Synthesis of liquid-crystalline oligotriacetylene derivatives

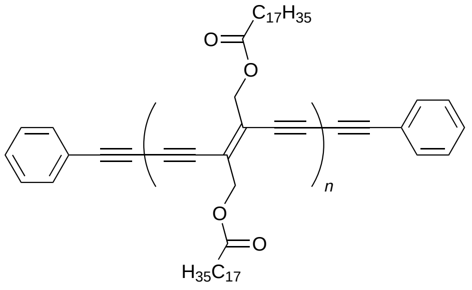
Jean-François Nierengarten,* Daniel Guillon, Benoît Heinrich and Jean-François Nicoud

Groupe des Matériaux Organiques, Institut de Physique et Chimie des Matériaux de Strasbourg, UMR C00460, CNRS, 23 rue du Loess, F-67037 Strasbourg, France

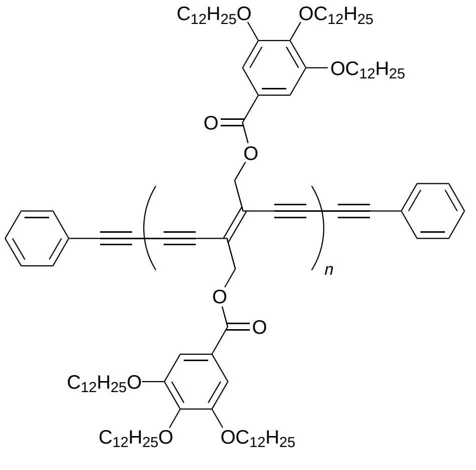
(*E*)-Hex-3-en-1,5-diyne derivatives with two or six pendant long alkyl chains have been prepared and their end-capping oligomerisation yields oligomers with a polytriacetylene conjugated backbone; whereas the end-capped mono- and di-mers do not exhibit any liquid-crystalline behaviour, the trimeric derivatives show mesomorphic properties.

The preparation of oligomers and polymers with extended conjugated carbon cores is currently being intensively pursued,[1] with the aim of generating advanced materials for electronic,[2] photonic,[3] and non-linear optical[4] applications. For many years, polyacetylenes (PA) and polydiacetylenes (PDA) were the only known single-strand conjugated polymers with a non-aromatic all-carbon backbone; however, Diederich and co-workers succeeded recently in the preparation of oligomers and polymers with a polytriacetylene (PTA) backbone.[5] Whereas introduction of bulky substituents in PA leads to loss of conjugation due to distortion from planarity for steric reasons,[6] side chains can be attached on PDA or PTA backbones without any loss of conjugation.[5] PDAs and PTAs are also considerably more stable than PAs.[5] However, the accessibility of PDAs is limited by the requirements resulting from their preparation by topochemical polymerisation of suitably pre-organised butadiynes,[7] while PTAs can be prepared by normal chemical reactions.[5] Here we report the synthesis of PTA oligomers **1**–**3** of defined length substituted with lateral long alkyl chains. The conjugated backbone is a rigid rod that can act as a mesogenic unit and liquid crystalline properties were observed for some of the reported oligomers. The advantage of such a liquid crystal is that many properties (electroluminescence, third order optical nonlinearity *etc.*) associated with the delocalised π-electron system can be enhanced due to the orientational effect induced by the liquid crystal ordering.[8]

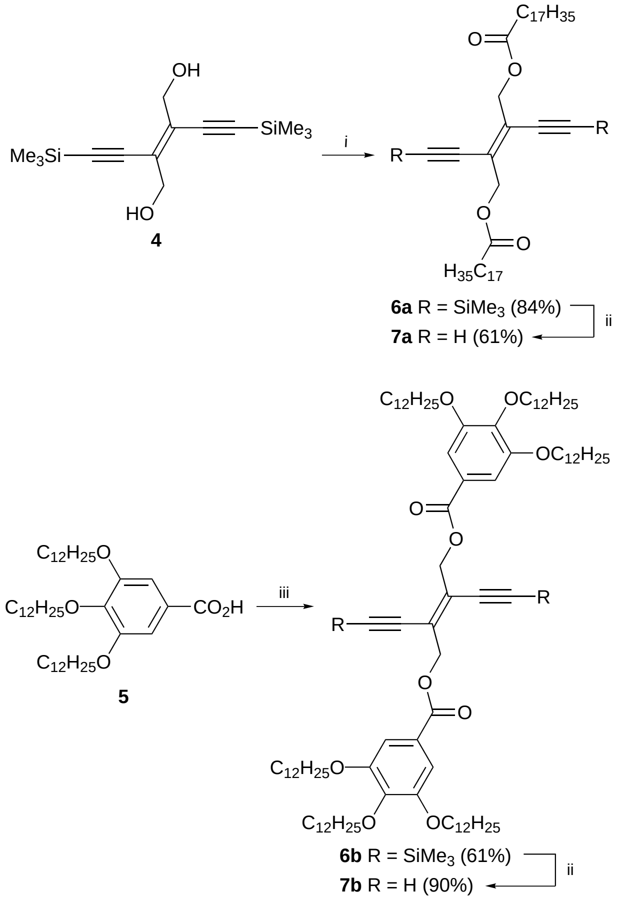
The synthesis of the monomers is described in Scheme 1. Diol **4** was prepared in three steps from dimethyl acetylenedicarboxylate as previously reported.[5b] The (*E*)-hex-3-en-1,5-diyne derivatives with pendant long alkyl chains were prepared by dicyclohexylcarbodiimide (DCC)-mediated esterification[9] of stearic acid and acid **5**[10] with diol **4** to give **6a** (84% yield) and **6b** (61% yield), respectively. Subsequent deprotection of **6a** and **6b** with Bu_4NF in wet THF afforded *trans*-endiyne **7a** (61% yield) and **7b** (90% yield), respectively. Whereas compound **7a** is relatively unstable in the neat state, **7b** is an air-stable solid that can be stored at ambient temperature for prolonged periods of time. As previously shown by X-ray



1a *n* = 1
2a *n* = 2
3a *n* = 3



1b *n* = 1
2b *n* = 2
3b *n* = 3



Scheme 1 *Reagents and conditions*: i, stearic acid, DCC, DMAP, CH_2Cl_2, 0 °C to room temp.; ii, Bu_4NF, wet THF, 0 °C; iii, **4**, DCC, DMAP, CH_2Cl_2, 0 °C to room temp.

crystal structure analysis of some related compounds,[11] the presence of bulky substituents in **7b** isolates the sensitive *trans*-endiyne units and prevents intermolecular reactions that would lead to decomposition.

The PTA oligomers **1a**–**3a** and **1b**–**3b** were prepared *via* end-capping oligomerisation of **7a** and **7b**, respectively. The *in situ* preparation of the Hay catalyst[12] [CuCl–TMEDA–O_2 (TMEDA = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine)] in CH_2Cl_2 in the presence of **7a** and phenylacetylene furnished a mixture of oligomers, from which **1a**–**3a** were isolated by column chromatography (SiO_2, hexane–CH_2Cl_2 3 : 2 to 1 : 2). When a large excess of phenylacetylene (10 equiv.) was used, **1a** and **2a** could be obtained in 25 and 5% yield, respectively. When **7a** and phenylacetylene were used in a 1 : 1 molar ratio, **1a** (9% yield), **2a** (5%) and **3a** (2%) could be isolated. End-capped oligomers **1b**–**3b** were prepared from **7b** and phenylacetylene under Hay coupling conditions in CH_2Cl_2 in a similar manner. Starting from phenylacetylene and **7b** in a 10 : 1 ratio, **1b** and **2b** were obtained in 64 and 7% yield, respectively. When a 1 : 1 molar ratio was used, **1b** (15% yield), **2b** (19%) and **3b** (12%) could be isolated by column chromatography (SiO_2, hexane–CH_2Cl_2 2 : 1 to 1 : 1). Higher oligomers could also be eluted by using CH_2Cl_2 but could not be separated into pure compounds. Whereas the yields for the preparation of **1b**–**3b** are similar to that reported for related reactions,[5a] the yields of **1a**–**3a** are limited by the instability of monomer **7a** as well as by their surprisingly low solubility. All of the spectroscopic studies and elemental analysis results were consistent with the proposed molecular structures.† In spite of the presence of bulky substituents in **2b** and **3b**, their absorption spectra are similar to those of **2a** and **3a**, respectively, showing that there is no loss of conjugation as a result of a distortion from planarity for steric reasons. Compounds **2a** and **2b** show end absorption around 450 nm, and **3a** and **3b** around 500 nm.

Whereas the end-capped mono- and di-mers do not exhibit any liquid-crystalline behaviour, the trimeric derivatives **3a** and **3b** show mesomorphic properties. These have been deduced from optical and X-ray diffraction investigations. Polarised optical microscopy revealed a fluid birefringent phase at room temperature for **3b** and between 80 and 115 °C for **3a**. The clearing temperature was determined to be 40 °C for **3b**. However, in both cases, the birefringent optical textures observed on cooling the samples from the isotropic phase were non-characteristic.[13] Furthermore, the X-ray diffraction pattern of **3b** is typical of a mesomorphic phase with a sharp diffraction peak in the small angle region and a diffuse band in the wide angle region (Fig. 1). For **3a**, the diffraction patterns recorded at various temperature are more complex. The exact structure determination of these mesophases is still in progress.

The preparation of PTA oligomers with pendant long alkyl chains leads to original liquid crystalline derivatives. The synthesis of the corresponding polymers is now under investigation in our laboratory.

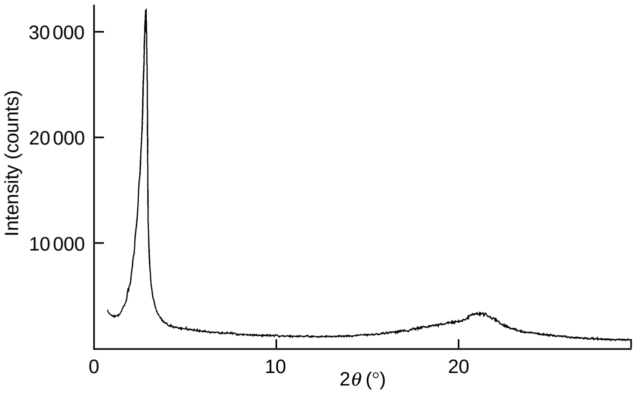


Fig. 1 X-Ray diffraction pattern of **3b** recorded at 25 °C

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Footnotes

* E-mail: niereng@michelangelo.u-strasbg.fr

† *Spectroscopic data* for **1b**: UV–VIS $\lambda_{max}(CH_2Cl_2)$/nm 243 (sh, 34140), 259 (49450), 360 (44560), 387 (sh, 35080); IR $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 2211 (C≡C), 1718 (C=O); ^1H NMR ($CDCl_3$, 200 MHz): 0.89 (m, 18 H), 1.26 (m, 108 H), 1.76 (m, 12 H), 4.02 (t, *J* 6.5, 4 H), 4.04 (t, *J* 6.5, 8 H), 5.21 (s, 4 H), 7.35 (s, 4 H), 7.37 (m, 6 H), 7.48 (m, 4 H); ^{13}C NMR ($CDCl_3$, 50 MHz): 14.09, 22.68, 26.11, 29.20, 29.38, 29.64, 30.34, 31.93, 64.16, 69.11, 73.44, 76.55, 87.47, 88.68, 108.11, 121.11, 124.14, 128.48, 129.16, 129.76, 132.48, 142.55, 152.84, 165.89; FAB-MS: *m*/*z* 1650 (MH^+). For **2b**: UV–VIS $\lambda_{max}(CH_2Cl_2)$/nm 271 (90210), 359 (sh, 52210), 388 (67090), 419 (sh, 50270); IR $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 2202 (C≡C), 1718 (C=O); ^1H NMR ($CDCl_3$, 200 MHz): 0.89 (m, 36 H), 1.26 (m, 216 H), 1.77 (m, 24 H), 4.02 (m, 24 H), 5.15 (s, 8 H), 7.31 (s, 4 H), 7.33 (s, 4 H), 7.36 (m, 6 H), 7.47 (m, 4 H); ^{13}C NMR ($CDCl_3$, 50 MHz): 14.09, 22.68, 26.09, 26.16, 29.38, 29.70, 30.37, 31.93, 63.95, 64.11, 69.12, 73.36, 73.47, 82.55, 87.34, 87.92, 89.54, 108.09, 108.18, 121.01, 123.95, 124.05, 127.68, 128.48, 129.83, 131.48, 132.50, 142.56, 142.68, 152.84, 165.73, 165.82; FAB-MS: *m*/*z* 3098.5 (M^+). For **3b**: UV–VIS λ_{max} (CH_2Cl_2)/nm 273 (117850), 396 (sh, 69310), 413 (71310); IR $\nu_{max}(CHCl_3)/cm^{-1}$ 2205 (C≡C), 1715 (C=O); ^1H NMR ($CDCl_3$, 200 MHz): 0.88 (m, 54 H), 1.25 (m, 324 H), 1.74 (m, 36 H), 3.98 (m, 36 H), 5.12 (s, 8 H), 5.16 (s, 4 H), 7.28 (s, 8 H), 7.32 (s, 4 H), 7.35 (m, 6 H), 7.42 (m, 4 H); ^{13}C NMR ($CDCl_3$, 50 MHz): 14.09, 22.88, 26.15, 26.22, 29.38, 29.55, 29.70, 30.37, 31.93, 63.85, 63.95, 64.10, 69.12, 73.35, 73.45, 77.19, 82.27, 82.97, 87.15, 87.99 (2C), 89.67, 108.07, 108.18, 123.88, 124.04, 127.01, 127.17, 128.39, 128.48, 129.34, 129.88, 132.22, 132.49, 142.56, 142.71, 152.83, 165.66 (2C), 165.79; FAB-MS: *m*/*z* 4547 (M^+).

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