

Special Polymers

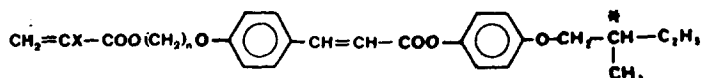
Chiral α substituted acrylates side-chain polymers with a cinnamate core

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SUMMARY

In this paper we report thermal studies and microscopic observations on optically active liquid crystalline monomers having the following general formula :



with X = H (acrylates), CH₃ (methacrylates) and Cl (chloroacrylates) and n = 2, 6, 11 (flexible spacer groups)

and a few corresponding side-chain polymers.

INTRODUCTION

Many studies in the field of thermotropic liquid crystalline polymers with mesogenic side groups have been reported (1,2,3).

Mainly, investigations about nematic, cholesteric, smectic A, C or other smectic polymers have been carried out (4,5,6,7).

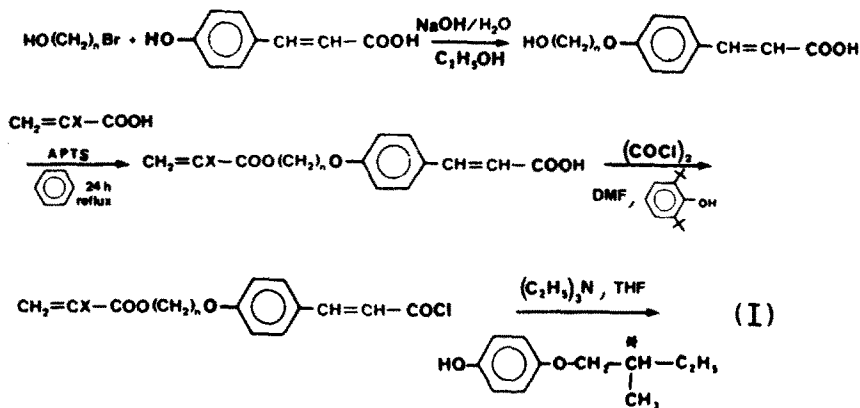
We focused our attention on chiral smectic polymers because of their capacity to give ferroelectric properties (8,9). Such polymers are expected to exhibit a non-zero polarization coefficient and by their non-centrosymmetrical structures, an interesting behaviour in non-linear optics (SHG : Second Harmonic Generation).

In parallel, research on low molecular weight liquid crystals with chiral mesogenic groups has shown potential applications (10,11). The initial-model, for our synthesis, is a new ferroelectric liquid crystal system already studied : the 4-(2-methylbutyloxy phenyl) 4'-n alkoxy cinnamate esters (12).

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RESULTS AND DISCUSSION

Monomers having the general structure (I) were synthesized.
Synthetic route :



Thermal properties of monomers (I)

In Tab. 1 the thermal properties of monomers (I) are summarized. The phase transitions of monomers and resulting polymers were studied by Differential Scanning Calorimetry (Perkin Elmer DSC4) and by polarization microscopy (Leitz Orthoplan) equipped with a Metler hot stage.

X-ray investigations and determination of structures will be published in further papers with "S. Esselin, C. Noel, Laboratoire de Physico-Chimie Structurale et Macromoléculaire, ESPCI, 10, rue Vauquelin, 75231 Paris Cedex 05, France".

When the spacer is equal to two, only crystalline monomers with no mesomorphic properties are observed. Each monomer with $n = 6$ and 11 exhibits enantiotropic smectic A phase comparing benzoate monomers already studied (13).

The double bond in the mesogenic core acts as a half a benzene ring stabilizing the smectic phase and increasing the melting points (12). Monomer (Ic) also exhibits a cholesteric phase. The influence of substituent X on the cinnamate esters is not appreciable when compared to the benzoate moieties. In the case of the benzoate monomers, the smectic behaviour was destabilized when $X = \text{Cl}, \text{CH}_3$.

The mesomorphism of the cinnamate monomers seems to be increased with the value of the spacer (n).

Tab. 1 Phase transitions for monomers (I) and phase transition enthalpies ΔH

Compound	n	X	Phase transition in °C
Ia	2	H	K 72 I_s (12)
Ib	2	CH ₃	K ₁ 107 K ₂ 112.5 I_s (16)
Ic	6	H	[S*] 49.4 S _A 75.1 N* ^α 76.5 ^β I_s mp : 48 (1.2) (2) (8.4)
Id	6	CH ₃	K 24 [S*] 36 S _A 69 I_s mp : 47 (5) (1) (1.8) (8.2)
Ie	11	H	[S* ₁] - 3 [S* ₂] 52.6 S _A 74.8 I_s mp : 63 (1) (1.3) (2.3) (17)
If	11	CH ₃	[S* ₁] - 7 [S* ₂] 49 S _A 73 I_s mp : 59.5 (1.2) (1) (2.3) (17.5)
Ig	11	Cl	[S* ₁] - 10 [S* ₂] 46.6 S _A 70 I_s mp : 56 (0.5) (1) (1.8) (14.5)

α : S_A - N* - I too close in temperature to be separated
 β : recorded optically
 [] : monotropic transitions
 () : ΔH in cal/gram.
 K : Crystalline, I_s : isotropic, S : smectic, * : chiral

Optical observations for monomers (I)

The case of monomer Ic summarizes all the textures we have observed for our materials.

On cooling the isotropic liquid, oily streaks appear at 76.5°C, this is characteristic of the plane cholesteric texture (plate 1) (14), this phase exists in a temperature range of about 1°C. At 75.1°C the texture changes in the form of bâtonnets which themselves consist of growing focal-conic fan domains (plate 2). This fan shaped texture can be unambiguously assigned to a smectic A phase. If the material is still cooled the focal conics become striated or banded at 49.4°C (plate 3), and leads to broken or grained fans. Such a texture is typical of a smectic tilted phase. Each smectic tilted phase following a smectic A phase has shown the same structure. The other smectic phases (S₁*) have not been optically observed.

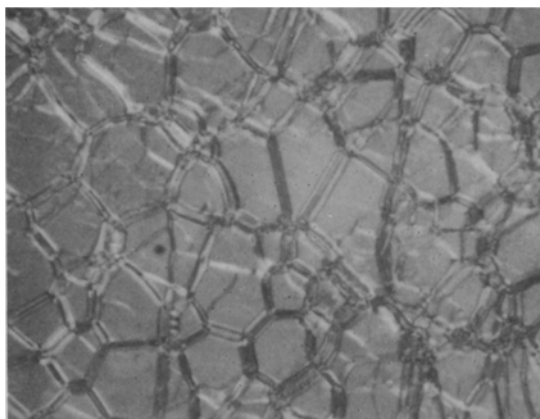


Plate 1 : Cholesteric texture of monomer Id at 76.4°C (crossed polarizers, 200 X)

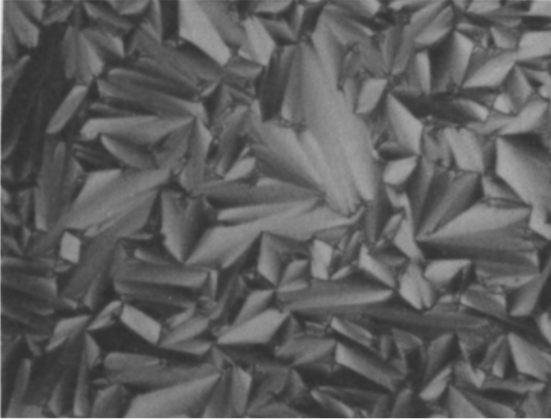


Plate 2 : Smectic A texture
of monomer Id at
74.8°C (crossed
polarizers, 200X)

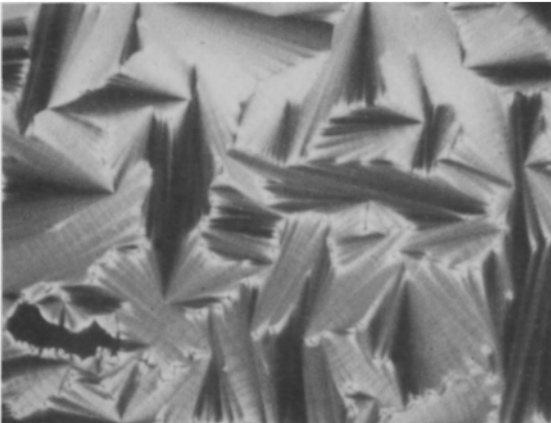


Plate 3 : Tilted smectic tex-
ture of monomer Id
at 50.2°C (crossed
polarizers, 200 X)

PROPERTIES OF THE POLYMERS (II)

The polymers (II) were prepared by radical polymerization in solution. Only the polymethacrylates and one polychloroacrylate (with $n = 11$) have been synthesized. Unfortunately, the acrylate monomers do not polymerize in such conditions of reaction (see experimental part).

Thermal properties

In Tab. 2, the transition temperatures of the polymers are listed. All the polymers investigated exhibit mesophases. The polymethacrylate with $n = 2$ leads to a mesophase between the glass transition T_g and the clarification transition T_c . When $n = 6$ the mesophase appears between the melting point T_m and T_c . When $n = 11$ a small endotherm is detected between T_m and T_c that shows the presence of two mesophases M1 and M2.

In the case of the polychloroacrylate with $n = 11$, only one mesophase appears between T_m and T_c .

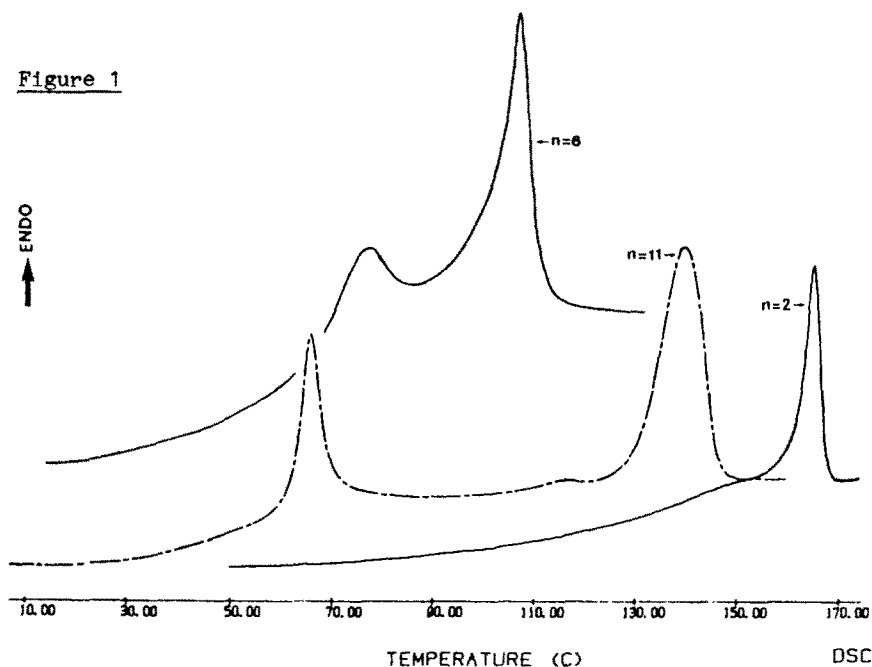
Tab. 2 Thermal properties of polymers

Polymer	Transition Temperature in °C					ΔH_c in cal/gram.	
	n	X	T _g	T _m	T _{M₁M₂}		T _C
IIb	2	CH ₃	120			162	1.6
IIId	6	CH ₃	40	83		110	1.9
IIIf	11	CH ₃	25	63	115 ^α	131	2.5
IIg	11	Cl	-10	69		131	2.0

α : lightly detectable in DSC. (Small endotherm)

We can make some remarks about the variation of the glass transition temperature as the length of the flexible spacer (n) varies. The polymethacrylate glass transition temperature decreases when the value of spacer increases, specially when n goes from 2 to 6. It is obvious that the bulky mesogenic group hinders the main chain motions. When the mesogenic group is closer to the main chain, this induces a stiffening of the polymer backbone. This is also due to the plasticizing effect of the aliphatic side chain. It is important to remark that the glass transition temperature of the polymer with n = 11 is higher than the expected temperature. The value of n authorizes a partial crystallization of the aliphatic side chains that seems to be more important than for n = 6 (semi-crystalline character). The polymethacrylate n = 2 has a non-crystalline character. (Figure 1)

These thermal results are in total agreement with those found for the polybenzoates (ref. : "Novel Smectic C Side-chain Polymers" to be published in Liq. Crystals).



Optical observations for polymers (II)

Birefringence is observed in both polymethacrylates with $n = 2, 6$ but textures are too fine and cannot be assigned to one texture or another. The X-ray studies will probably give more informations about their structures. The polymethacrylate with $n = 11$ exhibits two mesophases which show characteristic features of smectic phases. Upon cooling the isotropic liquid, bâtonnets begin to appear at 131°C and during 20 hours they grow and reorganize their shape in a fine focal-conic texture (plate 4). These microscopic observations are typical of a smectic A phase. As the temperature decreases below 120°C , the texture becomes poorly defined and suggests the formation of a tilted-smectic phase (plate 5) (same behaviour than polymethacrylate benzoate with a spacer equal to 11). In case of the polychloroacrylate $n = 11$, only one smectic A phase can be observed between 69 and 131°C . Bâtonnets appear from the isotropic liquid, grow and coalesce into a focal-conic fan texture.

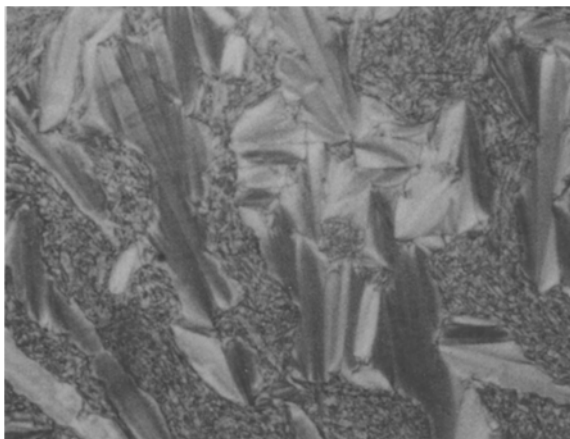


Plate 4 : Smectic A texture of polymer IIf at 131°C (crossed polarizers, 200 X)

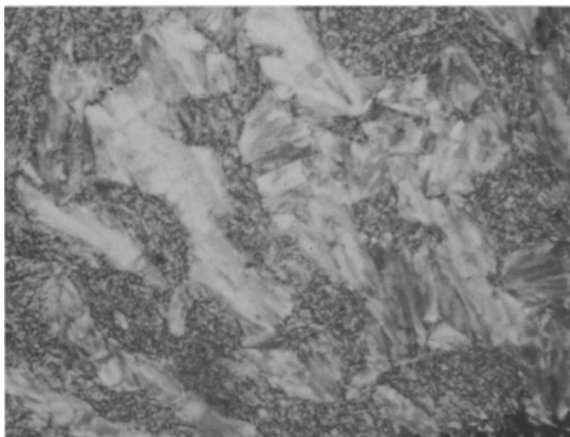


Plate 5 : Second smectic texture of polymer IIf at 115°C

EXPERIMENTAL PART

Preparation of the monomers (I)

The 4(hydroxyalkyloxy) cinnamic acids are prepared following the same way than for the 4(hydroxyalkyloxy) benzoic acids (13).

4(methacryloyloxy or chloroacryloyloxy or acryloyloxy) alkyloxy cinnamic acids : 4(hydroxyalkyloxy) cinnamic acids (0.045 mol) are esterified azeotropically in a Dean-Stark apparatus with a large excess (10 fold) of (methacrylic, chloroacrylic or acrylic) acid in 300 ml of benzene, 3 g p. toluenesulfonic acid and 3 g 2,6-diterbutylphenol during 20 hours. The benzene is then evaporated and the solution is washed a lot of times with hot water to eliminate the excess of acrylic acid. The solution is diluted with ether and dried with magnesium sulfate. The solid is precipitated by addition of hexane.

4(+)-2 methylbutyloxyphenyl ester of 4n(metha, chloro or acryloyloxy) alkyloxy cinnamic acids : the p(+) 2 methylbutyloxyphenol is synthesized by a standard method from hydroquinone and (+) 2 methylbutylbromide (15). The acid chlorides are prepared by a standard procedure with oxalylchloride (13). Monomers are purified by chromatography column over silicagel with dichloromethane as eluant and by recrystallization in ethanol.

Preparation of the polymers (II)

The polymers were prepared by free radical polymerization in toluene solution with 1 weight % azo-bis-isobutyronitrile as initiator in a sealed glass tube under vacuum for two days at 60°C. The polymers were precipitated by methanol.

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