the shear rate increases, the DNA molecules tend to align more towards the flow direction (see Fig. 4 legend).

Polymers extended in the direction of the shear flow have been qualitatively predicted by classical theories, and have been indirectly observed by using bulk birefringence. Partial stretching of individual polymers in the direction parallel to the flow direction is due to the viscous drag exerted on the molecule, which has been invoked to explain shear-thinning in polymer solutions. However, the existence of vertical conformations (such as those shown in Fig. 2a–c) is unexpected, and is not considered by classical models of polymer physics. Classically, it is assumed that in the plane parallel to the velocity and the velocity-gradient directions, shear orients polymers at an angle $\leq 45^\circ$ with the flow direction. Shear may also induce tumbling of the polymers within such a plane. However, in the plane parallel to the velocity and the vorticity directions (the present plane of visualization; see Fig. 1), neither shear-induced alignment nor polymer tumbling can explain the existence of vertical conformations. Although fluid-mechanics models—such as Jeffery orbits describing the motion of axisymmetric rigid particles in a shear flow—may serve as limiting cases in microtubule and actin dynamics, they cannot be directly applied to the dynamics of flexible polymers, as reported here. Further developments of classical polymer theories predict that a flexible polymer becomes stretched and oriented when the Weissenberg number, $W = \gamma t$, is equal to or larger than unity. But here we find shear-induced deformation of flexible polymers can occur at Weissenberg numbers much smaller than unity (Figs 1–4).

Our experimental results show that conventional approaches, such as birefringence and light scattering, which measure only ensemble-averaged molecular parameters (that is, $\langle \theta \rangle$, $\langle \phi \rangle$), overlook the extremely rich dynamics of individual polymers under shear. Our observations also provide an insight into the conformational and orientational changes of polymers in a shear flow, and a basis for further theoretical modelling. The molecular-level approach to non-equilibrium polymer physics that we describe here could be readily extended to many other polymer systems, including entangled solutions of flexible polymers and semiflexible polymers such as actin.

From seashells to DNA, chirality is expressed at every level of biological structures. In self-assembled structures it may emerge cooperatively from chirality at the molecular scale. Amphiphilic molecules, for example, can form a variety of aggregates and mesophases that express the chirality of their constituent molecules at a supramolecular scale of micrometres (refs 1–3). Quantitative prediction of the large-scale chirality based on that at the molecular scale remains a largely unsolved problem. Furthermore, experimental control over the expression of chirality at the supramolecular level is difficult to achieve, mixing of different enantiomers usually results in phase separation. Here we present an experimental and theoretical description of a system in which chirality can be varied continuously and controllably (‘tuned’) in micrometre-scale structures. We observe the formation of twisted ribbons consisting of bilayers of Gemini surfactants (two surfactant molecules covalently linked at their charged head groups). We find that the degree of twist and the pitch of the ribbons can be tuned by the introduction of opposite-handed chiral counterions in various proportions. This degree of control might be of practical value; for example, in the use of the helical structures as templates for helical crystallization of macromolecules.

Gemini surfactants, consisting of two identical (twin) surfactants joined by a hydrocarbon spacer of variable length, have been shown to have properties that are unusual compared to those of simple surfactants and lipids. Cationic Gemini surfactants having chiral counterions such as $\Delta$-tartaric (Fig. 1) form gels in both water and some organic solvents by creating extended networks of the multilamellar twisted ribbons reported here (Fig. 2, helix B). A feature of this system is that the chirality comes from the counterion rather than from the amphiphile itself, which allows us to both adjust the pitch and to introduce excess chirality in the form of sodium tartrate salts.

Similar structures to those that we observe are found for diacetylenic lipids, bile and glutamates, which form long helical strips of membranes with exposed edges (Fig. 2, helix A). However, these helical ribbons are unstable: they evolve into tubules (Fig. 2) consisting of a bilayer (or multilayer) membrane of amphiphilic molecules wrapped in a cylinder which exhibits a ‘barber’s-pole’ pattern on its surface as evidence of its chiral origin. The twisted ribbons that we observe have several original features. Geometrically, their saddle-like curvature differs from the cylinder.

Tuning bilayer twist using chiral counterions

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Received 21 October 1998; accepted 22 March 1999.


Acknowledgements. We thank M. Ferro, L. Archer, J. Harden, D. Lavan, and J. van Zanten for discussions. This work was supported by NASA (D.W.), ACS-PRF (D.W.), NSF (D.W.), the Whitaker Foundation (D.W.), Merck, Inc. (D.W.) ARO (G.B.), and IMRE (G.B.).

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How does the shape of the twisted ribbons arise from the particular molecular structure of the amphiphiles? To answer this, we examined the properties of structural variants of 16-2-16 tartrate, and came to the following conclusions.

First, the absence of twist for the malate derivative (Fig. 1), and the properties of the gels in organic solvents, strongly suggest a long-range alignment of the constituent anisotropic structures. For simple geometric reasons, such anisotropy can lead to a cylindrical shape.

Second, in water the twisted ribbons are stable for gemini surfactants with hydrocarbon chains ranging from 14 to 16 carbons. For shorter hydrocarbon chains, only micelles form for concentrations at least up to 40%. At 18 carbons, helical ribbons form instead of twisted ribbons, presumably as a result of the elevated chain melting temperature and the consequent solid phase, which will favour a cylindrical shape.

Third, the ability of the amphiphile to form such anisotropic aggregates (having ribbons with both long and short sides) appears to be directly linked to its dimeric character. For instance, the monomeric counterpart, cetyl trimethyl ammonium tartrate, fails to form any ribbon-like structure, whilst gemini surfactants having simple bromides as counterions form flat ribbons similar to those of Fig. 3a (ref. 12). Furthermore, these highly anisotropic structures strongly suggest a long-range alignment of the constituent geometrical parameters of these helices can be performed using very simple means.

| Table 1 Properties of ribbons formed by 16-2-6 tartrate |
|---|---|---|
| e.e. | $T$ (mM) | $W$ (mM) | $T/W$ |
| 0 | 0.0 ± 0.2 | 0.0 ± 0.2 | 100 |
| 0.2 | 5.0 ± 1.5 | 0.12 ± 0.04 | 43 ± 5.2 |
| 0.3 | 2.6 ± 0.9 | 0.11 ± 0.07 | 26 ± 7.0 |
| 0.5 | 1.0 ± 0.5 | 0.06 ± 0.01 | 17 ± 4.7 |
| 1 | 0.2 ± 0.04 | 0.04 ± 0.006 | 4.8 ± 0.51 |
| 1* | 0.12 ± 0.007 | 0.02 ± 0.002 | 7.0 ± 0.90 |
| 1† | 0.116 ± 0.01 | 0.02 ± 0.002 | 5.6 ± 0.86 |
| 1‡ | 0.115 ± 0.006 | 0.02 ± 0.002 | 5.9 ± 0.63 |

Shown are values of enantiomeric excess (e.e., defined as $(\phi_L - \phi_R)/(\phi_L + \phi_R)$) and the mean values and standard deviations of ribbon period ($T$), width ($W$), and period/width ($T/W$), for different proportions of L- and D-enantiomers of 16-2-16 tartrate. Statistics were derived from 10–20 measurements for each sample.

* In the presence of 1 equiv. of sodium L-tartrate.
† In the presence of 10 equiv. of sodium L-tartrate.
‡ In the presence of 3 equiv. of sodium L-tartrate.
molecules, which may be correlated with a hydrogen-bonded network of tartrate ions\(^\text{11}\).

In the model we propose, orientational order of the molecules within the membrane together with the chirality of the constituents provide a natural explanation for the observed twisted-ribbon shape, and can also account for the observed trends in the pitch and width of the ribbons on variation of the enantiomeric excess. In a membrane composed of gemini surfactants, an anisotropic fluid-like arrangement of head groups would be analogous to nematic order in bulk liquid crystals\(^\text{12}\).

The shape of the membrane is described by a curvature tensor \(K_{ij}\), whose eigen values \(\epsilon_1\) and \(\epsilon_2\) are the principal curvatures along two orthogonal directions in the membrane\(^\text{14}\). Including both bending energies and the coupling of membrane shape to the assumed nematic field\(^\text{13}\), \(Q_{ij} = S(n_i n_j - \frac{1}{2} \delta_{ij})\), the free energy per unit area of membrane is given by\(^\text{15,16}\):

\[
f = \frac{1}{2} \kappa (\text{Tr} K) + \kappa \text{Det} K + \lambda \epsilon_1 Q_{ij} K_{ij} + \frac{1}{2} \kappa' Q_{ij} K_{ij} K_{ij}
\]

\[
= \frac{1}{2} \kappa (\epsilon_1 + \epsilon_2)^2 + \kappa (\epsilon_1 + \epsilon_2) + \lambda S \sin(2\theta)(\epsilon_1 - \epsilon_2)
\]

\[
+ \frac{1}{2} \kappa' S \cos(2\theta)(\epsilon_1 + \epsilon_2)(\epsilon_1 - \epsilon_2)
\]

Here, the coupling \(\lambda\) characterizes the degree of chirality of the system (which should be proportional to the enantiomeric excess), \(\theta\) is the angle that the molecular orientation makes with respect to the principle curvature axes, \(\epsilon_j\) is the antisymmetric tensor and \(\kappa\), \(\kappa'\) and \(\lambda\) represent the mean, gaussian and anisotropic bending stiffness. Finally, we take into account the energy cost of the exposed edges of the ribbons by introducing an excess free energy \(\gamma\) per unit length of edge. This model assumes that the degree of nematic order \(S\) is fixed, by, for example, detailed molecular packing. Otherwise, it represents the most general continuum model that includes the curvature free-energy terms through quadratic order. It is thus expected to be valid provided that the membrane curvature is not too large (for example, on the molecular scale).

The analysis and results of this model will be described in greater detail elsewhere. Here we summarize the most relevant results for our experiments. First, for a given width of ribbon, the optimal shape (obtained by minimizing the bulk free energy \(f\) with respect to shape) for chiral systems is that of the twisted ribbon with saddle-like curvature (specifically, \(\epsilon_1 = -\epsilon_2\)) and the nematic director oriented at \(45^\circ\) with respect to the curvature axes. For a fluid membrane, cylindrical curvature—either as a complete tubule, or as a helical ribbon precursor to a tubule—is not expected. In contrast, solid-like order would strongly oppose saddle-like curvature and favor cylindrical curvature, as is observed in tubule-forming systems\(^\text{17}\).

Figure 3 TEM images of the ribbons. Shown are representative twisted ribbons formed by 16-2-16 tartrate at 0.1% in water for various values of \((\phi_1 - \phi_0) V(\phi_1 + \phi_0)\): a, 0 (racemate); b, 0.5; c, 1 (pure L); d, 1 (pure D) in the presence of 1 equiv. of sodium L-tartrate. Scale bar, 100 nm.

Figure 4 Predicted aspect ratio of twisted ribbons. Main figure, the calculated ratio of period to breadth, \(T/W\), as a function of reduced width \(\gamma W/\kappa\). This is shown for increasing values of \(\mu = S\chi/\gamma\), which is proportional to the enantiomeric excess. Curve a is for \(\mu = 0.02\); b is for \(\mu = 0.2\); and c is for \(\mu = 2\). For a given \(\mu\), only solutions lying along the corresponding line are possible. However, these are typically non-equilibrium solutions, evolving as shown by the arrows towards wider structures, which reduce the total edge energy. For narrow ribbons, the twist period \(T = \lambda_{\text{mac}}\) is constant. For \(\mu < 1/2\) (dashed line) no equilibrium solutions are possible, although \(T\) and \(W\) become strongly correlated: the ratio \(T/W\) approaches a value near 1/\(\mu\), even though polydisperse distributions of both \(W\) and \(T\) are expected. For \(\mu > 1/2\), the ribbons grow only until fixed, equilibrium values of \(T\) and \(W\) (shown by the filled circle) are reached. The equilibrium structures correspond to the upper boundary of the shaded region, within which no stable solutions are predicted. For all but a very narrow range of \(\mu\) near the critical value of 1/2, these are characterized by \(\gamma W/\kappa\) of the order of 1. Inset, measured ratio \(T/W\) (points with error bars representing standard deviations of 10–20 samples for ribbons of mixtures of 16-2-16 and L tartrate, without any salt added. Enantiomeric excess (chirality) \(\mu = S\chi/\gamma\). The precise relationship of the enantiomeric excess to \(\mu\) involves an unknown constant of proportionality, which has been chosen to fit the data.
As depicted in Fig. 4, minimization of the total free energy per surfactant predicts equilibrium ribbons if the chirality or enantio-
meric excess is large enough (specifically, if $\Delta S \gg \gamma/2$). Thus, despite the inevi-
table excess free energy associated with the edges, these ribbons may not grow beyond a certain preferred width $W$. In this case, the twist period $T$ and ribbon width $W$ are expected to vary inversely with the enantiomeric excess, to be well-defined (for example, their distributions are expected to be monodisperse), and the ratio $T/W$ is expected to be of the order of 1, and nearly independent of the enantiomeric excess. Before these equilibrium structures are attained, however, it is expected that $T$ varies inversely with the enantiomeric excess and is uncorrelated with $W$. Thus, the aspect ratio and monodispersity that we observe for ribbons formed by the pure 16–2–16 L-tartrate suggest that these are close to equilibrium.

The non-equilibrium structures predicted for weakly chiral systems (specifically, if $\Delta S \gg \gamma/2$) are expected to exhibit correlated values of $T$ and $W$: $T/W$ varies inversely with enantiomeric excess, although $T$ and $W$ are expected to have polydisperse distributions. This corresponds well to the twisted ribbons formed by mixtures of D and L enantiomers, which exhibit such correlated, though polydisperse, geometrical parameters, and large $T/W$ ratios. The observed stability for these helices probably results from kinetic effects which limit their growth.

Thus, on the basis of molecular parameters such as chirality and anisotropy of the surfactant polar heads, this simple yet general model predicts that the observed twisted-ribbon shape is optimal, and that both the pitch and the width are expected to follow the trends that we observe on varying the chirality. Also important are the apparently qualitatively different behaviours for strongly and weakly chiral systems. The experimental observations and the theoretical model reported here may open the prospect of creating stable structures of variable pitch in amphiphilic bilayer systems.

Received 4 January; accepted 24 March 1999.


Acknowledgements. This work was supported by the CNRS, INSERM, l’Hôpital Universitaire de Strasbourg, and Rhône-Poulenc. F.C.M. was supported in part by the CNRS, the Deutsche Forschungs-
gemeinschaft, the National Science Foundation, and the Petroleum Research Fund (administered by the ACS).