Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

Determination of the enantiomeric excess of ferroelectric liquid crystals derived from three natural amino acids

J. Schacht; P. Zugenmaier; F. Horii

Online publication date: 06 August 2010

To cite this Article Schacht, J. , Zugenmaier, P. and Horii, F.(1999) 'Determination of the enantiomeric excess of ferroelectric liquid crystals derived from three natural amino acids', Liquid Crystals, 26: 4, 525 — 533
To link to this Article: DOI: 10.1080/026782999204967
URL: http://dx.doi.org/10.1080/026782999204967

LIQUID CRYSTALS, 1999, VOL. 26, NO. 4, 525–533

Determination of the enantiomeric excess of ferroelectric liquid crystals derived from three natural amino acids

J. SCHACHT*, P. ZUGENMAIER† and F. HORII

Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011, Japan
†Institute of Physical Chemistry, Clausthal University of Technology,
Arnold-Sommerfeld-Straße 4, D-38678 Clausthal-Zellerfeld, Germany

(*Received 27 August 1998; in final form 12 October 1998; accepted 23 October 1998*)

The synthesis and ^{1}H NMR spectra are presented for diastereoisomeric esters based on chiral α-chloro acids which are derived from natural available α-amino acids (L-valine, L-leucine and L-isoleucine) and commonly employed for the synthesis of ferroelectric liquid crystals possessing a high spontaneous polarization. Partial racemization is established as occurring within the formation of the chiral α-chloro acids and their esterification procedure. The enantiomeric excess exceeds 90% for L-isoleucine and L-valine derivatives, whereas an enantiomeric excess of 60% is found for L-leucine derivatives. On the basis of existing data in the literature, the differences in the spontaneous polarization of these derivatives is discussed with regard to the determined enantiomeric excess and their conformational freedom affecting the average lateral dipole moment of a single molecule.

1. Introduction

The synthesis of chiral liquid crystal materials possessing smectic phases of C_2 symmetry, like the SmC* phase, has gained considerable interest due to their expected ferroelectric properties. α-Chloro acids derived form chiral natural amino acids, e.g. L-valine, L-leucine and L-isoleucine (figure 1), have been utilized in synthesizing low molecular mass liquid crystalline esters as well as side chain polymers possessing a large spontaneous polarization [1–6]. The large spontaneous polarization, exceeding 200 nC cm^{-2}, of some of these compounds with the α-chloro ester moiety was almost simultaneously published by Sakurai *et al.* [7] and Bahr and Heppke [8].

The origin of the large spontaneous polarization of these compounds with an α-chloro ester group was ascribed to a large lateral overall molecular dipole moment caused by a superposition of the C–Cl and C=O dipole moments. Steric interactions are supposed to prevent the cancelling of the C–Cl and C=O dipole moments: these molecules prefer a conformation where the bulky aliphatic chain is located near the carbonyl group. Two possible conformations are depicted in figure 2, where conformation (*a*) is favoured for steric reasons. In consequence, both, the C=O and the C–Cl dipoles form a chiral dipolar unit (after averaging all accessible conformations), and both contribute to the average lateral dipole moment. In this model, the bulky

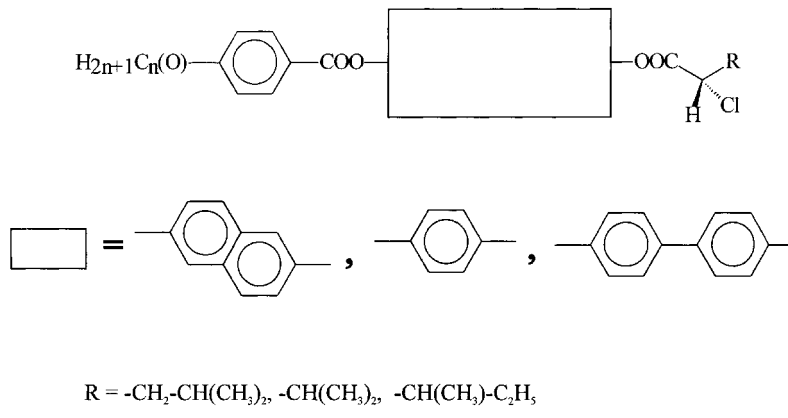
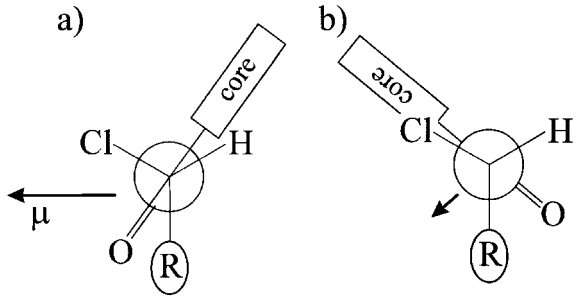


Figure 1. Chemical constitution of some ferroelectric liquid crystal materials derived from naturally available α-amino acids. The integer *n* determines the number of carbon atoms in an alkyl or alkoxy group and *R* represents the aliphatic tail of L-isoleucine, L-valine and L-leucine, respectively, as indicated.

*Author for correspondence.

Journal of Liquid Crystals ISSN 0267-8292 print/ISSN 1366-5855 online
http://www.tandf.co.uk/JNLS/lct.htm
http://www.taylorandfrancis.com/JNLS/lct.htm



R = -CH_2-$CH(CH_3)_2$, -$CH(CH_3)_2$, -$CH(CH_3)$-C_2H_5

Figure 2. Schematic representation of conformations of the chiral (Cl)C*–CO unit of the molecules depicted in figure 1 (projection normal to the single bond to the dipolar unit). For steric reasons, the bulky aliphatic residue *R* of the α-amino acid (see figure 1) and the aromatic core are placed approximately antiperiplanar. This can be realized in two ways: (*a*) the mesogenic core is placed near the H atom, hence, forcing the dipole moments of the C–Cl and the C=O groups to add up to a large lateral dipole moment μ, and (*b*) the mesogenic core is paced near the comparably bulky chlorine atom, in which case the C–Cl and the C=O dipoles almost compensate and the overall lateral dipole moment is almost cancelled.

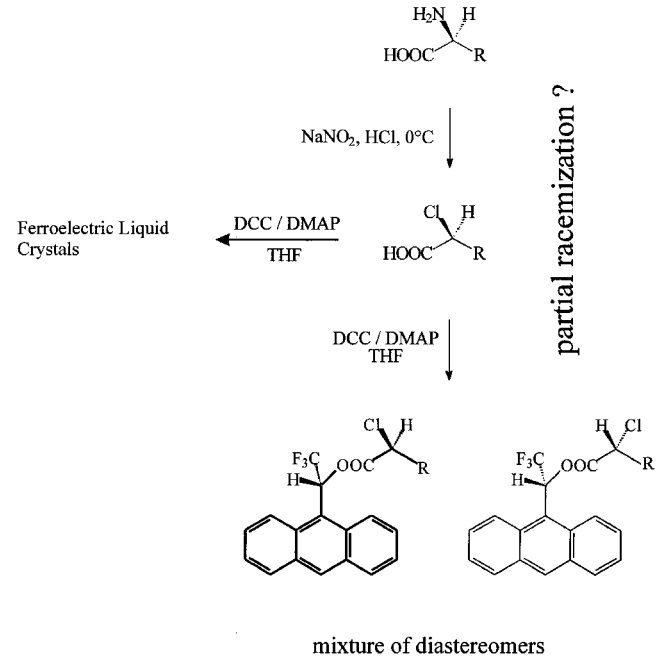


Figure 3. Pathway of synthesis: substitution of the amino group by chlorine affords an α-chloro acid. Using dicyclohexylcarbodiimide (DCC) and dimethylaminopyridine (DMAP), esterification of these acids with aromatic alcohols forms ferroelectric liquid crystal materials, or with chiral 1-(9-anthryl)-2,2,2-trifluoroethanol creates diastereomers. The degree of partial racemization determines the composition of the mixture of diastereomers. (The aliphatic group *R* has been defined in figure 1.)

aliphatic chain clicks this chiral dipolar unit into place. This effect was realized very early, because Sakurai *et al.* [7] stated: 'Though the origin of this novel ferroelectricity in these new materials is not clear at this stage, it may be due to the existence of large bulky groups, e.g. branched alkyl, aralkyl, or phenyl groups, near the chiral centre.' The lower spontaneous polarization of compounds derived from L-leucine in comparison with those derived from L-valine or L-isoleucine was reported by Twieg *et al.* [9]: 'The leucine tail displays the lowest P_S value in the series, presumably because the C–Cl group is separated from the bulky isopropyl group by an additional methylene unit, and thus their steric interactions are minimal.' The significance of this effect on the spontaneous polarization of α-chloro esters has been established by computer simulations [10].

The enantiomeric excess and the synthesis of different α-chloro esters derived from optically pure L-valine, L-leucine and L-isoleucine are reported in this work. It is shown that partial racemization occurs for L-leucine derivatives in a synthetic route that is commonly applied to produce ferroelectric liquid crystals. This result is discussed with respect to the origin of the high spontaneous polarization of these derivatives in relation to the average shape of the chiral dipole of molecules and its averaged lateral dipole moment (see figure 3). The influence of conformational changes on the average shape of the chiral dipole is discussed qualitatively, and new measurements of the spontaneous polarization of different compounds are compared with existing measurements and computer simulations reported in literature.

2. Experimental

The spontaneous polarization and its temperature dependence was investigated by the triangle wave method [11]. An electric field with a frequency of 210 Hz and an amplitude of 2 MV m^{-1} is used to achieve saturated switching in the SmC* phase. Ionic impurities do not affect the polarization reversal current at this considerably high frequency, but, due to the low viscosity of these materials, saturated ferroelectric switching occurs up to 2.5 kHz at an amplitude of the electric field of 2 MV m^{-1}.

^{1}H NMR spectra were obtained from a Brucker ARX (400 MHz) spectrometer with tetramethylsilane (TMS) as internal standard and deuteriochloroform ($CDCl_3$) as solvent. Mass spectra were obtained from a HP 4989B mass spectrometer (70 eV, direct injection probe). All chemicals and solvents were obtained from Sigma-Aldrich GmbH and were used without further purification. Dry THF was used as a solvent for the esterifications.

2.1. *(2S)-2-Chloro-4-methylpentanoic acid*

The synthesis of α-chloro acids [12] given by Fu *et al.* [13] was modified as follows: 0.2 mol (25 g) of L-leucine was dissolved in a mixture of 550 cm^3 of 37% HCl and 260 cm^3 of water at room temperature. The solution was cooled to − 3°C. During a period of 5 h, 0.32 mol (22 g) of solid $NaNO_2$ was added in small portions with vigorous stirring. The solution turned yellow and phase separation of the crude product from the inorganic medium occurred. Stirring was continued for another 4 h and the temperature was allowed to increase to room temperature. The solution was quenched with 1200 cm^3 of an ice/water mixture and shaken with chloroform ($3 \times 300\ cm^3$). The combined organic extracts were washed with water ($2 \times 100\ cm^3$) and dried over anhydrous $MgSO_4$. The solvent was evaporated and the crude product distilled under reduced pressure to afford 18 g of (2*S*)-2-chloro-4-methylpentanoic acid, yield 18 g (60%); b.p. 109°C, 10 mm Hg (lit.: b.p. 110–112°C, 10 mm Hg [14]); $n_D^{25} = 1.4441$. ^{1}H NMR δ ($CDCl_3$, 400 MHz): 0.94 (3H, d, $J = 6.1$ Hz, C**H**$_3$), 0.98 (3H, d, $J = 6.1$ Hz, C**H**$_3$), 1.05 (1H, m, C**H**(CH$_3$)$_2$), 1.87 (2H, m, **H**CH–CH(CH$_3$)$_2$), 4.35 (1H, m, C**H**(Cl)), 8.8 (1H, broad, COO**H**). ^{13}C{^{1}H} NMR δ ($CDCl_3$, 100 MHz): 21.0 (**C**H$_3$), 22.6 (**C**H$_3$), 25.1 (**C**H(CH$_3$)$_2$), 43.3 (**C**H$_2$), 55.6 (**C**H(Cl)), 175.9 (**C**OOH); *m/z* 150, 152 (M^+, 10%), 133 (9), 94 (32), 73 (48), 69 (75), 57 (70), 43 (100), 39 (45).

2.2 *Synthesis of diastereomers*

2.2.1 *(2S)-[(1R)-1-(9-Anthryl)-2,2,2-trifluoroethyl] 2-chloro-4-methylpentanoate (1RS)*

Quantities 0.17 mmol (26 mg) of (2*S*)-2-chloro-4-methylpentanoic acid and 0.15 mmol (41 mg) of (*R*)-1-(9-anthryl)-2,2,2-trifluoroethanol [15, 16] were dissolved in 2 cm^3 of dry THF; 0.2 mmol (41 mg) of DCC and 1 mg of DMAP were added and the reaction mixture was stirred overnight at room temperature. The white precipitate was filtered off. THF was evaporated under reduced pressure, and the crude product purified by column chromatography (CH_2Cl_2 as eluant) to yield 46 mg (66%) of 1RS in the form of a colourless oil. ^{1}H NMR δ ($CDCl_3$, 400 MHz): 0.76 (3H, d, $J = 6.6$ Hz, CH(C**H**$_3$)), 0.785 (3H, d, $J = 6.6$ Hz, CH(C**H**$_3$)), 1.65 (1H, dd, $J = 6.6$ Hz, HC**H**–CH(CH$_3$)$_2$), 1.73 (1H, dd, $J = 6.6$ Hz, **H**CH–CH(CH$_3$)$_2$), 1.79 (1H, m, HCH–C**H**(CH$_3$)$_2$), 4.38 (1H, dd, $J = 6.6$ Hz, C**H**(Cl)), 7.38–7.60 (4H, m), 7.74 (1H, m), 7.96 (2H, m), 8.27 (1H, d), 8.50 (1H, s), 8.61 (1H, d). ^{13}C{^{1}H} NMR δ ($CDCl_3$, 100 MHz): 21.7, 22.8 (CH(**C**H$_3$)$_2$), 25.4 (**C**H(CH$_3$)$_2$), 43.7 (**C**H$_2$CH(Cl)), 55.7 (**C**H(Cl)), 120.6–132.1 (**C** arom.), 168.7 (H(Cl)C–**C**OO); *m/z* 408, 410 (M^+, 94%), 389 (0.5), 372 (1), 259 (100), 239 (20), 207 (80), 179 (23), 178 (25), 151 (10), 97 (8), 69 (10), 55 (13), 43 (15).

2.2.2 *(2S)-[(1R)-1-(9-anthryl)-2,2,2-trifluoroethyl] 2-chloro-3-methylbutanoate (2RS)*

Esterification of (1*R*)-1-(9-anthryl)-2,2,2-trifluoroethanol with (2*S*)-2-chloro-3-methylbutanoic acid afforded (2*S*)-[(1*R*)-1-(9-anthryl)-2,2,2-trifluoroethyl]-2-chloro-3-methylbutanoat (2RS): yield: 75%. ^{1}H NMR δ ($CDCl_3$, 400 MHz): 0.87 (3H, d, $J = 6.6$ Hz, CH(C**H**$_3$)), 0.94 (3H, d, $J = 6.6$ Hz, CH(C**H**$_3$)), 2.30–2.40 (1H, m, C**H**(CH$_3$)$_2$), 4.28 (1H, d, $J = 6.1$ Hz, C**H**(Cl)), 7.43–7.70 (4H, m), 7.82 (1H, q), 8.04 (2H, m), 8.34 (1H, d), 8.58 (1H, s), 8.70 (1H, d); *m/z* 394, 296 (M^+, 100%), 375 (0.5), 358 (0.5), 259 (92), 239 (15), 207 (68), 179 (17), 178 (21), 151 (10), 97 (7), 69 (12), 55 (17), 43 (21).

2.2.3 *(2S,3S)-[(1R)-1-(9-anthryl)-2,2,2-trifluoroethyl] 2-chloro-3-methyl-pentanoate (3RSS)*

Esterification of (1*R*)-1-(9-anthryl)-2,2,2-trifluoroethanol with (2*S*,3*S*)-2-chloro-3-methylpentanoic acid afforded 3RSS, yield 90%. ^{1}H NMR δ ($CDCl_3$, 400 MHz): 0.68 (3H, t, $J = 7.1$ Hz, CH$_2$C**H**$_3$), 0.92 (3H, d, $J = 6.6$ Hz, H$_5$C$_2$CH(C**H**$_3$)), 1.12–1.41 (2H, m, C**H**$_2$(CH$_3$)), 2.11 (1H, m, H$_5$C$_2$C**H**(CH$_3$)), 4.34 (1H, d, $J = 6.6$ Hz, C**H**(Cl)), 7.45–7.69 (4H, m), 7.84 (1H, q), 8.04 (2H, dd), 8.36 (1H, d, $J = 9.2$ Hz), 8.59 (1H, s), 8.70 (1H, d, $J = 8.1$ Hz); *m/z* 408, 410 (M^+, 100%), 372 (2), 259 (90), 239 (15), 207 (67), 179 (19), 178 (25), 151 (9), 97 (7), 69 (12), 55 (22), 43 (10).

3. Results and discussion

The α-amino acid L-isoleucine contains two asymmetric C atoms, one of which (the β-C atom) is located in the aliphatic chain and assumed to be unaffected by the chemical reactions carried out under the conditions described in the experimental section. Therefore, a mixture of diastereomers, namely (2*S*,3*S*)-2-chloro-3-methylpentanoic acid and (2*R*,3*S*)-2-chloro-3-methylpentanoic acid, will be formed, if partial racemization occurs during the substitution of the amino group by chlorine. Only one of these diastereomers, (2*S*,3*S*)-2-chloro-3-methylpentanoic acid, is detected in the ^{1}H NMR spectrum of the product; therefore, the degree of partial racemization is low in this case, assuming that the ^{1}H NMR spectra of both diastereomers do not completely overlap by chance.

However, esterification of a pure diastereomer, say (2*S*,3*S*)-2-chloro-3-methylpentanoic acid, with the pure (*R*) enantiomer of 1-(9-anthryl)-2,2,2-trifluoroethanol affords an ester, 3RSS, containing three asymmetric carbons, as can be seen from figure 4. In the range of chemical shifts of the methyl groups, the ^{1}H NMR spectrum of compound 3RSS is depicted in the lower part of the panel in figure 4. The methyl group located at one of the asymmetric carbons (β-C atom) appears as a doublet with its centre at $\delta = 0.937$, whereas the signal

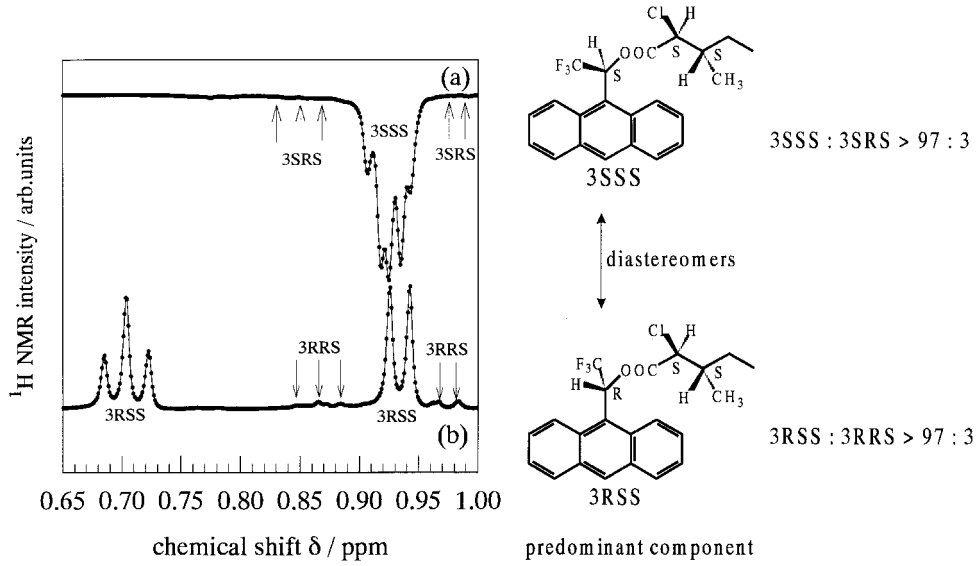


Figure 4. ^{1}H NMR spectra displayed in the region of chemical shift for the methyl groups of the diastereomers obtained from the α-chloro acid derived from L-isoleucine. Esterification with (*a*) pure (1*S*)-1-(9-anthryl)-2,2,2-trifluoroethanol affords the esters 3SSS and, due to partial racemization, 3SRS (spectrum is turned upside down); with (*b*) pure (1*R*)-1-(9-anthryl)-2,2,2-trifluoroethanol a mixture of 3RSS and 3RRS is formed.

of the primary methyl group appears (approximately) as a triplet located at $\delta = 0.705$. The small peaks marked by the arrows in this spectrum might be assigned to the different diastereomer 3RRS, where the configuration of the α-C atom carrying the chlorine atom has been changed. This diastereomer (3RRS) is formed by partial racemization during the synthesis of these compounds, but its content is determined as lower than 3%, which is close to the resolution limit of this method.

On the other hand, esterification of the α-chloro acid previously used, (2*S*,3*S*)-2-chloro-3-methylpentanoic acid, with the mirror image of the aromatic alcohol, (1*S*)-1-(9-anthryl)-2,2,2-trifluoroethanol, yields the diastereomer 3SSS whose ^{1}H NMR spectrum is depicted in the upper part of the panel in figure 4. In this case, the signals of both methyl groups overlap in the region between $\delta = 0.900$ and $\delta = 0.955$. Again, the small peaks marked by the arrows might be assigned to the 3SRS diastereomer, which is formed by partial racemization and whose content is less than 3% with respect to the total amount of product formed in the esterification step. The following conclusions have to be drawn:

(1) The enantiomeric excess of the chiral aromatic alcohol used for esterification is larger than 94% in accordance with the reference given by Aldrich-Sigma GmbH.
(2) In the case of L-isoleucine derivatives, the degree of partial racemization during the formation of the α-chloro acid and its esterification with aromatic alcohols using the DCC/DMAP method is very small. Therefore, the diastereomeric excess of the corresponding esters exceeds 94%.

L-Valine contains a single asymmetric carbon (α-C atom). Therefore, both methyl groups of the isopropyl group attached to the chiral centre are diastereotopic, and two well-separated doublets are assigned to them in their ^{1}H NMR spectrum, each of which shows a normalized integral intensity equal to three protons. After substitution of the amino group by chlorine, esterification of (2*S*)-2-chloro-3-methylbutanoic acid with pure (1*R*)-1-(9-anthryl)-2,2,2-trifluoroethanol affords 2RS. Part of the ^{1}H NMR spectrum of 2RS is depicted in the lower part of the panel in figure 5: the two large doublets located at $\delta = 0.905$ and $\delta = 0.968$ are assigned to the 2RS diastereomer. Partial racemization causes the formation of the diastereomer 2RR whose two diastereomeric methyl groups can be seen at $\delta = 0.967$ and $\delta = 1.050$, as indicated by the arrows. (Compound 2SS is the mirror image of 2RR, and their ^{1}H NMR spectra are equivalent in a non-chiral solvent. Hence, the doublet of 2RR at $\delta = 0.967$ overlaps with the doublet of 2RS at $\delta = 0.968$.) Comparing the integral intensity of the pairs of doublets, the large excess of the 2RS compound in the mixture of the diastereomers can be noted (>95 : 5). In consequence, the degree of partial racemization is concluded to be small for the valine derivatives as well. This is only correct if chiral differentiation, which defines the preferred formation of a specific diastereomer during the synthesis, as well as

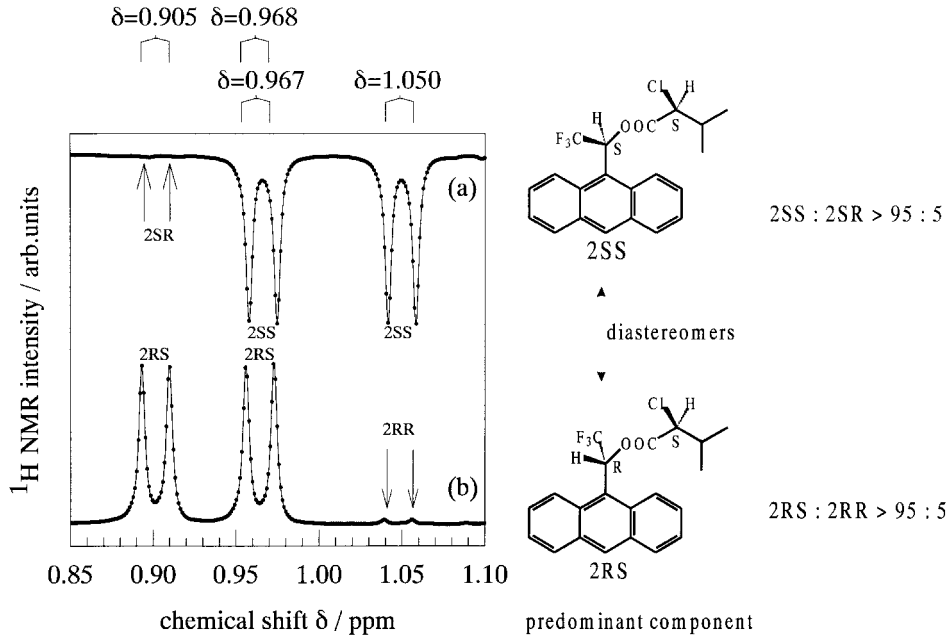


Figure 5. ^{1}H NMR spectra displayed in a similar way to that in figure 4. Esterification of the α-chloro acid derived from L-valine with (*a*) pure (1*S*)-1-(9-anthryl)-2,2,2-trifluoroethanol affords a mixture of 2SS and 2SR (spectrum is turned upside down), whereas a reaction with (*b*) pure (1*R*)-1-(9-anthryl)-2,2,2-trifluoroethanol affords a mixture of compounds 2RS and 2RR.

enrichment of one of these diastereomers during the purification steps, is negligible.

As a proof, esterification of (2*S*)-2-chloro-3-methylbutanoic acid with (1*S*)-1-(9-anthryl)-2,2,2-trifluoroethanol affords the diastereomer 2SS with the ^{1}H NMR spectrum depicted in the upper part of the panel in figure 5. The two big doublets are related to the 2SS diastereomer (mirror image of 2RR), which is the predominant component in this mixture. As a consequence of partial racemization, the 2SR diastereomer (mirror image of 2RS) is formed. The doublets due to the absorption of the methyl groups are indicated by the arrows. In accordance with the previous result, the ratio of both diastereomers can be deduced from integration of the spectrum; 2SS : 2SR = 95 : 5 and chiral differentiation is excluded. Two important results are worth summarizing:

(1) Chiral differentiation is negligible during the synthesis of these diastereoisomers and an enrichment of a particular diastereomer during the purification steps cannot be verified experimentally.
(2) The diastereomeric excess of the α-chloro esters derived from L-valine exceeds 90%.

Esterification of (2*S*)-2-chloro-4-methylpentanoic acid derived from L-leucine with pure (1*R*)-1-(9-anthryl)-2,2,2-trifluoroethanol yields the compound 1RS whose diastereotopic methyl groups exhibit two well separated doublets at $\delta = 0.762$ and $\delta = 0.785$ as shown in figure 6. In contrast to the spectra previously discussed, two additional doublets of considerably high intensity occur at $\delta = 0.760$ and $\delta = 0.839$, the former as a shoulder. These ^{1}H NMR signals have to be assigned to the 1RR diastereomer, which is formed by partial racemization in this case. The ratio of the concentration of both diastereomers is determined from integration of this ^{1}H NMR spectrum; 1RS : 1RR = 80 : 20. The diastereomeric excess of ee = 60% is significantly lower compared to that for the L-isoleucine and L-valine derivatives.

As proof, esterification of (2*S*)-2-chloro-4-methylpentanoic acid with pure (1*S*)-1-(9-anthryl)-2,2,2-trifluoroethanol leads to the diastereomer 1SS (80%) being the mirror image of the 1RR ester discussed above. The compound 1SS displays two doublets located at $\delta = 0.760$ and $\delta = 0.839$ as depicted in figure 7, whereas partial racemization causes the formation of diastereomer 1SR (20%, mirror image of 1RS) showing two doublets located at $\delta = 0.762$ and $\delta = 0.785$, with the former appearing again as a shoulder. The composition of this mixture is determined from integration of these doublets; 1SS : 1SR = 80 : 20. In accordance with the results described above, chiral differentiation during the synthesis, as well as any enrichment of a particular diastereomer during the purification of these compounds can be excluded. In consequence, the degree of partial racemization due to the synthesis of these esters depends on the specific α-amino acids from which the synthesis starts: for esters based on L-isoleucine, the diastereomeric

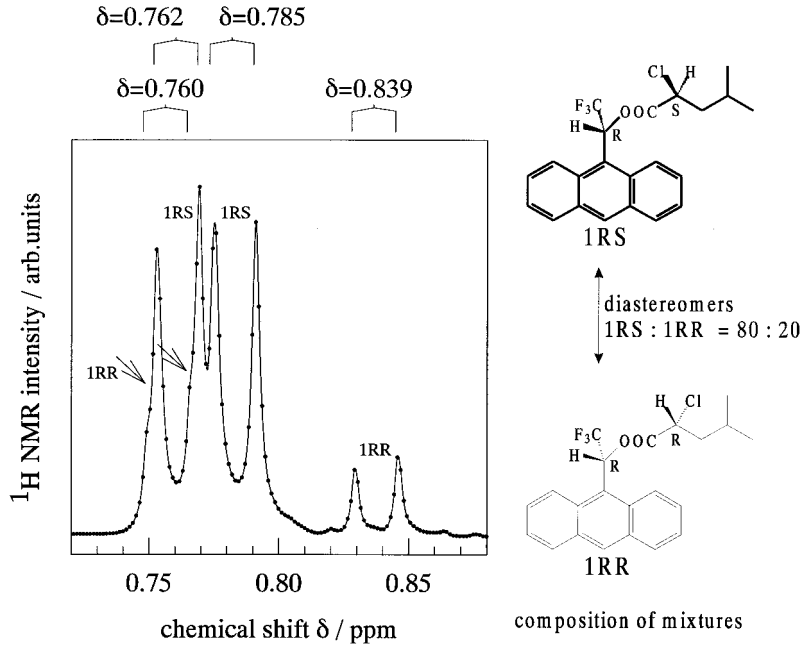


Figure 6. ^{1}H NMR spectra depicted in the region of the diastereotopic methyl groups of the mixture of esters obtained from esterification of the α-chloro acid derived from L-leucine and (1*R*)-1-(9-anthryl)-2,2,2-trifluoroethanol. The product contains 80% of 1RS and 20% of 1RR formed by partial racemization; thus, a diastereomeric excess of 60% is obtained.

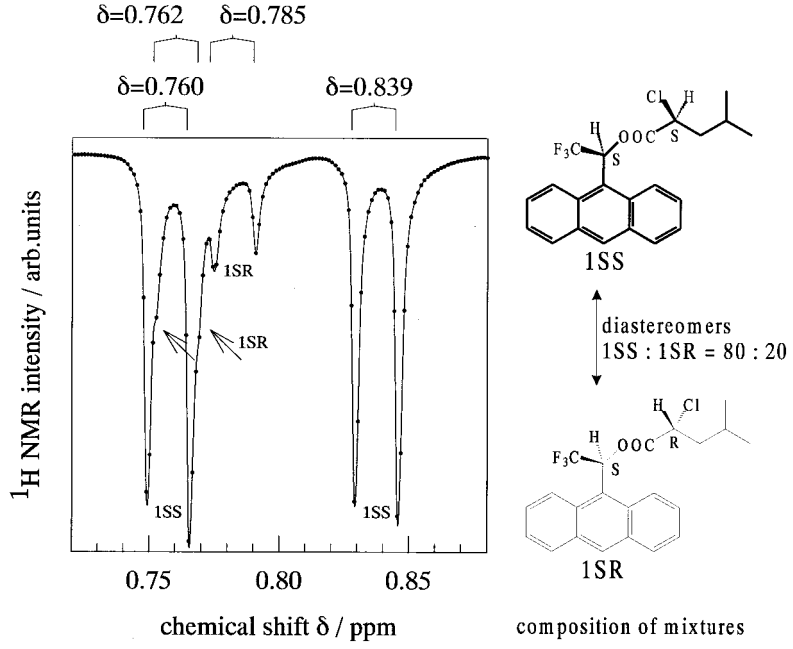


Figure 7. ^{1}H NMR spectra of esters obtained from esterification of the α-chloro acid derived from L-leucine and (1*S*)-1-(9-anthryl)-2,2,2-trifluoroethanol: a diastereomeric excess of 60% is determined.

excess exceeds 97%; it amounts to approximately 95% for L-valine derivatives; a significantly lower diastereomeric excess of 60% has been verified for the esters derived from L-leucine.

It has to be stressed that these results provide evidence that partial racemization within the two step straightforward synthesis of these esters does occur (see figure 3), and that it depends on the particular α-amino acid being used. At present it is not clear in which of the two steps of the synthesis partial racemization occurs, or whether it occurs in both, namely in the formation of the α-chloro acid via a double inversion process of the S_N2 type depicted in figure 8 or/and in the esterification employing the DCC/DMAP method. However, for (2*S*)-2-chloro-4-methylpentanoic acid an enantiomeric excess larger than 95% is reported by Koppenhoefer and Schurig [14]. On the basis of this result, the partial racemization may predominantly occur in the esterification procedure.

Here it is assumed that the degree of partial racemization for the respective α-amino acid is a characteristic of the pathway of synthesis outlined in figure 3. This degree of racemization is assumed to be independent

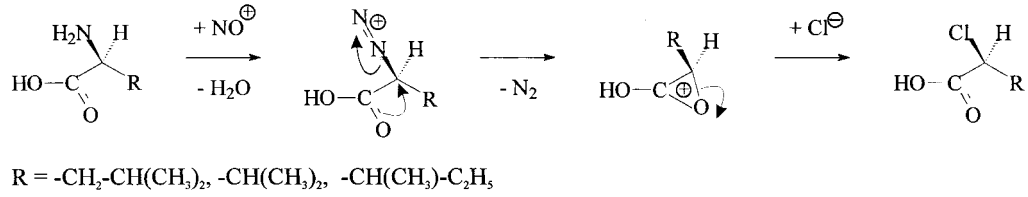


Figure 8. Synthesis of the α-chloro acids: a double inversion process is involved during the substitution of the amino group by chlorine.

of the chemical structure of the aromatic alcohol that is used in the esterification step. This aromatic alcohol might be a building block of ferroelectric liquid crystal compounds such as those schematized in figure 1. It is interesting that ferroelectric liquid crystals derived from L-isoleucine exhibit a diastereomeric excess larger than 97%, those synthesized from L-valine an enantiomeric excess of approximately 95%, whereas L-leucine derivatives exhibit an enantiomeric excess of only 60%. The consequences of this for the spontaneous polarization of ferroelectric liquid crystal materials is discussed below.

The spontaneous polarization of a chiral liquid crystal depends on the enantiomeric excess, the director tilt angle, the number of molecules in the unit volume, the biasing of the rotation around the molecular long axis, and the average lateral molecular dipole moment, quantities which are interrelated to some extent. To compare the spontaneous polarization of SmC* materials with respect to the average lateral dipole moment, compounds of equal molecular mass, of approximately equal density, and of a similar evolution of their temperature dependent tilt angle should be selected. The spontaneous polarizations of different homologous series of the type depicted in figure 1 are taken from literature searches and depicted in figure 9 for comparison. As Twieg *et al.* [9] pointed out, a comparison of L-isoleucine, L-leucine and L-valine derivatives shows that the L-isoleucine derivatives exhibit the highest spontaneous polarization, closely followed by the L-valine derivatives, whereas the L-leucine derivatives exhibit a significantly lower spontaneous polarization of *c.* 60%, independent of the mesogenic core that has been used, which confirms the initial assumption.

The enantiomeric excess of ferroelectric liquid crystal materials might be influenced by slightly different reaction conditions that are reported, but the significant differences in the spontaneous polarizations of the various compounds depicted in figure 9, stemming from a comparison of the results of independent work reported by different authors, are significant.

For the spontaneous polarization, a linear dependence with regard to the enantiomeric excess [19] has been established, as can be inferred from figure 10. Therefore, the lower spontaneous polarization of the L-leucine derivatives is predominantly caused by the smaller enantiomeric excess, as a result of partial racemization

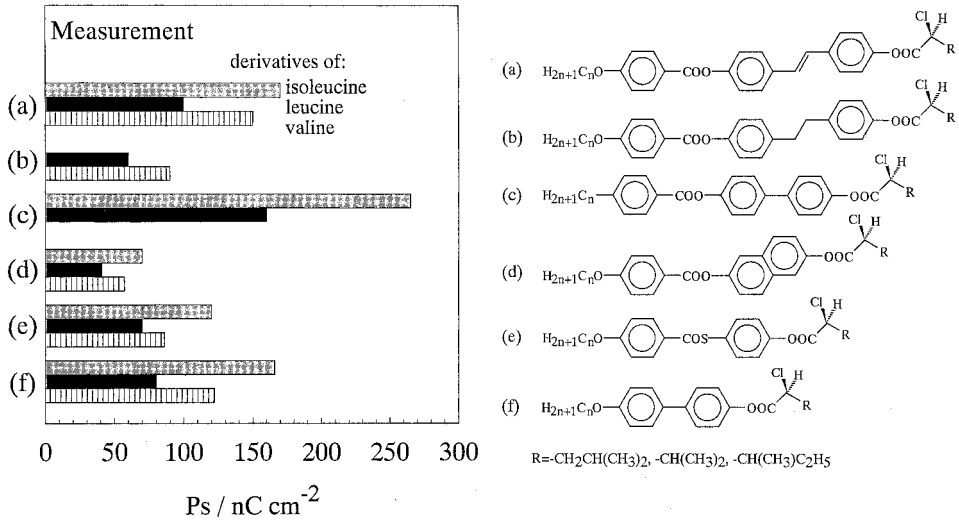


Figure 9. Spontaneous polarizations of different homologous series of the type depicted in figure 1. The mesogenic core and the length of the non-chiral aliphatic chain are altered: (*a*) *trans*-stilbene derivatives [17], (*b*) bibenzyl derivatives [5, 17], (*c*) biphenyl derivatives (three aromatic rings) [17, 18], (*d*) 2,6-disubstituted naphthyl derivatives [10], (*e*) phenyl derivatives [9], (*f*) biphenyl derivatives (two aromatic rings) [8].

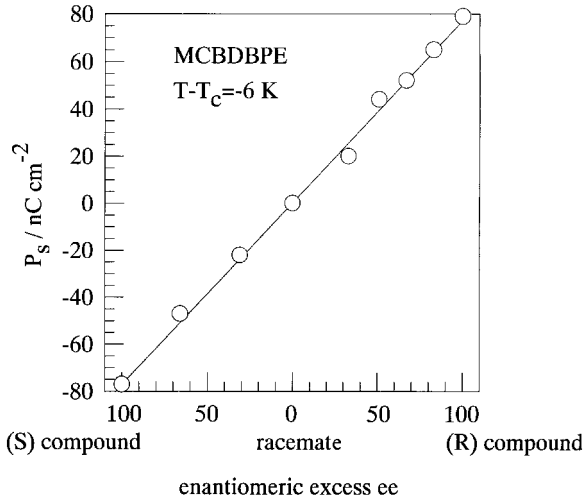


Figure 10. Linear dependence of the spontaneous polarization on the enantiomeric excess measured for binary mixtures of 4-[(2*R*)-2-chloro-3-methylbutanoyloxy]phenyl 4-decyloxybenzoate (MCBDBPE [20]) and its mirror image.

during synthesis. On the basis of a linear dependence, the values of the spontaneous polarization shown in figure 9 are extrapolated to the corresponding pure enantiomer (ee = 100%) for each particular compound and the results are depicted in figure 11. The differences in spontaneous polarization of the derivatives of the three α-amino acids are then much less pronounced.

In general, the effect of the bulky aliphatic chain clicking the chiral dipole composed of the C=O and C–Cl dipoles into a position, such that the dipole moments do not compensate each other, might be responsible for the formation of the comparably large spontaneous polarizations of these compounds. By taking the enantiomeric excess into account, the effect of some additional conformational freedom in the aliphatic tail connected with the insertion of a methylene group between the isopropyl group and the asymmetric carbon (α-C atom), so reducing the average lateral dipole moment of the L-leucine derivatives in comparison with L-valine derivatives, has much less influence on the spontaneous polarization than the computer simulation reveals [10].

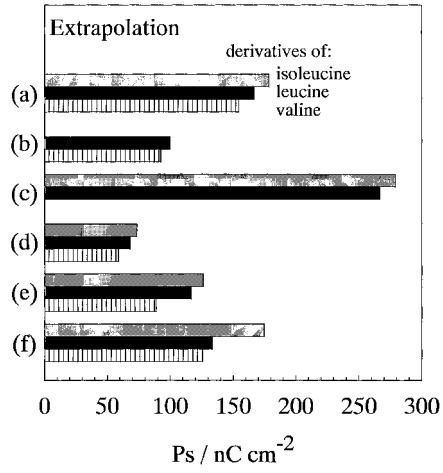


Figure 11. Extrapolated values of the spontaneous polarizations depicted in figure 9.

4. Summary and conclusion

Ferroelectric liquid crystal materials derived from naturally available α-amino acids, L-isoleucine, L-valine and L-leucine, exhibit a large spontaneous polarization, probably due to reinforcement of the C=O and the C–Cl dipoles, both of which form a chiral dipolar unit stabilized by the bulky aliphatic group directly attached to this unit [7, 9]. The insertion of a methylene group between the C–Cl group and the isopropyl group, as in L-leucine derivatives, has been reported to increase the flexibility of these molecules and reduce the average contribution of the C=O dipole to the chiral dipolar unit. In consequence, this conformational effect explains the significantly smaller spontaneous polarization of L-leucine derivatives in comparison with those of L-valine and L-isoleucine derivatives.

In this work, diastereomers are produced by application of exactly the synthetic route commonly applied for ferroelectric liquid crystal materials. Their disastereoisomeric excess is determined by evaluation of the ^{1}H NMR spectra and reveals that almost no partial racemization occurs in the case of the L-isoleucine and L-valine derivatives, whereas partial racemization leads to a smaller diastereomeric excess of 60% in the case of the L-leucine derivative. Application of this result to ferroelectric liquid crystals produced generally by this synthetic route means that the enantiomeric excess of L-leucine derivatives cannot exceed 60%. Consequently, this result provides a simple explanation for the smaller spontaneous polarization observed for all L-leucine derivatives in comparison with L-valine or L-isoleucine derivatives. Therefore, the insertion of a methylene group between the C–Cl dipole and the isopropyl group affects the spontaneous polarization less than the computer simulation predicts [10].

J.S. is indebted to the Alexander von Humboldt Foundation for a Feodor–Lynen Fellowship and to the Japan Society for the Promotion of Science (JSPS) for a Postdoctoral Fellowship for Foreign Researchers.

References

[1] Yoshino, K., Ozaki, M., and Kisho, S., 1987, *Mol. Cryst. liq. Cryst.*, **144,** 87.

[2] Mohr, K., Köhler, S., Worm, K., Pelzl, G., Diele, S., Zaschke, H., Demus, D., Andersson, G., Dahl, I.,

LAGERWALL, S. T., SKARP, K., and STEBLER, B., 1987, *Mol. Cryst. liq. Cryst.*, **146,** 151.
[3] SLANEY, A. J., and GOODBY, J. W., 1995, *J. mater. Chem.*, **5,** 663.
[4] BREHMER, M., and ZENTEL, R., 1994, *Macromol. Chem. Phys.*, **195,** 1891.
[5] DIERKING, I., GIEßELMANN, F., KUßEROW, J., and ZUGENMAIER, P., 1994, *Liq. Cryst.*, **17,** 243.
[6] SCHACHT, J., DIERKING, I., GIEßELMANN, F., MOHR, K., ZASCHKE, H., KUCZYNSKI, W., and ZUGENMAIER, P., 1995, *Liq. Cryst.*, **19,** 151.
[7] SAKURAI, T., MIKAMI, N., HIGUCHI, R., HONMA, M., OZAKI, M., and YOSHINO, K., 1986, *J. chem. Soc. chem. Commun*, 978.
[8] BAHR, CH., and HEPPKE, G., 1987, *Mol. Cryst. liq. Cryst.*, **148,** 29.
[9] TWIEG, R. J., BETTERTON, K., NGUYEN, H. T., TANG, W., and HINSBERG, W., 1989, *Ferroelectrics*, **91,** 243.
[10] SIERRA, T., SERRANO, J. L., ROS, M. B., EZCURRA, A., and ZUBIA, J., 1992, *J. Am. chem. Soc.*, **114,** 7645.
[11] MIYASATO, K., ABE, S., TAKEZOE, H., FUKUDA, A., and KUZE, E., 1983, *Jpn J. appl. Phys.*, **22,** L661.
[12] KARRER, P., RESCHOWSKY, H., and KAASE, W., 1947, *Helv. Chim. Acta*, **30,** 271.
[13] FU, C. S. J., BIRNBAUM, S. M., and GREENSTEIN, J. P., 1954, *J. Am. chem. Soc.*, **76,** 6054.
[14] KOPPENHOEFER, B., and SCHURIG, V., 1987, *Org. Synth.*, **66,** 151.
[15] PIRKLE, W. H., and SIKKENGA, D. L., 1977, *J. org. Chem.*, **42,** 1370.
[16] PIRKLE, W. H., SIKKENGA, D. L., and PAVLIN, M. S., 1977, *J. org. Chem.*, **42,** 384.
[17] SCHACHT, J., 1997, PhD thesis, Clausthal University of Technology, Clausthal-Zellerfeld, Germany.
[18] SCHACHT, J., BAETHGE, H., GIEßELMANN, F., and ZUGENMAIER, P., 1998, *J. Mater. Chem.*, **8,** 603.
[19] BAHR, CH., HEPPKE, G., and SABASCHUS, B., 1988, *Ferroelectrics*, **84,** 103.
[20] GIEßELMANN, F., and ZUGENMAIER, P., 1993, *Mol. Cryst. liq. Cryst.*, **237,** 121.