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Patrick Keller [a]
[a] Laboratoire Léon Brillouin, C.E.N. Saclay, 91191, Gif sur Yvette Cedex, France
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# Synthesis of New Mesomorphic Polyesters by Polymerization of Bifunctional Monomers†

PATRICK KELLER

*Laboratoire Léon Brillouin,‡ C.E.N. Saclay, 91191 Gif sur Yvette Cedex (France)*

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New polyesters have been synthesized by high temperature polycondensation of *bifunctional* monomers (4-(ω-(4-acetyloxyphenyloxy)alkyloxy)benzoic acids). Their mesomorphic properties have been studied. By analogy with the chemistry of polypeptide polymers (use of bifunctional monomers and of protective groups), a step by step polymerization has been performed in order to obtain model compounds sketching a "monomer," a "dimer" and a "trimer." Preliminary results are given on the mesomorphic properties of the model compounds.

## INTRODUCTION

The thermotropic liquid crystalline behaviour of polymers having rigid mesogenic groups linked by flexible spacers along the main chain has been predicted theoretically[1] and is well demonstrated experimentally from reports over the past several years.[2–4]

Among all the interesting problems posed by these new materials, one is the influence of the molecular weight of the mesomorphic entities forming the liquid crystalline phases on the physical properties of these phases (i.e. order parameter; enthalpies and entropies of transitions; elastic properties . . .).[5–16]

Clearly, studies in that field require the synthesis of mesomorphic materials of increasing molecular weight from low molecular weight

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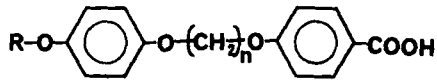
‡Laboratoire commun CEA-CNRS.

compounds ("classic" liquid crystalline compounds) to relatively high molecular weight compounds (liquid crystalline "main chain" polymers). Model compounds related to a "monomer" or a "dimer" have been obtained by classical synthetic methods,[16-20] but for intermediary compounds ("oligomers"), chromatographic technics have been used which give, at best, materials with narrow distributions in molecular weight.[15,19,21-23]

Keeping in mind these difficulties, we have tried to design a new type of compound which could, in principle, give the opportunity to prepare model compounds related to a "monomer," a "dimer," a "trimer" and so on up to the polymer.

This type of "step by step" polymerization is well known in the case of polypeptides which are formed by a well-defined succession of amino-acids. The selective linkage of one amino-acid to the end of a polypeptide chain is based on the use of *protective groups*:[24,25] one reactive function (amine or acid) of the amino-acid is protected from reaction by a suitable group (i.e. the protective group) and the other, remaining free, reacts with the terminal function of the peptide chain to give the usual peptidic bond. By using a selective method, the protective group is removed and the function thus released will be available for subsequent reactions.

We have tried to adopt similar synthetic schemes for the preparation of liquid crystalline polymers. We have prepared compounds of type (**1**) which, like amino-acids, are *bifunctional* compounds (acid and alcohol or derived functions).

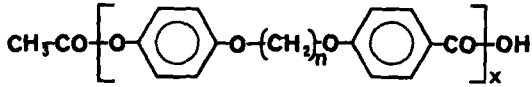



**1** n = 3 to 11

R = H; $CH_3CO$; $\phi$–$CH_2$;

Starting from these compounds, we have been able to prepare:

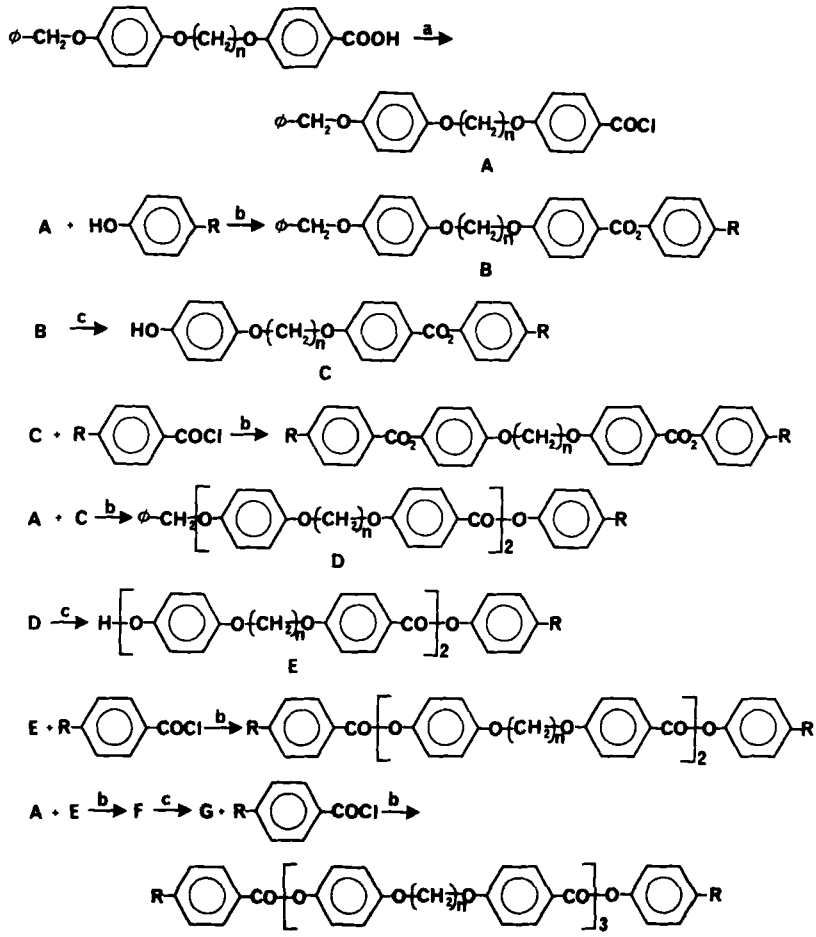
-polyesters (**2**) by high temperature polycondensation of compounds (**1**; R = $CH_3-CO-$).




**2**

-model compounds sketching a "monomer," a "dimer," a "trimer," . . . by the synthetic way summarized in Scheme 1.

In this article, we present the synthesis and mesomorphic properties



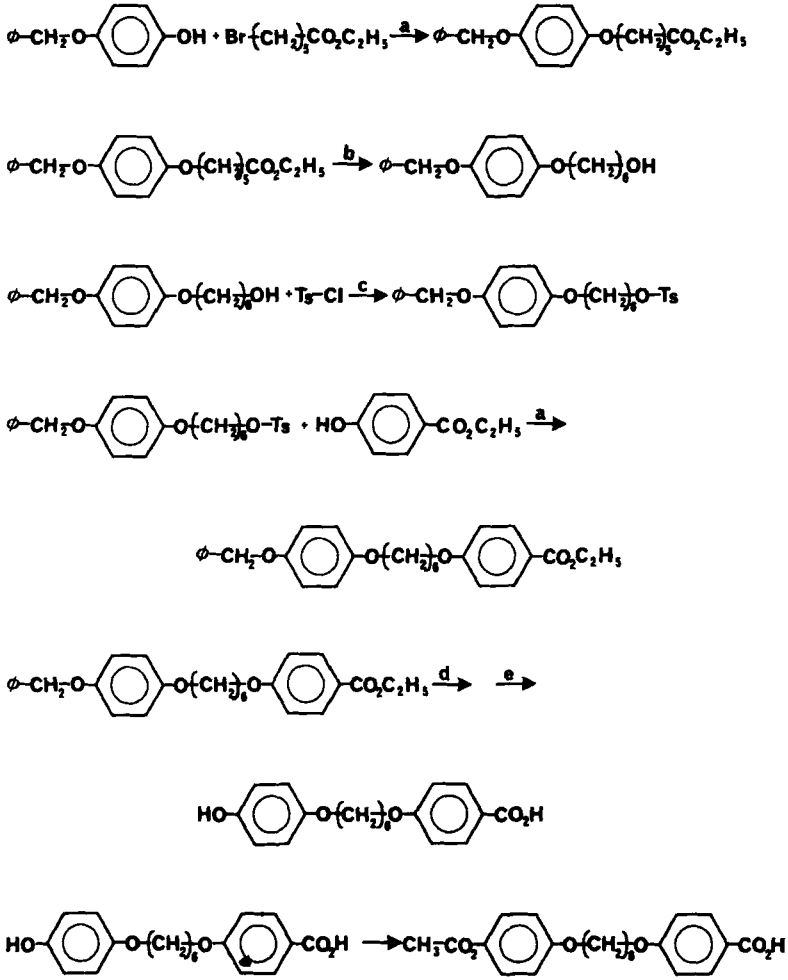
SCHEME 1 (a)$SOCl_2$; (b)pyridine, room temperature, 24h.; (c)$H_2$-Pd/C, ethyle acetate.

of compounds (**1**) and polymers (**2**) and our first results concerning the synthesis of model compounds.

## EXPERIMENTAL

Synthesis of compounds (**1**)

The procedure followed for the synthesis of these compounds will be illustrated by the detailed description of the preparation of compound (1) with n = 6. This procedure is summarized in the Scheme 2.



SCHEME 2 (a)$K_2CO_3$, cyclohexanone; (b)$LiAlH_4$; (c)pyridine, room temperature, 24h.; (d)KOH, ethanol; (e)$H_2$-Pd/C, dichloroacetic acid.

**Preparation of ethyl 6-(4-benzyloxyphenyloxy)hexanoate**

A mixture of 4-benzyloxyphenol (10g;0.05mole), ethyl 6-bromohexanoate (16.7g;0.075mole), potassium carbonate (30g;0.21mole) in cyclohexanone (60 ml) was refluxed for 4 h. After removal of the salts by filtration, the solvent was distilled and the solid residue recrystallized from hexane/ethanol. Yield = 15.3g; mp = 62°C (IR; $\nu_{CO}$ = 1770 $cm^{-1}$).

**Preparation of 6-(4-benzyloxyphenyloxy)hexanol**

To a suspension of lithium aluminium hydride (1.6g) in diethyl ether (150ml) was added portionwise solid ethyl 6-(4-benzyloxyphenyloxy) hexanoate (15.3g;0.044mole). The mixture was heated under reflux for 4 h after completion of the addition, and, after cooling, was poured onto ice and 6M hydrochloric acid. After extraction with chloroform, followed by washing of the organic phases with water and drying ($Na_2SO_4$), the solvents were distilled off to leave a white solid. Recrystallisation from ethanol gave 13g of 6-(4-benzyloxyphenyloxy)hexanol, mp = 96°C (IR;$\nu_{OH}$ = 3340cm$^{-1}$, no $\nu_{CO}$).

**Preparation of 6-(4-benzyloxyphenyloxy)hexyl tosylate**

To a solution of 6-(4 benzyloxyphenyloxy)hexanol (13g;0.043mole) in pyridine (50ml) cooled in iced water, was added portionwise the tosyl chloride (16.5g;0.086mole). The mixture was stirred at 0°C for 12 h, and poured into 100ml of water and 200g of ice. The solution was shaken with chloroform; the organic phase was washed with dilute hydrochloric acid (2M) and then with water, and dried ($Na_2SO_4$). Evaporation of the solvent gave 19.9g of the tosylate which was used in the next step without further purification.

**Preparation of 4-(6-(benzyloxyphenyloxy)hexyloxy)benzoic acid (1,R = Φ-$CH_2$-)**

A mixture of ethyl 4-hydroxybenzoate (7.1g;0.042mole), 6-(benzyloxyphenyloxy)hexyl tosylate (19.9g;0.043mole), and potassium carbonate (25g;0.18mole) in cyclohexanone (65ml) was heated under reflux for 6 h. The heterogeneous mixture was filtered hot to remove salts, and the solvent distilled. To the residue, dissolved in ethanol (140ml), was added potassium hydroxide (10g) in water (10ml), and the resulting solution was boiled for 6 h. During the course of the reaction, a precipitate appeared. After cooling the reaction mixture, the precipitate was filtered off, washed well with ethanol and then with ether; yield = 11.2g. The IR spectrum was consistent with the potassium salt of 4-(6-benzyloxyphenyloxy)hexyloxy) benzoic acid. (IR;$\nu_{CO_2^-}$ = 1560cm$^{-1}$ and 1410cm$^{-1}$).

The salt was suspended in water (130ml) and concentrated hydrochloric acid (15ml) was added. After stirring at room temperature for 12 h, the precipitate was filtered off, washed with water and crystallized from acetic acid; yield = 8.5g; mp = 250°C (IR;$\nu_{CO}$ = 1710cm$^{-1}$).

### Preparation of 4-(6-(4-hydroxyphenyloxy)hexyloxy)benzoic acid (1,R = H-)

A solution of 4-(6-(benzyloxyphenyloxy)hexyl)benzoic acid (2g) in dichloroacetic acid (50ml) was hydrogenated at room temperature and atmospheric pressure in the presence of Pd catalyst (Pd-5% on charcoal;0.35g). After hydrogen consumption had ceased, the catalyst was filtered off and the filtrate poured onto ice and water. The resulting precipitate was filtered, washed with water and dried; yield = 1.4g; mp = 107°C (IR;$\nu_{OH}$ = 3360cm$^{-1}$; $\nu_{CO}$ = 1680cm$^{-1}$).

### Preparation of 4-(6-(4-acetyloxyphenyloxy)hexyloxy)benzoic acid (1,R = $CH_3$-CO-)

To a solution of the phenol (**1**,R = H−) (0.8g;2.4.10$^{-3}$mole) in pyridine (15ml), was added acetic anhydride (1g). After stirring for 24h at room temperature, the solution was poured onto ice (50g) and hydrochloric acid (5ml). The mixture was extracted with chloroform, the organic phase was washed with water and dried ($Na_2SO_4$), and the solvent was distilled. The residue was recrystallized from ethanol; yield = 0.8g; K 149 N 158 I (IR;$\nu_{CO_2H}$ = 1680cm$^{-1}$; $\nu_{CO}$ = 1740cm$^{-1}$).

### Preparation of polyesters (2)

The polyesters (**2**) were prepared by high temperature transesterification of the monomers (**1**,R = $CH_3CO$-) as described by Strzelecki and Liebert.[26] The case of polymer (**2**) with n = 6 will be given as a typical procedure.

Transesterification was performed by placing the monomer (**1**,R = $CH_3$-CO-;n = 6) (0.7g;1.88.10$^{-3}$mole) along with zinc acetate (0.24mg) and antimony(III) oxide (0.32mg) in a polymerization tube fitted with a side arm and a capillary tube which served as a nitrogen inlet. After flushing out with nitrogen, the polymerization tube was plunged in a metallic bath at 180°C. The temperature was raised from 180 to 280°C in ½ h, with a continuous stream of nitrogen passing through the polymerization tube. After 1 h at 280°C, the stream of nitrogen was stopped, and the pressure reduced to ~20mm Hg. Half an hour later, the pressure was reduced again to ~1mm Hg and heating was continued for ½ h. The metallic bath was removed and the polymer cooled down under reduced pressure. The polymer had an inherent viscosity of 0.46dl.g$^{-1}$ in dichloroacetic acid ($c$ = 0.5g.dl$^{-1}$).

Transition temperatures were measured by optical microscopy us-

ing a polarizing microscope (Leitz) fitted with a Mettler FP82 heating stage and FP80 control unit. They were checked by differential thermal analysis (DTA 2000, Mettler).

Structural checks were carried out using a Shimadzu IR408 instrument for IR spectra. Satisfactory elemental analysis results were obtained for all the materials.

Inherent viscosities of the polyesters were determined at 30°C using 0.5g.dl$^{-1}$ solutions in dichloroacetic acid. KPG Ubbelohde microviscometers were used with an AVS 300 automatic viscometer assembly (Schott-Gerate).

## RESULTS AND DISCUSSION

The melting and transition points for the monomers (**1**,R = $CH_3$-CO-) are listed in Table I. Identification of the mesophases has been achieved by examination of the textures exhibited by thin samples sandwiched between two glass slides.

For these compounds, the change in the mesomorphic properties with lengthening of the chain is similar to that encountered for *para*-substituted benzoic acids:[27] a nematic phase alone occurs for the shorter substituents, a nematic and a smectic C phase for intermediate lengths of substituent, and a smectic C phase alone for the longer substituents.

Table II lists the transition temperatures for the polymers synthesized by high temperature polycondensation of the precursor monomers and their inherent viscosities in dichloroacetic acid.

Except for the product with n = 11, all polyesters have similar inherent viscosities which could indicate, to a rough approximation,

TABLE I

Transition temperatures (°C) for 4-(ω-(4-acetyloxyphenyloxy)alkyloxy) benzoic acids (**1**, R = $CH_3$-CO-).

| n | K | SC | N | I |
|---|---|---|---|---|
| 3 | · 175 | | | · |
| 4 | · 195 | | | · |
| 5 | · 160 | | | · |
| 6 | · 149 | | · 158 | · |
| 7 | · 90 | · 93 | · 116 | ·· |
| 8 | · 60 | · 115 | | · |
| 9 | · 62 | · 100 | | · |
| 10 | · 76 | · 110 | | · |
| 11 | · 70 | · 120 | | · |

TABLE II

Transition temperatures (°C) and inherent viscosities of the polyesters (2)

| n | ηinh. | $t_1$ | $t_2$ |
|---|---|---|---|
| 5 | 0.49 | 150 | |
| 6 | 0.46 | 60 | 120 |
| 7 | 0.40 | 70 | 160 |
| 8 | 0.44 | 70 | 135 |
| 9 | 0.45 | 75 | 200 |
| 10 | 0.44 | 60 | 210 |
| 11 | 0.25 | 70 | 110 |

that their average molecular weights are of the same order of magnitude.

Temperatures $t_1$ listed in Table II are the temperatures at which the solid phase transforms to a birefringent state which is deformable when the cover slide is slightly depressed; $t_2$ are the temperatures at which the system becomes isotropic.

Transition temperatures determined by hot stage microscopy and DTA were in reasonable agreement. In Figure 1, typical DTA curves for the polyester with n = 6 are presented.

Identification of the mesophases by optical observations is very difficult since non-classical textures are obtained. Textures exhibited by these very viscous mesophases could be related to those described by other authors[26] who have classified the mesophases as nematic.

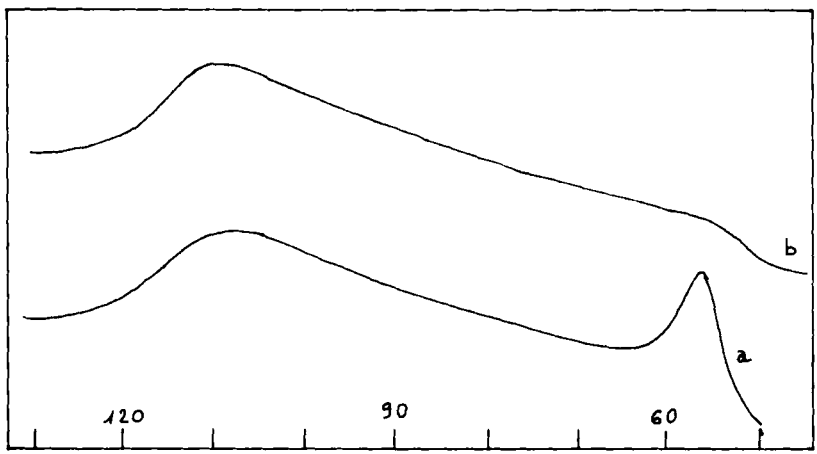



FIGURE 1 DTA curves for the polyester with n = 6 (heating rate:5°C.min$^{-1}$). (a) First heating; (b)Second heating.

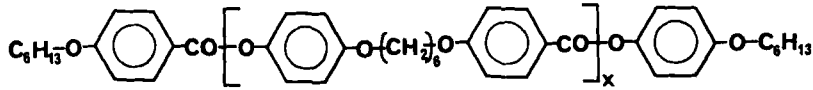
We have tried unsuccessfully to confirm this identification by performing X-ray diffraction experiments: in fact, a sample of the polymer with n = 6 heated at 100°C and submitted to a magnetic field of 1.7*T*. does not align as shown by the X-ray diagrams.[28] Clearly, other experiments with higher magnetic fields are required and these are now in progress.

## CONCLUSION

We have prepared a new family of *bifunctional* monomers (**1**) which give, by polycondensation, new liquid crystalline polyesters (**2**).

By analogy with the chemistry of polypeptide polymers,[24] a step by step polymerization is, in principle, possible starting with these bifunctional monomers (or related compounds) (see Scheme 1).

By the synthetic Scheme 1, model compounds (3), sketching a monomer (x = 1), a dimer (x = 2) and a trimer (x = 3), have actually been obtained.



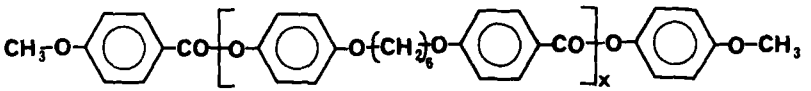
**3** x=1,2,3

The pseudomonomer (**3**, x = 1) exhibits the following transitions: K 85 $S_C$ 106 N 126,5 I, as determined by optical observations and DTA.

Surprisingly, the pseudodimer (**3**, x = 2) and the pseudotrimer (**3**, x = 3) are *not* mesomorphic (K 150 I for x = 2; K 155 I for x = 3).

However, Blumstein *et al.*[19] have found in another series, that ~6 repeating units are required for the appearance of a stable nematic phase. A similar length might also be necessary for our compounds. Work is in progress to confirm this hypothesis.

Another possible way to favour the existence of a stable nematic phase would involve using shorter end substituents as currently used for "small" mesomorphic molecules.[27] Compounds such as (**4**) might be better candidates for the appearance of a stable N phase.



**4**

Work is being pursued in that field and results will be forthcoming.

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