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Columnar order in thermotropic mesophases of oligophenylenevinylene derivatives

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Abstract

Oligophenylenevinylene derivatives substituted with long alkyl chains on one end and a carboxylic acid function on the other end have been prepared and the dimeric polycatenar calamitic supramolecules resulting from hydrogen bonding of their acid functions show columnar liquid crystalline phases. © 2000 Elsevier Science Ltd. All rights reserved.

Although conjugated oligomers and polymers have been extensively investigated in previous years for their electronic properties (conductivity, optical properties, etc),[1] structural studies of these materials have received less attention and appear today as a very important issue in their application. Of particular interest are derivatives exhibiting liquid crystalline properties.[2,3] Such materials are not only ordered assemblies easy to process for various applications, but many properties associated with the delocalized π-electron system (electroluminescence, third order optical nonlinearity, etc.) can be enhanced due to the orientational effect induced by the liquid crystal ordering.[2] A particularly appealing challenge is the preparation of liquid crystalline conjugated oligomers displaying columnar mesophases with the aim of generating fibers that could act as conducting nanowires similar to those obtained from discotic derivatives.[4] In this paper, we report the preparation of new liquid crystalline *all-trans*-oligophenylenevinylene (OPV) derivatives giving rise to columnar order in thermotropic mesophases.

The synthesis of the OPV derivatives is depicted in Scheme 1. Benzaldimines **1a**[5] and **1b**[6] were subjected to the Siegrist reaction with stilbene **2**[6] to give protected trimers **3a** and **3b**, respectively. Subsequent deprotection of **3a** and **3b** with CF_3CO_2H in CH_2Cl_2/H_2O afforded aldehydes **4a** and **4b**, respectively. Reaction of **4a** and **4b** with methyl (triphenyphosphoranylidene)acetate under Wittig conditions followed by the saponification of the resulting esters yielded carboxylic acids **6a** and **6b**, respectively. Reduction of **4a** and **4b** with $LiAlH_4$ to the corresponding alcohols followed by a Mitsunobu reaction with methyl *p*-hydroxybenzoate afforded **8a** and **8b**, respectively.

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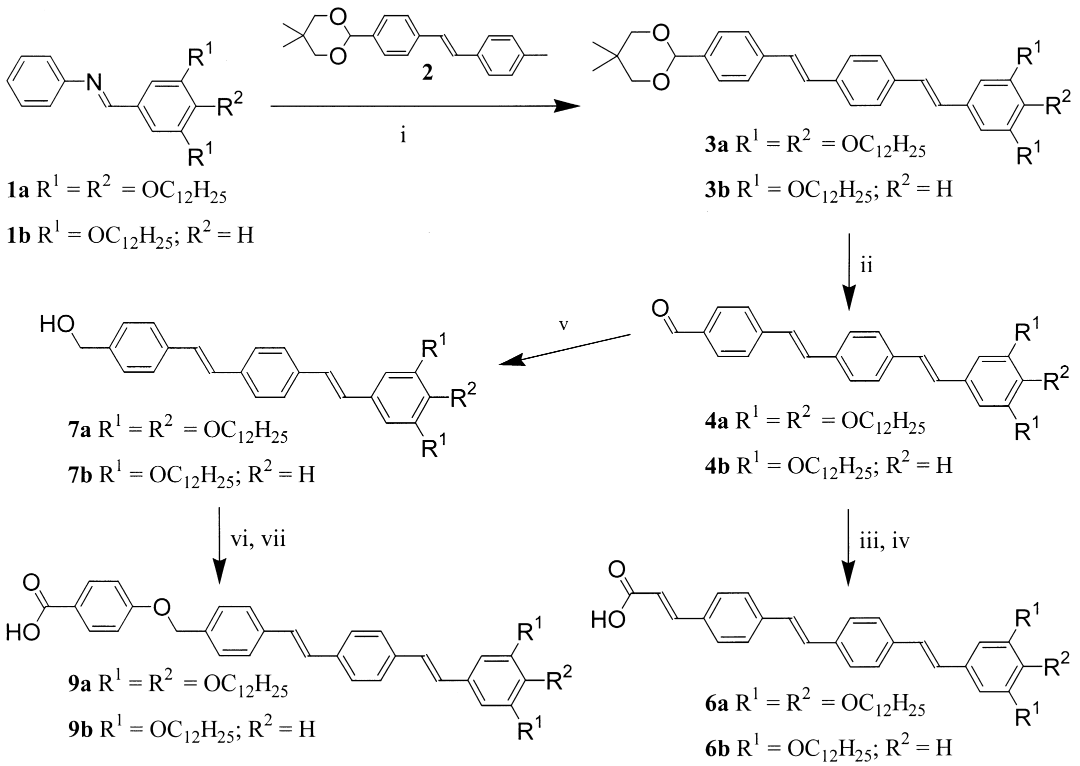

Scheme 1. *Reagents and conditions*: (i) *t*-BuOK, DMF, 80°C, 2 h (**3a**: 91%; **3b**: 91%); (ii) TFA, CH_2Cl_2, H_2O, room temp., 4 h (**4a**: 96%; **4b**: 96%); (iii) methyl (triphenyphosphoranylidene)acetate, THF, Δ (**5a**: 80%; **5b**: 84%); (iv) KOH, THF, H_2O, Δ, 48 h (**6a**: 90%; **6b**: 90%); (v) $LiAlH_4$, THF, 0°C, 1 h (**7a**: 90%; **7b**: 86%); (vi) methyl *p*-hydroxybenzoate, diethyl azodicarboxylate (DEAD), PPh_3, THF, Δ, 24 h (**8a**: 72%; **8b**: 85%); (vii) KOH, THF, H_2O, Δ, 48 h (**9a**: 90%; **9b**: 90%)

Subsequent treatment with KOH in THF/H_2O yielded the corresponding carboxylic acids **9a** and **9b**. All of the spectroscopic studies and elemental analysis results were consistent with the proposed molecular structures.[7]

The liquid crystalline properties of the OPV derivatives **6a**–**b** and **9a**–**b** have been studied by differential scanning calorimetry (DSC), X-ray diffraction and optical investigations. Furthermore, thermogravimetric analyses (TGA) show that these oligomers remain stable up to 350°C. The results are summarized in Table 1.

Columnar mesophases have been observed with polycatenar calamitic molecules composed of long rigid aromatic cores (containing in general five rings) with two or three paraffinic chains at both ends.[8] In our case, the OPV derivatives **6a**–**b** and **9a**–**b** are all able to form dimers through hydrogen bonding[9] of their acid functions to give polycatenar calamitic supramolecules containing up to seven and nine rings, respectively. In fact, the polymorphism of the resulting supramolecules appears to be similar to that of polycatenar calamitic molecules in spite of the increased length of the rigid core. Effectively, columnar mesophases have been observed for all the OPV derivatives **6a**–**b** and **9a**–**b**. Fig. 1 shows an optical texture observed for one of the derivatives. This optical microscopy texture contains developable units that are characteristic of a columnar mesophase.[10]

Table 1
Phase behavior of **6a–b** and **9a–b** (K, crystalline phase; Col_H, hexagonal columnar phase; Col_R, rectangular columnar phase; I, isotropic phase)

Compound	Transitions (temperature)	
6a	K-Col_R (36°C)	Col_R-I (219°C)
6b	K-Col_H (125°C)	Col_H-I (237°C)
9a	K-Col_R (111°C)	Col_R-I (236°C)
9b	K-Col_H (143°C)	Col_H-I (245°C)

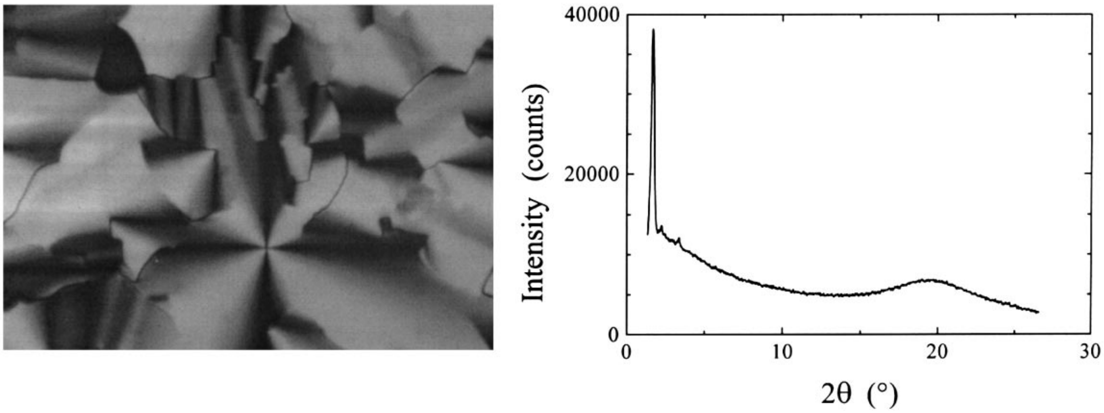

Figure 1. Left: optical texture observed with a polarizing microscope at 100°C for compound **6a**; right: X-ray diffraction pattern of compound **6a** recorded at 100°C

The columnar structure of the mesophases was confirmed by X-ray diffraction investigations for all the OPV derivatives **6a–b** and **9a–b**. For example, the diffraction pattern recorded at 100°C for compound **6a** is depicted in Fig. 1. Whereas a columnar phase with hexagonal symmetry was found for both biforked derivatives **6b** and **9b**, a columnar phase with P_{2gg} rectangular symmetry and a *pseudo*-hexagonal lattice ($a/b = 3^{0.5}$) was observed for the corresponding derivatives with tridodecyloxyphenyl groups.

Two types of columnar mesophases have been observed for OPV derivatives substituted with long alkyl chains on one end and a carboxylic acid function on the other end. Further structural studies of these new OPV derivatives, their incorporation in light emitting devices and determination of their conducting properties are now under investigation.

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