

Detection of Chiral Disorder in Langmuir Monolayers Undergoing Spontaneous Chiral Segregation

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Abstract: Acid–base interactions between two different chiral amphiphilic molecules (*p*-pentadecylmandelic acid and *p*-tetradecylphenylethylamine) are used in order to achieve spontaneous chiral segregation from a racemic mixture at the air–water interface, as shown by grazing incidence X-ray diffraction. The extent of possible chiral disorder for both acid and base components is examined. We show that an oblique lattice symmetry is insufficient to guarantee spontaneous segregation of chiral molecules in two-dimensional crystals because of possible chiral disorder.

Introduction

Spontaneous separation of chiral molecules from a racemic mixture into two-dimensional crystals of opposite handedness echoes Pasteur's famous experiment with sodium ammonium tartrate tetrahydrate crystals performed 150 years ago.¹ Definitive evidence on spontaneous separation in bulk crystals can be easily obtained by common experimental tools such as optical rotation measurements, chromatography on chiral columns, phase diagrams, or X-ray structure analysis. Determination of chiral separation in monolayer films is far less straightforward.² Early surface pressure–molecular area (π – A) isotherm measurements provided indirect evidence for spontaneous resolution of some racemates in two dimensions.^{3–5} Much more direct observation of spontaneous separation of enantiomers became possible only with the advent of modern techniques such as grazing incidence X-ray diffraction (GIXD) and atomic force (AFM), scanning tunneling (STM), Brewster angle (BAM), and epifluorescence microscopies. The latter two methods are optical and provide information on the shape of monolayer domains at least a few micrometers in size. Observations of asymmetric shapes of the polycrystalline monolayer domains in racemic mixtures were ascribed to the separation into crystalline clusters of opposite handedness.⁶ A comparative GIXD and epifluorescence microscopy study of racemic diol monolayers on water showed, however, that such a correlation does not necessarily hold.⁷

In this work, we have made use of known acid–base interactions involving two different chiral molecules to induce

chiral separation in two dimensions. Moreover, the use of this acid–base binary system has allowed us to probe the extent of possible chiral disorder.

Experimental Section

General Procedures. ¹H NMR spectra were recorded on a Bruker spectrometer (270 MHz) in CDCl₃ using OTS as internal standard. Multiplicities in ¹H NMR are reported as broad (br), singlet (s), doublet (d), triplet (t), double doublet (dd), quartet (q), double quartet (dq), and multiplet (m). Thin-layer chromatography (TLC) was performed on Merck silica gel plates. Column chromatography was performed on silica gel columns.

***p*-Tetradecylacetophenone (1).** A chloroform solution containing tetradecylbenzene (15.4 g, 56.2 mmol) and acetyl chloride (11.7 g, 0.169 M) was slowly dripped into a chloroform solution of AlCl₃. The mixture was stirred for 1 h while the temperature was kept below 10 °C and then stirred for another hour at 25 °C. The solution was poured into ice. The chloroform layer was separated from the aqueous solution and the latter washed several times with ether. The ether extracts were collected and combined with the chloroform fraction, treated with sodium bicarbonate, and dried with MgSO₄. The organic solvent was evaporated and the solid residue was recrystallized from ethyl acetate/hexane/methanol to yield white solid **1** (13.8 g, 80% yield), mp 54–55 °C. ¹H NMR (CDCl₃) δ 7.88 and 7.23 (dd, 4H, aromatic A₂B₂ system), 2.66 (t, 2H, PhCH₂), 1.60 (s, 3H, COCH₃), 1.28 (m, 24H, aliphatic CH₂), 0.90 (t, 3H, CH₂CH₃).

(*R,S*)-*p*-Tetradecylphenylethylamine (2). Compound **1** (12.5 g, 41.4 mmol), ammonium acetate (31 g, 378 mmol), and NaBH₃CN (1.76 g, 0.279 M) were dissolved in absolute methanol (20 mL) in an inert N₂ atmosphere. The solution was stirred for 3 days at 60 °C until the reaction was complete. The mixture was acidified with concentrated HCl to pH 2.1. Methanol was evaporated, and the remaining aqueous solution was washed with CH₂Cl₂. The hydrochloride salt of **2** was reacted in water with KOH to release the free amine that was extracted with CH₂Cl₂ and dried to yield **2** (8.0 g, 60% yield), mp 68–69 °C. ¹H NMR (CDCl₄) δ 7.24 (dd, 4H, aromatic A₂B₂ system), 4.08 (q, 1H, NCH), 2.58 (q, 2H, PhCH₂), 1.37 (d, 3H, NCCH₃), 1.25 (m, 24H, aliphatic H), 0.88 (t, 3H, CH₂CH₃).

(*R*)-(or *S*)-*p*-Tetradecylphenylethylamine (3). Racemic **2** was optically resolved via cocrystallization with optically pure (*R*)- or (*S*)-mandelic acid. Racemic **2** (23.5 g, 11 mmol) and (*R*)-(–)mandelic acid (1.5 g, 10 mmol) were dissolved in ethyl acetate (250 mL) at 60 °C.

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Thin crystalline plates precipitated upon cooling. The salt was recrystallized several times. The free amine was released in 10% aqueous solution of KOH, extracted with pure CH_2Cl_2 , and washed repeatedly with water, until all the mandelic acid was removed as indicated by TLC ($\text{CH}_2\text{Cl}_2/\text{ethanol}$ 2:1 solution on silica plates). The solution was dried with MgSO_4 to yield (*R*)-**3** with an optical rotation of $[\alpha]_{25}^{\text{D}} = +12.95^\circ$ ($c = 2$, CH_2Cl_2). The ^1H NMR spectrum is identical to that of racemic **2**. The *S*-enantiomer of **2** was obtained analogously using (*S*)-(+)-mandelic acid, $[\alpha]_{25}^{\text{D}} = -12.77^\circ$ ($c = 2$, CH_2Cl_2).

α -Keto- β -(*p*-pentadecylphenyl)ethyl Propionate (4**).** AlCl_3 (6.86 g, 51.5 mmol) dissolved in chloroform (14 mL) was placed in a three-neck flask in an inert dry N_2 atmosphere. A solution of pentadecylbenzene (10 g, 34.2 mmol) and ethyl oxalyl chloride (7.03 g, 51.5 mmol) in chloroform (7 mL) was slowly added from a dropping funnel at 0–5 °C. During the exothermic reaction, the yellow reaction mixture turned dark brown. The reaction was then stirred in the ice bath for 1 h and then for 3 h at ambient temperature. The reaction mixture was poured into ice, and organic components were extracted three times with ether. The organic fractions were combined and washed with an aqueous solution of sodium bicarbonate and dried with MgSO_4 , and the solvent was evaporated. The yellow oil was chromatographed on a silica column with $\text{CH}_2\text{Cl}_2/\text{hexane}$ (1:1) to yield **4** (12 g, 91%), mp 129–131 °C. ^1H NMR (CDCl_3) δ 7.16 and 7.30 (dd, 4H aromatic A_2B_2 system), 5.12 (s, 1H, CH), 4.20 (dq, 2H, COOCH_2), 2.59 (t, 2H, ArCH_2), 1.73 (b, 1H, OH), 1.59 (t, 3H, OCH_2CH_3), 1.25 (m, 26H, aliphatic CH_2), 0.87 (t, 3H, CH_2CH_3).

(*R*)-*p*-Pentadecylmandelic Acid (5**).** An asymmetric reduction of **4** was performed in the following steps. NaBH_4 (1.47 g, 38.7 mmol) and (*R,R*)-tartaric acid (5.55 g, 38.0 mmol) were dissolved in THF (130 mL) in a three-necked flask and heated in an inert dry N_2 atmosphere at 70 °C for 3 h. The resulting white suspension was cooled to –20 °C. Compound **4** (9 g, 0.023 M) in THF (10 mL) was added dropwise (exothermic reaction) and the reaction mixture was stirred for 15 h at –20 °C. Ethyl acetate (60 mL) and 1 M HCl (30 mL) were slowly added to the mixture at 0 °C. After adding water (50 mL), the organic layer was separated, washed several times with an aqueous solution of sodium bicarbonate, and dried with MgSO_4 . The organic solvent was evaporated to yield an oil that was chromatographed on a silica column with ethyl acetate/hexane mixture (1:6). The solvent was evaporated to yield white crystalline ethyl ester of *p*-pentadecylmandelic acid (7.5 g, 87%).

The ester (6.1 g, 15.3 mmol) was added in 5 M KOH/methanol solution (55 mL) with a few drops of water and stirred for 2.5 h at ambient temperature. White crystals of the salt started precipitating after several minutes. After 2 h, the solution with crystals was acidified with HCl and the white crystalline substance was filtered and washed with water and hexane. The solid was recrystallized from THF to yield **5** (3.0 g, 56%), $[\alpha]_{25}^{\text{D}} = -63.21$ ($c = 1.01$, THF). The acid was further optically purified via crystallization with (*R*)-(+)-phenylethylamine for several times until reaching the constant rotation value of $[\alpha]_{25}^{\text{D}} = -83.11$ ($c = 0.965$, THF), mp 119–121 °C. ^1H NMR (CDCl_3) δ 7.08 and 7.27 (dd, 4H, aromatic A_2B_2 system), 5.06 (s, 1H, CH), 2.49 (t, 2H, ArCH_2), 1.16 (m, 26H, aliphatic CH_2), 0.78 (t, 3H, CH_2CH_3).

(*R,S*)-*p*-Pentadecylmandelic Acid (6**).** NaBH_4 (0.44 g, 11.61 mmol) was suspended with THF (40 mL) in a three-neck flask in an inert N_2 atmosphere. The mixture was cooled to 0 °C, and **4** (2.84 g, 7.73 mmol) was added in THF (5 mL) dropwise. The reaction mixture was left to stir in the bath for 1 h at 0 °C and overnight at ambient temperature. Ethyl acetate (20 mL) and 1 M HCl (10 mL) were slowly added to the mixture at 0 °C. Water was added and the organic layer separated, washed with sodium bicarbonate, dried with MgSO_4 , and recrystallized in THF to yield the racemic ethyl ester of *p*-pentadecylmandelic acid (1.06 g, 90%). Hydrolysis of the ester was done in the same way as for (*R*)-**5**. ^1H NMR of the final product demonstrated the same spectrum as for **5** and zero optical rotation.

X-ray Crystal Structure Determination. A platelike needle of $\{(xR, (1-x)S)\text{-C}_{15}\text{-MA}, S\text{-PEA}\}$ (x was found in the refinement) of dimensions $0.2 \times 0.4 \times 0.8 \text{ mm}^3$ was grown by slow cooling of equimolar mixture of (*R*)-*p*-pentadecylmandelic acid (95% ee) and commercial (*S*)-PEA from Aldrich (99% ee) dissolved in tetrahydrofuran. Crystallographic measurements were performed at ambient

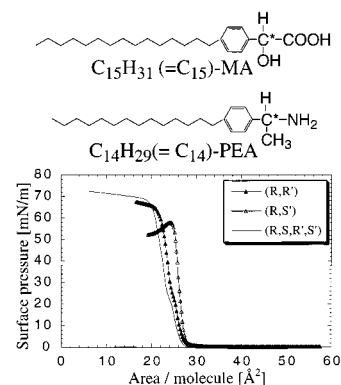


Figure 1. (Top) Structural formulas of the C_{15} -MA and C_{14} -PEA molecules. The asterisk marks the chiral carbon center. (Bottom) Surface pressure–molecular area (π - A) isotherms at 5 °C for *R,R'*, *R,S'*, and *R,S,R',S'* diastereomeric films formed by C_{15} -MA and C_{14} -PEA molecules in a 1:1 molar ratio. The molecular area A was calculated per one amphiphilic molecule, disregarding the difference between MA and PEA.

temperature (17 °C) on a four-circle Rigaku single-crystal diffractometer with a 18-kW rotating anode generator. The intensity data of 4015 reflections ($0 \leq h \leq 67$, $-10 \leq k \leq 0$, $0 \leq l \leq 8$) were measured. After merging equivalent reflections, 1066 observed reflections remained with $I \leq 2\sigma(I)$. The structure was solved with SHELXS97⁸ and refined isotropically with use of SHELXL97 programs.⁹ Hydrogen atoms at C and N atoms were positioned in calculated positions and refined as riding on the corresponding nonhydrogen atoms with fixed $U = 0.08$. The α -hydroxy oxygen atom was found to be disordered over two sites (xR and yS in the above formula) was close to 1 and constrained in the further refinement ($y = (1 - x)$) while the U factor variable was common for both the oxygen sites. The final refinement resulted in 0.45 : empirical formula $\text{C}_{31}\text{H}_{47}\text{O}_3\text{N}$, $M_r = 481.70$ g, orthorhombic, $P2_12_12_1$, $a = 52.140(10)$ Å, $b = 8.450(2)$ Å, $c = 6.8040(10)$ Å, $V = 2997.7(10)$ Å³, $Z = 4$, $D_x = 1.067$ g/cm³, $\text{Mo K}\alpha$ (0.710 73 Å, $2\theta_{\text{max}} = 55^\circ$, $F(000) = 1056$, $R = 0.139$, and $S = 0.884$).

Grazing Incidence X-ray Diffraction. The GIXD measurements were conducted on the liquid surface diffractometer at the undulator beam line BW1 in HASYLAB at Deutsches Elektronen-Synchrotron (DESY). The synchrotron radiation beam monochromated to wavelengths of 1.336 and 1.452 Å that were used in two synchrotron sessions. The incident angle was adjusted to $\alpha_f = 0.85\alpha_c$, where $\alpha_c \approx 0.14^\circ$. A detailed explanation of the method and experimental setup is given elsewhere.^{10,11} The diastereomeric mixtures were prepared by dropwise spreading of chloroform solutions at ambient temperature in a Langmuir trough and then cooled to 5 °C.

Results and Discussion

Mandelic acid (MA) and phenylethylamine (PEA), each with one chiral center (Figure 1, top), can be used for mutual chiral resolution of their racemic *R,S* mixtures. All the reported (MA,-PEA) three-dimensional crystal structures with various chiral composition have a bilayer arrangement with one crystallographically independent (MA,PEA) unit in each layer.^{12–15} The

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molecules are interconnected by multiple hydrogen bonds within a two-dimensional network. It is important to note that, in all these crystal structures, the MA (or PEA) molecules within a layer have the same absolute configuration. The same structural feature is also preserved in the 3D structures of the MA salts with substituted PEA all assuming very similar packing arrangements.¹⁶ Thermodynamic properties and crystal structures of various PEA–MA compositions demonstrated a higher stability of diastereomeric crystals, in which MA and PEA are of the same absolute configuration. This structural feature should, in principle, be preserved in analogous long-chain compounds which can be used for monolayer studies. Thus, for 1:1 mixtures of racemic long-chain amphiphiles bearing mandelic acid and phenylethylamine head groups, we may expect the monolayer to be separated into crystalline islands composed of (MA,PEA) units of the same absolute configuration, i.e., R,R' or S,S' rather than their diastereomeric¹⁷ pairs R,S' or S,R' , where R and S denote the absolute chiral configuration of MA and R' and S' that of PEA.

Para-substituted analogues of PEA and MA bearing long hydrocarbon chains C_nH_{2n+1} (labeled C_n) were synthesized to form racemic and chiral resolved amphiphilic compounds C_{14} -PEA and C_{15} -MA (Figure 1, top). Surface pressure–molecular area (π - A) isotherms of three different mixtures ((R)- C_{15} -MA, (R)- C_{14} -PEA), ((R)- C_{15} -MA, (S)- C_{14} -PEA), and ((R,S)- C_{15} -MA, (R,S)- C_{14} -PEA) on Millipore water indicate formation of stable monolayers with a limiting area per molecule of 25–28 Å² (Figure 1). All three isotherms have similar shapes. The GIXD spectra for the three compositions were measured at a surface pressure $\pi = 1$ mN/m. All the three measured GIXD patterns display seven narrow Bragg peaks (Figure 2a–c, left) as is evident from their full width at half-maximums (average fwhm in Table 1). These diffraction patterns were fully indexed yielding cell dimensions (Table 1). Each unit cell of area ~ 51 Å² contains two symmetry-independent long-chain molecular units corresponding to one acid and one amine molecule. The GIXD patterns for the R,R' and R,S' mixtures are clearly different both in terms of positions of the Bragg peaks, their integrated intensities (Figure 2a,c, left) and, in particular, the shapes of the corresponding Bragg rods (Figure 2d), whereas the mixture R,S,R',S' (Figure 2b, left) displays a diffraction pattern almost identical to that of the R,R' monolayer. Since the oblique unit cell for R,S,R',S' contains only two independent molecules and the monolayer is highly crystalline in view of the narrow Bragg peaks, it is highly plausible that the R,S,R',S' mixture segregates into R,R' and S,S' crystalline islands of opposite handedness. The crystallization process for the three systems is schematically shown in Figure 2a–c (right).

Racemic mixtures of amphiphilic molecules bearing a long hydrocarbon chain and a chiral hydrophilic head group would seem, when compared with their water-soluble analogues in the bulk, to have a lower tendency to separate in two dimensions since hydrocarbon chains readily pack in a herringbone motif in which R (right-hand) and S (left-hand) molecules are related by glide symmetry. Most of the examples of chiral separation in two dimensions, based on GIXD^{18,19} and in other reports by AFM²⁰ and STM,²¹ have rested primarily upon the finding of an oblique lattice with one amphiphilic molecule per unit cell

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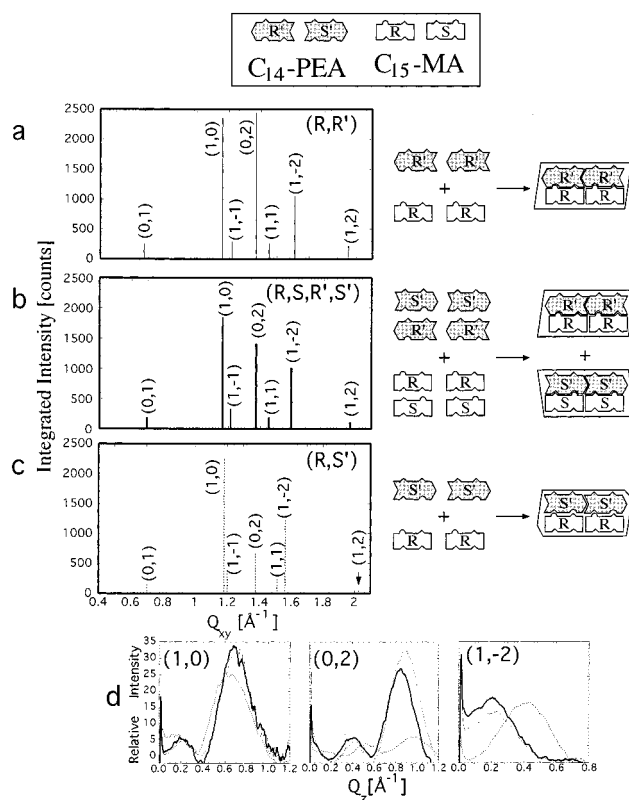


Figure 2. GIXD patterns for the three diastereomeric films R,R' (thin line), R,S' (dotted line), and R,S,R',S' (thick line) measured at 5 °C and surface pressure $\pi = 1$ mN/m. (a–c, left) The observed Bragg peaks represented by lines of corresponding integrated intensities with assigned (h,k) indices. (d) Comparison of Bragg rods of the three diastereomeric systems corresponding to the most intense (1, 0), (0, 2), and (1, -2) reflections, where the type of line corresponds to that as in (a–c, left). (a–c, right) Schematic views of the molecular assembly into crystals corresponding to the three diffraction patterns.

Table 1. Crystallographic Data for the Monolayers

| parameters | R,R' | R,S' | $0.5(R,S)-R'$ | R,S,R',S' |
|--|--------|--------|---------------|-------------|
| lattice spacings (Å) | | | | |
| d_{01} | 9.26 | 9.25 | 9.25 | 9.28 |
| d_{10} | 5.48 | 5.38 | 5.46 | 5.47 |
| $d_{1\bar{1}}$ | 5.19 | 5.28 | 5.25 | 5.24 |
| d_{02} | 4.61 | 4.62 | 4.62 | 4.63 |
| d_{11} | 4.37 | 4.20 | 4.31 | 4.35 |
| $d_{1\bar{2}}$ | 3.94 | 4.05 | 3.99 | 3.98 |
| d_{12} | 3.25 | 3.13 | 3.22 | 3.22 |
| av fwhm ^a (Å ⁻¹) | 0.0124 | 0.0197 | 0.0142 | 0.0143 |
| av coherence length ^b (Å) | 560 | 320 | 480 | 470 |
| unit cell dimens | | | | |
| a (Å) | 5.59 | 5.56 | 5.60 | 5.60 |
| b (Å) | 9.40 | 9.55 | 9.47 | 9.48 |
| γ (deg) | 101.5 | 104.8 | 102.8 | 102.4 |
| tilt angle (deg) | 40 | 39 | 41 | 40 |
| tilt azimuth ^c (deg) | 42 | 49 | 43 | 42 |
| unit cell area, A_{xy} (Å ²) | 51.5 | 51.3 | 51.7 | 51.8 |
| chain cross-section area | 19.7 | 20.0 | 19.5 | 19.9 |
| A_{\perp} (Å ²) | | | | |

^a fwhm, full width at half-maximum of the Bragg peak in Q_{xy} units.

^b The coherence length L has been calculated using the standard Sherrer equation:²² $L = (0.9 \times 2\pi) / (\text{fwhm}^2 - \Delta^2)^{1/2}$, where the resolution of the Soller collimator, $\Delta = 0.0081$ Å⁻¹ (in Q_{xy} units). ^c The angle between the projection of the hydrocarbon chain vector onto the xy plane and the reciprocal vector a^* as determined from the positions of the maximums q_z of the three Bragg rods corresponding to (1, 0), (0, 2), and (1, -2) reflections.¹⁰

leading to an assumption that all molecules are related by translation symmetry and, therefore, of the same handedness.

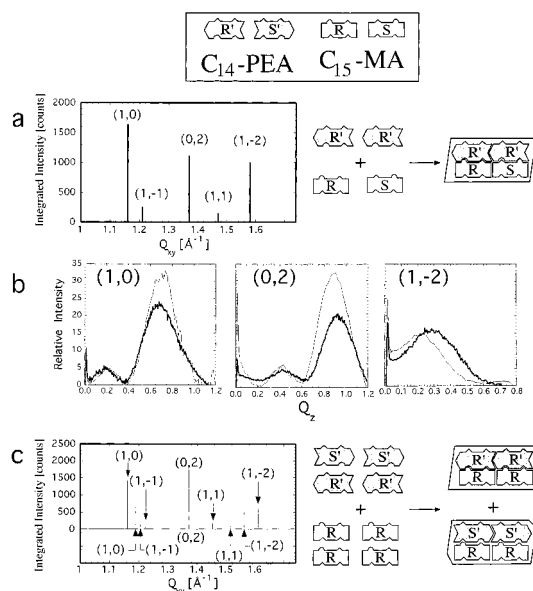


Figure 3. GIXD Bragg peaks (lines) for the two diastereomeric mixtures: (a, left) $0.5(R,S)-R'$ and (c, left) $R-0.5(R',S')$, where the diffraction pattern for $R-0.5(R',S')$ is a combination of the R,R' and R,S' phases with the h, k indices denoted above for R,R' and below for R,S' . (b) Bragg rod profiles of the $0.5(R,S)-R'$ mixture (solid bold line) vs the corresponding Bragg rods of the R,R' composition (thin solid line), originally shown in Figure 2d. (a,c, right) Schematic views of the molecular assembly into crystals corresponding to the two diffraction patterns.

Such an assumption neglects potentially high molecular disorder in monolayer films that are often mesophases rather than crystalline aggregates. Thus we may envisage, in the ultimate, a racemic 2D crystal ($R:S = 1:1$) with the R and S chiral head groups randomly distributed, although the long hydrocarbon tails pack in an oblique unit cell by translation symmetry only.

In order to help evaluate the extent of chiral molecular disorder for both the acid and amine moieties, two chiral compositions $R-0.5(R',S')$ and $0.5(R,S)-R'$ with a 1:1 acid to amine molar ratio were inspected. Both mixtures display π - A isotherms similar to those previously described. The GIXD measurements gave two qualitatively different results. The mixture $0.5(R,S)-R'$ composed of the acid molecules of both handedness and the amine molecules of single handedness gave rise to a diffraction pattern (Table 1 and Figure 3a, left, and b) very similar to that of the R,R' system. Since there is only one crystalline phase and the corresponding diffraction pattern has approximately the same intensity distribution as for R,R' , we deduce that the $(0.5(R,S), R')$ phase is isomorphous with R,R' , but where half the R sites are randomly occupied by S molecules, as schematically shown in Figure 3a (right).

The diffraction spectrum for the $R-0.5(R',S')$ mixture, composed of an acid of single chirality and amine molecules of both handedness, combines two overlapping GIXD patterns, characteristic of the R,R' and R,S' crystalline phases (Figure 3c, left). The relative amount of crystalline material of these two phases is approximately 1.5:1 according to the intensity ratio of the corresponding diffraction patterns.

The diffraction results for the 1:1 mixtures $R-0.5(R',S')$ and $0.5(R,S)-R'$ suggest that R,S,R',S' separates into enantiomor-

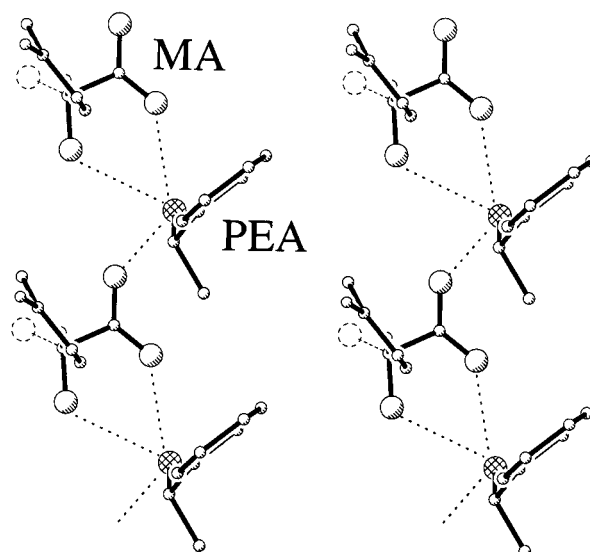


Figure 4. Layer packing of MA and PEA moieties in the observed 3D crystal structure of $((0.5R,0.5S)-C_{15}-MA,(R)-PEA)$ with the observed chiral disorder of the OH group. All hydrogen atoms and hydrocarbon chains are omitted.

phous domains of composition $([(1-x)R, xS], R')$ and $([(1-x)S, xR], S')$, where x is a fraction of "foreign" C_{15} -MA molecules within the R,R' and S,S' domains. For the three compositions R,R' , R,S,R',S' , and $0.5(R,S)-R'$ there is no significant difference in the Q_{xy} positions of the corresponding Bragg peaks. Nonetheless, comparison of the sensitive $(1, -2)$ Bragg rod of these three mixtures suggests that the R,S,R',S' is much closer to R,R' than to $0.5(R,S)-R'$ (cf. Figure 2d and Figure 3b).

Strong support for the possibility of chiral disorder for the MA moiety may be drawn from the reported 3D structure of $((R)-MA,(S)-C_{15}-PEA)$ with intralayer cell dimensions of $a = 6.0 \text{ \AA}$, $b = 9.1 \text{ \AA}$, and $\gamma = 90^\circ$,¹⁶ which compares with those of the diastereomeric monolayers (Table 1). The interchange of the OH group and the hydrogen atom at the chiral carbon center with the concomitant switch in chirality leads to formation of an extra hydrogen bond and does not impair van der Waals contacts. Experimental proof for such a type of chiral disorder is provided by observed chiral disorder in the 3D crystal structure $((0.45R,0.55S)-C_{15}-MA,(R)-PEA)$, grown from tetrahydrofuran solution with a large excess of $(S)-C_{15}$ -MA molecules ($R:S = 5:95$) and enantiomerically pure $(R)-PEA$. The structure refinement revealed $\sim 50\%$ chiral disorder for the OH group (Figure 4). This structure is therefore a 3D analogue of the Langmuir phase with the $0.5(R,S)-R'$ chiral composition.

Conclusions

Diastereomeric interactions between two different chiral molecules were used for the first time to achieve two-dimensional spontaneous chiral separation into crystalline islands of opposite handedness at the air-water interface. The extent of chiral disorder, as assessed from the GIXD pattern analysis, was shown to be always low for the amine component and in some cases high (up to 50%) for the acid component. The results show that an oblique lattice symmetry, even for highly crystalline monolayers, is insufficient proof for spontaneous separation of chiral molecules in two dimensions. One way to ascertain whether such a separation occurred would require a determination of the monolayer crystal structure making use of the Bragg rod diffraction data, complemented by lattice energy calculations.

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Supporting Information Available: Tables of crystal data, atomic coordinates, bond lengths and angles, isotropic displacement parameters for $((xR,(1-x)S)\text{-C}_{15}\text{-MA},(S)\text{-PEA})$ ($x = 0.45$) (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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