer is dried with magnesium sulfate. After evaporating the
solvent, the solid is recrystallized from a mixture (2/1) hexane : ethanol.

4' (+)2 methylbutyloxyphenyl ester of 4n (methacryloyloxy or a
chloroacryloyloxy or acryloyloxy) alkyloy benzoic acids (3).

Tab. 2: Temperature of the glass transition of polymers 4 at various frequencies

Polymer	n	x	Temperature of α relaxation at different frequencies °C			DSC 1Hz
			120 Hz	10^3 Hz	10^4 Hz	
4a	2	H	x	90	100	85
4b	2	CH₃	x	145	170	120
4c	2	Cl	x	x	x	90
4d	6	H	x	35	45	10
4e	6	CH₃	x	70	80	40
4f	6	Cl	x	x	x	30
4g	11	H	x	35	45	25
4h	11	CH₃	x	58	75	45
4i	11	Cl	55	60	65	50

X not yet determined

The p(+)2 methylbutyloxyphenol is synthesized by a standard method from hydroquinone and (+)2 methylbutyl bromide (10). 0,017 mol of 4(metha cryloyloxy, a chloroacryloyloxy or acryloyloxy) alkyloxybenzoic acids are stirred during 20 min with 13 ml of thionyl chloride, few drops of N,N dimethyl formamide and a small amount of 2,6 diterbutyl p phenol. The excess of thionyl chloride is removed in vacuo ; the acid chloride is dis solved in THF and added dropwise to a solution of 0,011 mol of (+) 2 methyl butyloxyphenol and 4 ml of triethylamine in THF at·10°C. The mixture is stirred during 20 h at room temperature, then diluted with methylene chlo ride and the organic layer is washed several times with water, dried with magnesium sulfate.

The methylene chloride is evaporated and the residue is purified by columm chromatography over silicagel with dichloromethane as eluant.

SYNTHESIS OF POLYMERS (4)

Radical polymerization with 1 mole % 2,2' azoisobutyronitrile in toluene was carried out in a sealed glasstube under nitrogen for two days at 70°C. The polymers are precipitated by methanol.

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