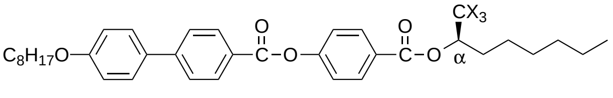
Direct transition from S_A to antiferroelectric, ferroelectric or unknown phases of diastereomeric liquid-crystalline molecules with varying enantiomeric purities

Koichi Mikami,*[a]† Tomoko Yajima,[a] Masahiro Terada,[a] Yoshiichi Suzuki[b] and Ichiro Kobayashi[b]

[a] *Department of Chemical Technology, Tokyo Institute of Technology, Meguro-ku, Tokyo 152, Japan*
[b] *Central Research and Development Laboratory, Showa Shell Sekiyu K.K., 123-1 Shimokawairi, Atugi, Kanagawa 243-02, Japan*

The phase sequences of diastereomeric α-trifluoromethyl-β-methyl-substituted liquid-crystalline molecules critically depend on the enantiomeric purities (% ee) not only for *ul*- but also for *lk*-diastereomers, to show eventually an unknown phase in the racemic region of either an *ul*- or an *lk*-diastereomer.

New types of liquid-crystalline (LC) phases such as ferroelectric[1] (F) (S_{C^*}), antiferroelectric[2] (AF) ($S_{C_A^*}$), ferrielectric[3] ($S_{C_\alpha^*}$ and $S_{C_\gamma^*}$), and twist-grain boundary[4] (TGB) phases have recently been discovered in chiral LC molecules. Amongst these, the AF phase has been studied intensively both experimentally and theoretically, due to its potential applications in electro-optic devices.[5,6] However, only a limited number of AFLC molecules have been reported so far (Fig. 1) such as the methyl-substituted aryl ester (MHPOBC)[5a] and its trifluoromethyl analogue (TFMHPOBC),[5b] which bear a chiral alkyl terminus with a single stereogenic centre. In these, the direct phase transition from S_A to $S_{C_A^*}$ takes place in high enantiomeric excess (% ee) and the S_{C^*} phase occurs between the S_A and $S_{C_A^*}$ phases in the racemic region.[7] In order to investigate the relationship between molecular asymmetry and AFLC properties, we designed α-trifluoromethyl-β-methyl-substituted aryl esters which are diastereomers with double stereogenic centres. We report the intriguing feature that their phase sequence critically depends on the enantiomeric excesses (% ee) not only for *ul*- but also for *lk*-diastereomers.[8] Surprisingly, we also found a direct phase transition from S_A to an unknown phase which shows an intriguing electro-optic response in the racemic composition for both diastereomers.

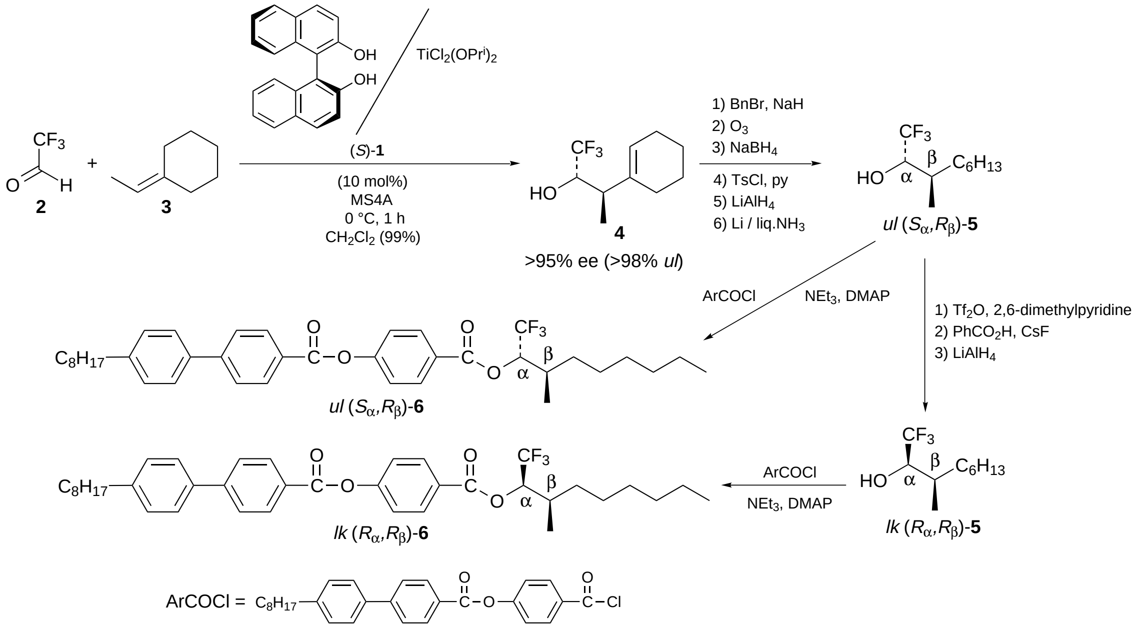


X = H MHPOBC
X = F TFMHPOBC

Fig. 1

Both enantiomers of diastereomeric LC molecules were synthesised through a chiral titanium complex-catalysed carbonyl–ene reaction[9] of fluoral **2** with ethylidenecyclohexane **3**,[10] using an (*S*)- or (*R*)-binaphthol-derived chiral titanium catalyst [(*S*)- or (*R*)-**1**][11] (Scheme 1). The *ul*(S_α,R_β)-alcohol **4** was thus obtained in an almost quantitative yield in more than 95% ee and 95% de, by the use of the (*S*)-binaphthol–titanium catalyst [(*S*)-**1**]. Protection of the alcohol, ozonolysis, reduction and deprotection led to the *ul*(S_α,R_β)-diastereomer **5** in an essentially stereopure form (> 95% ee, > 95% de). Inversion of the stereochemistry of a α-hydroxy group through the triflate derivative with benzoic acid by catalysis with caesium fluoride[12] produced an *lk*(R_α,R_β)-diastereomer **5** again in a stereochemically pure form (> 95% ee, > 95% de). Condensation of *ul*- and *lk*-**5** with 4-chlorocarbonylphenyl 4′-octyloxybiphenyl-4-carboxylate gave the diastereomeric LC molecules *ul*(S_α,R_β)- and *lk*(R_α,R_β)-**6**, respectively.

The phase sequences and transition temperatures for **6** were measured for varying enantiomeric excesses for the *ul*- and *lk*-



Scheme 1

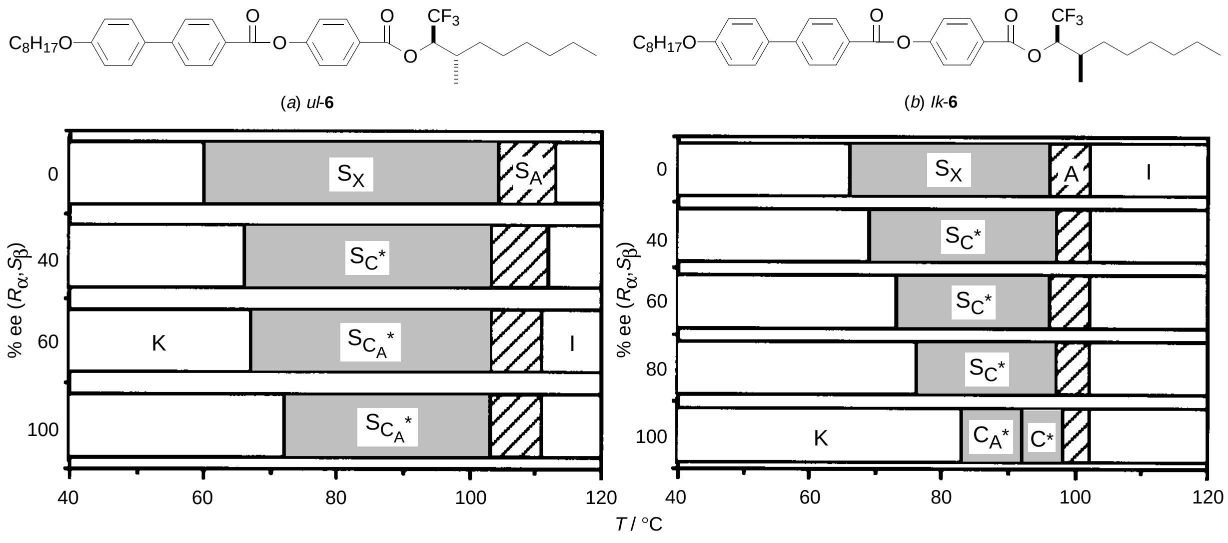


Fig. 2

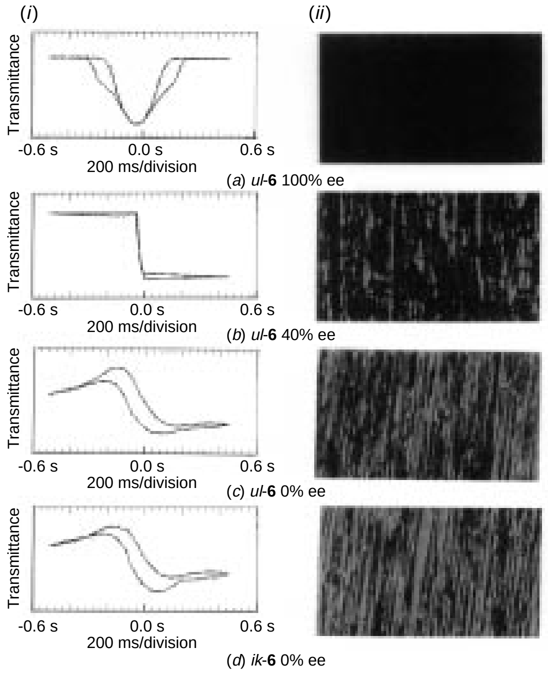


Fig. 3 (*i*) Electro-optic switching characteristic at 90 °C and (*ii*) photomicrographs of the liquid-crystalline phases at 90 °C

diastereomers (Fig. 2). The phase transition from S_A to S_{C_A*} takes place for medium-to-high enantiomeric excesses (60–100% ee) of the *ul*-diastereomer [Fig. 2(*a*)]. Interestingly, the transition from S_A to S_{C*} takes place without any transition from S_{C*} to S_{C_A*} at low enantiomeric excess (40% ee). By contrast, the opposite *lk*-diastereomer shows the transition from S_A to S_{C*} even in the enantiopure form (100% ee) [Fig. 2(*b*)]. Thus, the S_{C_A*} phase is likely to be stabilised in the *ul*-diastereomer. Surprisingly, an unknown phase appears in the racemic region of either the *ul*- or the *lk*-diastereomer. The phase in question is, therefore, referred to as S_X.

The *ul*-diastereomer **6** shows an AF double-loop hysteresis [Fig. 3(*i*)(*a*)] in the medium-to-high enantiomeric range (60–100% ee) and, by contrast, in the low enantiomeric purity (40% ee), a single-loop-hysteresis, characteristic of FLC [Fig. 3(*i*)(*b*)]. However, the electro-optic responses of S_X phases of racemic LC diastereomers show an intriguing type of hysteresis for both *ul*- and *lk*-diastereomers [Fig. 3(*i*)(*c*) and (*d*)]. Furthermore, the kinds of texture in the S_X phases [Fig. 3(*ii*)(*c*), (*d*)] are quite different from those in the S_{C_A*} [Fig. 3(*ii*)(*a*)] and S_{C*} [Fig. 3(*ii*)(*b*)] phases.

In summary, we have demonstrated the first proof that the appearances of antiferroelectric, ferroelectric and unknown phases are controlled by tuning the enantiomeric excesses in diastereomeric liquid-crystalline molecules.

Footnote

† E-mail: kmikami@o.cc.titech.ac.jp

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