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Synthesis of New Polymerizable Liquid-Crystal Molecules

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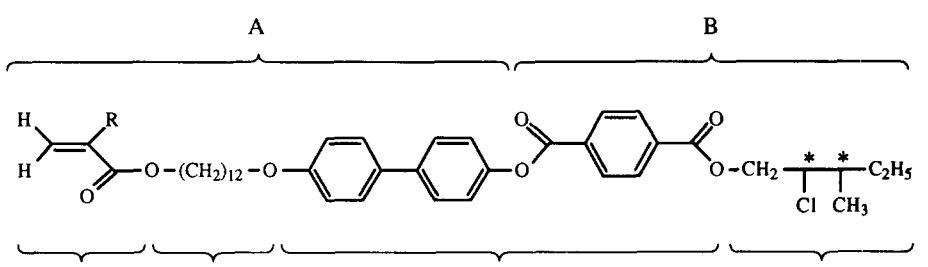
Abstract: On the way to get a comparison between different side-chain liquid-crystal polymers bearing the same lateral mesogenic group, in order to show the influence of the nature of the polymer backbone on their thermal behaviors, we present here the synthesis of new liquid-crystal acrylate and methacrylate monomers.

Liquid-crystal polymers showing ferroelectric properties at room temperature are of great interest for many chemists in the field of display devices[1]. Such molecules have to present a chiral smectic C phase (S_C^*). Architectural considerations about the relationship between the structure of molecules and their mesophases led us to propose a model structure favorable to S_C^* phase. This model molecule, terminated with different polymerizable moieties, here acrylate and methacrylate ones, will be studied later on under its polymerized form to study the influence of the nature of the main chain on the mesomorphic properties.

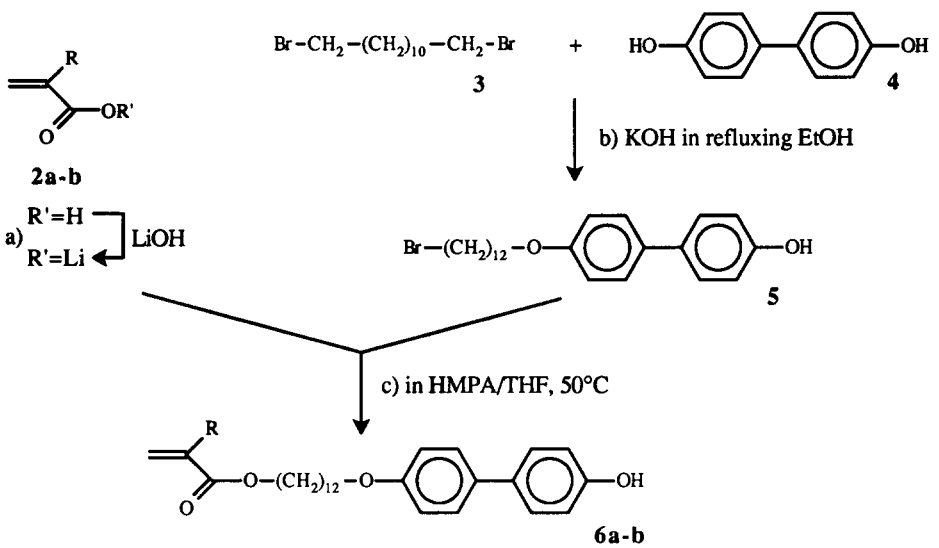
We present here the synthesis of these model molecules[2] :



1, R = H (**1a**) or CH_3 (**1b**)

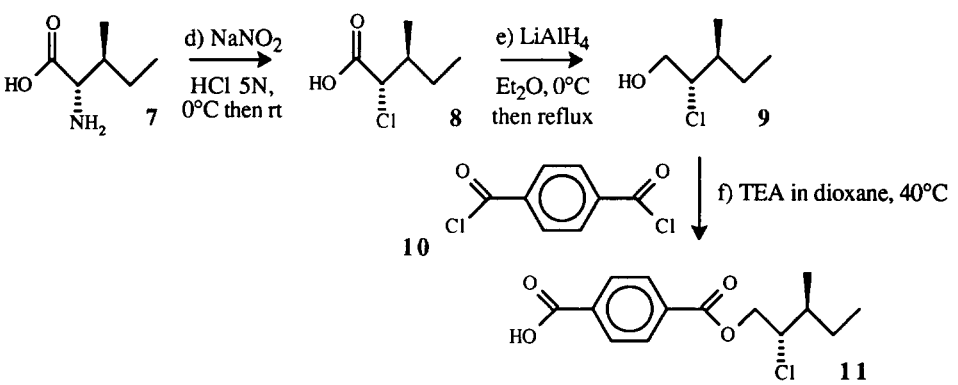
The synthesis has been divided into two steps : synthesis of part A, containing the spacer and the polymerizable function, and synthesis of part B, containing the chiral group.

The preparation of part A[3] is described in Scheme 1. The monosubstitution of 1,12-dibromododecane **3** with 4,4'-biphenol **4** is accomplished in an equimolecular solution of KOH in ethanol[4], the molar ratio biphenol/KOH being 1/1 to avoid a bisubstitution of biphenol. The product **5** is obtained in a yield of 50%. The coupling of the lithium salt of acrylic acid **2** with the compound **5**, rather insoluble in common solvents, is performed in a solution 1/1 v/v HMPA/THF to afford the acrylate **6** in a 91% yield.



Scheme 1 : Synthesis of part A.

The synthesis of part B[3] is outlined in scheme 2. Two reasons have determined the choice of L-isoleucine **7** as the chiral precursor : (i) the presence of two stereogenic neighboring centers, (ii) the steric bulkiness of the CH_3 group, which decreases the mobility of the C-Cl polar group, reinforcing the rigidity of the end-group.

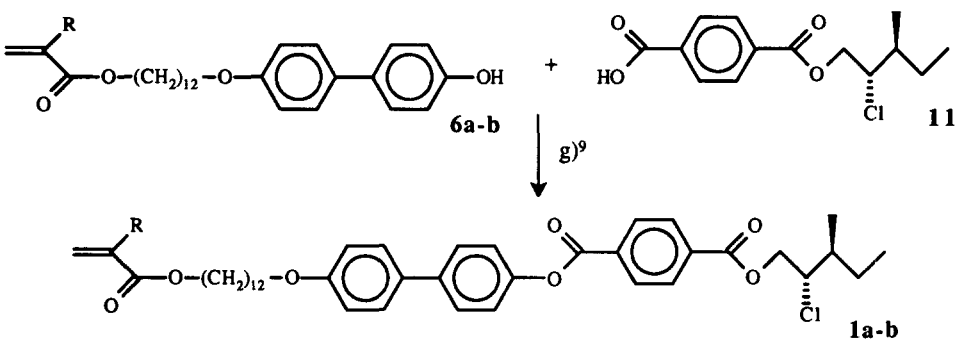


Scheme 2 : Synthesis of part B.

L-Ileu **7** is transformed into its diazonium salt[5] which is transformed into the chlorinated compound **8** ($[\alpha]_D^{25}$= -4.4 neat). Baillon-Moussel[6], confirming the studies of Neuberger[7], has shown that this double substitution took place with a retention of configuration. Thus, the carbon atom bearing the chlorine atom will be considered as in a "S" absolute configuration, this stereogenic carbon remains unmodified during further reactions. The acid **8** is then reduced with $LiAlH_4$[8] to obtain the alcohol **9** ($[\alpha]_D^{25}$= -7.9 neat). The monoesterification of terephtaloyl chloride **10** by the alcohol **9**, using triethylamine to quench HCl, has been run using the dichloride in large excess to avoid its disubstitution. The moderate yield of this step is due to the

difficult removal of the terephtalic acid formed in this reaction. Compound **11** is obtained in a 67% yield ($[\alpha]_D^{25}$ = -15, c 2, $CHCl_3$).

Esterification[9] of acid **11** with alcohol **6** completes the preparation of the monomers **1**, presented in scheme 3. Compounds **6** and **11** are coupled in presence of DCC and DMAP[10] to afford **1** with 30% yield[11].



Scheme 3 : Synthesis of the monomers.

We have thus succeeded in obtaining a molecule featuring the main structural characteristics necessary to generate a S_C^* phase in a mesogenic molecule : (i) a long spacer group, up to 12 carbons, which is a challenge because the bad solubility of the reactants generates two problems : a difficult accessibility of the active centers in an heterogeneous medium, and thus a rather weak conversion, and difficulties in the separation between substrates and reactants which are both very slighly soluble in general and, still worth, soluble only in the same solvents (steps b-c), (ii) three aromatic groups containing a reversed ester bond which is very sensitive to even slightly acidic conditions, but is giving a configuration more favorable[12] to a smectic phase generation than a normal ester bond which induces the apparition of a nematic phase, (iii) two neighboring stereogenic carbons which allow the formation of the chiral phase.

The thermal analysis of the products **1a** and **1b** has shown a liquid crystal behavior for both molecules[2] and a S_C^* phase has been identified between 64 and 71°C for the acrylate **1a** and between 79 and 104°C for the methacrylate **1b**. Their mesogenic properties will be more detailed in a later paper.

REFERENCES AND NOTES

1. Hachiya, H.; Tomoike K.; Yuasa K.; Togawa S.; Sekiya T.; Takahashi K.; Kawasaki K. *Journal of the SID.* **1993**, *1/3*, 295-299.
2. Bezou, P. *Synthèse et Caractérisation de Nouveaux Polymères Cristaux Liquides à Chaînes Latérales Chirales*, Thesis, Université P. et M. Curie, Paris, 1994.
3 All compounds were fully characterized by ^1H and ^{13}C-NMR, infrared, mass spectroscopy and elementary analysis.
4 Klarmann, E.; Gates, L.W.; Shternov, V.A. *J. Am. Chem. Soc.* **1932**, *54*, 1204-1211.
5. Schurig, V.; Leyrer, U.; Wistuba, D. *J. Org. Chem.* **1986**, *51*, 242-245.
6. Baillon-Moussel, C. *Synthèse et caractérisation de nouvelles molécules chirales : application aux mélanges smectiques C* ferroélectriques*, Thesis, Université P. et M. Curie, Paris, 1989.
7. Neuberger, A. *Advances Protein Chem.* **1948**, *4*, 297-383.
8. Koppenhoefer, B.; Weber, R.; Schurig, V.; *Synthesis Com.* **1982**, 316-318.

9. The mixture of **11** (1.23 mmol), **6** (1.62 mmol), in presence of DCC and DMAP in $CHCl_3$, filtered over basic alumina, is stirred under N_2 during 24h at rt. After removal of the solvent, the product is purified by flash chromatography on neutral alumina gel (petroleum ether/ethyl acetate v/v 95/05 to 90/10).

10. Hassner, A.; Alexanian U. *Tetrahedron Lett.* **1978**, *46*, 4475-4478

11 Spectral properties of monomers are :

1a : white powder, ^{1}H-NMR (200 MHz, $CDCl_3$) δ 0.9 (3H, t), 1.1 (3H, d), 1.2-1.5 (16H, m), 1.6-1.9 (7H, m), 3.9 (2H, t), 4.2 (3H, m), 4.6 (2H, m), 5.8 (1H, dd), 6.1 (1H, dd), 6.4 (1H, dd), 6.9 (2H, d), 7.3 (2H, d), 7.55 (2H, d), 7.65 (2H, d), 8.2 (2H, d), 8.35 (2H, d), IR (neat) 2924, 2854, 1738, 1501, 1270 cm^{-1}, MS (*m/z*) calcd for $C_{41}H_{51}O_7Cl$ 690, found 663 (M-27 (CH_2=$CH^•$)), 648, 441, 279, Anal calcd C, 71.24; H, 7.44; O, 16.2; Cl, 5.13, found C, 71.68; H, 7.97; O, 15.34; Cl, 4.19, $[\alpha]_D^{25}$= +7 (c 2.8, $CHCl_3$).

1b : white powder, ^{1}H-NMR (200 MHz, $CDCl_3$) δ 0.9 (3H, t), 1.1 (3H, d), 1.2-1.5 (16H, m), 1.6-1.9 (7H, m), 2 (3H, s), 3.9 (2H, t), 4.2 (3H, m), 4.6 (2H, m), 5.6 (1H, s), 6.1 (1H, s), 6.9 (2H, d), 7.3 (2H, d), 7.55 (2H, d), 7.65 (2H, d), 8.2 (2H, d), 8.35 (2H, d), IR (neat) 2924, 2854, 1738, 1501, 1270 cm^{-1}, MS (*m/z*) calcd for $C_{42}H_{53}O_7Cl$ 704, found 704, 662, 647, 614, 441, Anal calcd C, 71.52; H, 7.57; O, 15.88; Cl, 5.03, found C, 72.24; H, 7.83; O, 15.69; Cl, 4.66, $[\alpha]_D^{25}$= +9 (c 2.8, $CHCl_3$).

12 Rodekirch, G.; Rubner, J.; Zschupper, V.; Wolff, D.; Springer, J. *Makromol. Chem.* **1993**, *194*, 1125-1135.

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