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Chiral Induction

Chiral Induction in Lyotropic Liquid Crystals: Insights into the Role of Dopant Location and Dopant Dynamics**

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In the nematic phase N of a lyotropic liquid crystal (LLC), anisometric amphiphile micelles, which are surrounded by a solvent (mostly water), exhibit long-range orientational order along the director **n**. Chiral dopants induce the chiral nematic (cholesteric) phase N* with a helical superstructure of the director field (Figure 1) without any concentration threshold.

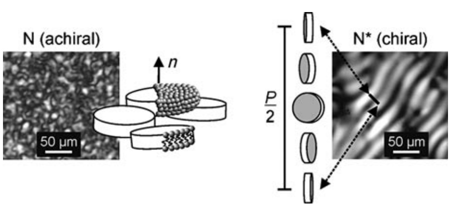

Figure 1. Schlieren texture and model of the nematic (N) LLC host phase with disk-like micelles (left). Fingerprint texture and model of the chiral nematic (N*) phase; micelles represent the helical modulation of the director **n** with pitch *P* induced by doping the host phase with 4.37% *R*-MA (right).

The pitch *P* of the helix can be directly observed in the polarizing optical microscope as the periodic pattern of the "fingerprint texture". Chiral induction in liquid crystals (LCs) is one of the most sensitive methods for the detection of chirality.[1] The unique chirality effects in LCs have been studied widely,[2] including the molecular induction mechanism in thermotropic LCs[3] and in a self-assembled two-dimensional model system.[4]

For LLCs, however, the molecular induction mechanism in the N* phase has been a matter of discussion for more than 20 years.[5–11] There are two proposed mechanisms: a) a dispersive chiral interaction between dopants in adjacent micelles (the dopant should preferentially be located at the micellar surface), and b) a steric dopant–amphiphile interaction yielding distorted micelles (in this case the solubilization of the chiral dopant within the micelle should be favorable).[6,10,11] The temperature dependence of the pitch $P(T)$ is expected to differ for the two mechanisms: in (a), P increases linearly with T, whilst in (b), P may decrease hyperbolically (with T^{-1}; see Supporting Information). Experimental studies on the chiral induction mechanism include pitch measurements of varied guest–host systems[6,7] and X-ray diffraction, however, the latter has not provided clear evidence of distorted micelles.[8] The pitch was found to depend on the chemical composition of the LLC host phase, the temperature, the dopant concentration and, in particular, the chemical nature of the dopant.[6] A general correlation between properties of the chiral dopant and its chiral induction power in a host phase has not yet been established for LLCs, in contrast to the molecular concepts developed for thermotropic LCs (see, for example, Ref. [1] and Ref. [12]), which are also important for LLCs, as we will discuss later.

A crucial point of discussion regarding LLCs, especially in view of the suggested mechanisms, is the actual location of the chiral dopants in the N* phase: within the apolar core of the micelle or at the micellar surface. The dopant location is proposed to play an important role for the chiral induction power,[6,13] but locating the dopants experimentally has not yet been successful.

Recently, a magnetic resonance method suitable for studying dopants present at low concentrations, avoided-level-crossing muon spin resonance (ALC-µSR), was used to reveal the dopant location in lamellar LLC phases. The ALC-µSR technique[14,15] involves the formation of a radical by the addition of muonium, Mu, a light hydrogen isotope ($m_{\mathrm{H}} = 9\, m_{\mathrm{Mu}}$) with a positive muon μ^+ as the nucleus, to an unsaturated bond (Scheme 1). The time-integrated muon spin polarization, which is proportional to the muon decay asymmetry A, is measured as a function of an external magnetic field. Resonances occur when there is coupling between eigenstates of the three-spin-$\frac{1}{2}$ system composed of the radical electron, the muon, and the proton bound to the same carbon as the muon. The resonance field B_{res} is determined by the hyperfine coupling constants of the radical; these coupling constants are, among other factors, sensitive to the polarity of the surroundings, and B_{res} is shifted to higher values with increasing polarity.[15] The polarity of the local environment and thus the location in the LLC is determined by comparing B_{res} in the LLC with the values in a

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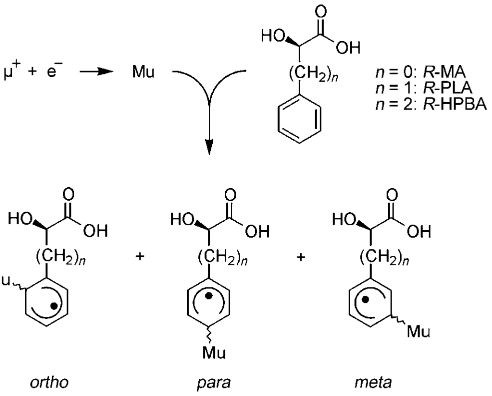

Scheme 1. Formation of muonium Mu from a positive muon and an electron, and addition of Mu to the phenyl ring of the dopants *R*-MA, *R*-PLA, and *R*-HPBA in the *ortho*, *para*, or *meta*-position to yield diastereomeric radicals.

polar reference (herein water) and in an apolar reference (decanol). ALC-μSR also delivers information on the reorientational dynamics of the radical. If this is anisotropic, on a characteristic time scale of about 50 ns herein,[15a] so-called Δ_1 resonances occur, which is a further indication that the dopant is trapped in an anisotropic environment, for example, a micelle.[14,15]

We present the first application of ALC-μSR to a chiral nematic LLC phase to reveal new aspects of the still unexplained chiral induction mechanism in nematic LLC phases, and begin with the actual location and reorientation dynamics of chiral dopants. ALC-μSR cannot directly measure a chiral, that is, a mathematically pseudoscalar quantity. However, it will be shown that μSR results can contribute valuable indirect information on the chiral induction mechanism, namely concerning the role of the dopant location and the dopant dynamics.

We selected the nematic host phase of disk-like micelles formed in the system cetyldimethylethylammonium bromide (CDEA)/decanol/water with mass fractions 0.283/0.674/0.043.[6,9,16] As dopants we chose a homologous series of chiral amphiphiles with the same chiral polar head group but increasing aliphatic segment length (see Scheme 1): (*R*)-mandelic acid (*R*-MA), (*R*)-3-phenyllactic acid (*R*-PLA), and (*R*)-2-hydroxy-4-phenylbutanoic acid (*R*-HPBA). Experimental details are described in the Supporting Information.

A linear $P(T)$ behavior was found for the *R*-MA sample (see Supporting Information), indicating that induction mechanism (a) applies and that the dopant should reside at the micellar surface. The increasing hydrophobicity of the higher homologues can be expected to promote their solubilization within the micelle. Therefore, if the dopant location is in fact important for the chiral induction, the series should show a uniform trend of, for example, the helical twisting power (HTP),[17] a quantitative measure for the chiral induction of a dopant in a given host phase.[5,10,18] It can be derived from the concepts described for thermotropic LCs[1,12] that the macroscopic HTP and its sign, which indicates the handedness of the induced helix, is the sum over the individual $\mathrm{HTP_i}$ contributions from each molecule. Furthermore, it has been shown theoretically[12] and experimentally[1] that the chiral induction is an anisotropic (tensorial) property. Value and sign of the $\mathrm{HTP_i}$ depend on the molecular structure and conformation, and also on the dopant orientation with respect to the host phase molecules and to the director. Therefore, the dynamics of the dopant is proposed to have an important influence on the chiral induction. In lyotropic LCs, the dopant location can be assumed to be an additional determining factor for the $\mathrm{HTP_i}$.

Interestingly, *R*-MA, *R*-PLA, and *R*-HPBA exhibit alternating HTP values and signs (see Figure 2), despite the structural similarity. Comparable odd–even effects, that is, alternating properties throughout a homologous series of molecules, have been observed for thermotropic LCs (see, for example, Ref. [18a]) and were correlated with an alternating molecular geometry. In our case, the effect could also be related to the dopant location or its dynamics; both factors can be addressed by ALC-μSR.

Figure 2 shows the ALC-μSR spectra of each dopant in the nematic LLC phase at a concentration of 4.37 mol % (with

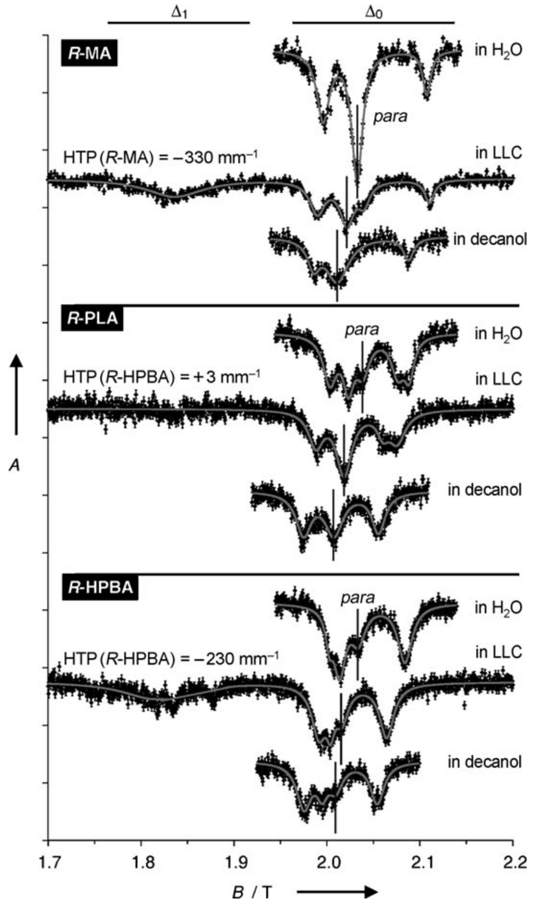

Figure 2. ALC-μSR spectra and *HTP* values (from references [6,7,19]) of the chiral dopants *R*-MA, *R*-PLA and *R*-HPBA dissolved in H_2O, the nematic LLC host phase and decanol. The ALC-μSR spectra are fit by multiple Lorentzian functions (gray lines). Note that for *R*-HPBA/LLC, apart from the broad resonance (see the fit curve), there are individual Δ_1 resonances present. These resonances are significant but not relevant in the present context, and will be discussed elsewhere. The experimental asymmetry *A* has arbitrary units; *B* is the magnetic field.

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respect to the aggregated material) and in the isotropic reference solvents H_2O and decanol. The spectra and the HTP values[19] are taken at the same relative temperature $T_{rel} = T_{N*I} - 3$ K (T_{N*I} is the transition temperature from the chiral nematic to the isotropic phase; see Supporting Information).

A qualitative comparison of the three spectra of each dopant reveals that the resonances in the LLC phase appear mostly at lower field than in water but not as low as in decanol. This result strongly indicates that the dopants are located at the micellar surface (Figure 3), with the polar part between the CDEA head groups and the phenyl ring just below the micellar surface, which supports the validity of the chiral induction mechanism (a) for these dopants. Two *R*-MA resonances are shifted to higher field in the LLC than in water, which suggests the solubilization of the short *R*-MA molecule close to the highly polar CDEA head groups.

A closer look at the Δ_0 region of the spectra reveals that all dopants show three to five resonances whilst similarly substituted benzenes exhibit usually only three resonances with an intensity ratio of 2:1:2.[14c,15] The number and intensity distribution of resonances found herein is a consequence of the dopant chirality[20] and observed in ALC-μSR for the first time. Owing to the dopant chirality, the muoniated *ortho* and *meta* radicals are diastereomers with potentially different resonance positions. Mu addition at the *para* position leads to only one isomer assuming fast rotation of the phenyl ring around the bond indicated by arrows in Figure 3 bottom), and a maximum of five resonances is found (see *R*-PLA/water). Overlapping of resonances lowers this number and changes the usual intensity ratios (see *R*-MA/water), which hinders the resonance assignment. Based on large experience with similarly substituted radicals,[14c,15] the resonances are assigned as *ortho*, *para*, and *meta* with increasing field. DFT calculations of the hyperfine coupling constants, which will be published elsewhere, support the assignment.

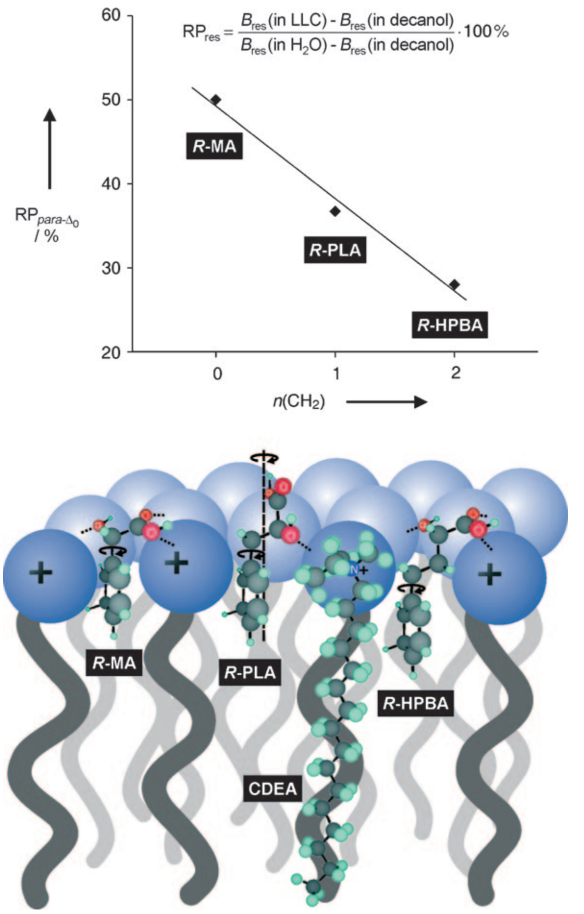

Figure 3. Top: Linear decrease of the relative polarity (RP) for the para Δ_0 resonance with increasing methylene chain length $n(CH_2)$ of the dopants. B_{res} = resonance field. Bottom: Schematic model of the dopant location at the micellar surface. O red, C gray, H bright green; NH_4^+ or N blue. The bromide counterions and decanol are omitted for clarity.

With increasing hydrophobicity, the aromatic ring of the dopants is solubilized deeper in the micelle, which is clearly revealed by plotting the relative polarity (RP, a measure for the polarity of the muon surroundings relative to a polar and apolar reference) of the LLC *para* Δ_0 resonance over the number *n* of methylene groups per dopant (Figure 3 top). This finding indicates that the dopant location is not the crucial factor for the alternating HTP values.

Regarding the reorientation dynamics of the dopants, broad Δ_1 resonances are clearly present in the spectra of *R*-MA and *R*-HPBA in the LLC phase, which indicates decreased but still relatively high dynamics of the dopants and confirms the dopant location in the micelle. The absence of Δ_1 resonances in the *R*-PLA sample (even at a 10 °C lower temperature) indicates high and isotropic dopant dynamics. This alternation of the dynamic properties is intriguing, as it is strikingly similar to the alternating HTP values and suggests a coupling between the dynamics of a chiral dopant and its chiral induction. This coupling is, in fact, sensible within the molecular concepts for thermotropics discussed above:[1,12] Owing to the fast isotropic motion of the *R*-PLA molecule, the different HTP_i values, which account for different molecule orientations, may be averaged to an effective HTP value close to zero.

The results are summarized in a model representation of the micellar surface (Figure 3, bottom). To reveal the role of molecular geometry and packing effects, on which many odd–even phenomena are known to be at least qualitatively based, the dopant geometry was optimized using a DFT calculation. The resulting dopant geometries are indeed substantially different for the strong chiral inducers *R*-MA and *R*-HPBA compared to the low-HTP dopant *R*-PLA. With the phenyl rings entering the micellar surface, the chiral polar head groups of *R*-MA and *R*-HPBA lie in between those of CDEA. This orientation certainly favors interactions between the positively charged CDEA head groups and the negatively polarized oxygen atoms of the dopants. The head group of *R*-PLA, however, protrudes from the surface and may interact less with CDEA. This effect may allow increased dynamics of the whole *R*-PLA molecule (such as rotation about the axis indicated by the dashed line) and thereby effectively reduce both the Δ_1 resonance intensity and the chiral induction.

For the first time, the actual location and local reorientation dynamics of chiral dopants in the micellar N* phase of a

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LLC could be unambiguously determined using a promising tool in LLC research, namely the magnetic resonance method ALC-μSR. Both results contribute important indirect information on the chiral induction mechanism. The role of the dopant location was found to be inferior to the role of the dopant dynamics; fast isotropic reorientation dynamics leads to a spherical appearance of the dopant and thus to isotropic coupling with the environment, which reduces the chiral induction to zero.

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