Pitch of a polymer cholesteric

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This result is in sharp contrast to what was observed in micelles[2] where the following order was obeyed:

$$\tau_{1/2}(\text{Mi}^+) < \tau_{1/2}(\text{Mi}^0) < \tau_{1/2}(\text{Mi}^-)$$

Two important factors—obviously not independent from each other—intervene in the redox reactions responsible for the TMB$^+$ decay: the electric field intensity and the respective location and local concentrations of the reactants.

A negatively charged interface, as in DHP vesicles or anionic micelles, would control the localization of the aqueous nucleophile Cl$^-$, hence the analogous behavior or Ve$^-$ and Mi$^-$ systems with regard to the electron-transfer reactions involved in the TMB$^+$ decay.

Such a picture cannot hold for DODAC vesicles, however, since the TMB$^+$ decay in DODAC is found slower than in DHP. In DODAC vesicles the electrostatic contribution susceptible to increase the reaction rate by the presence of Cl$^-$ in the Stern layer would not be the most important one, and a localization of TMB$^+$ deeper in the lipid bilayer, increasing the distance between the reactants, would be the determining parameter. It may then be speculated that the combined influence of the repulsive interfacial positive charge, of the TMB$^+$ hydrophobicity, and possibly of a viscosity gradient across the bilayer would result in a relative stabilization of TMB$^+$ in the core of the membrane. It may also be envisaged that the TMB$^+$ anchoring could be facilitated by some structural distortion of the surfactant chains around the cation as recently advocated.[24]

The electrostatic repulsive effect would be attenuated upon salt addition, the TMB$^+$ anchoring loosen, and the decay accelerated in accordance with what was observed.

It should be noted that the addition of NaCl, even at low concentrations, has been reported to increase notably the hydrodynamic radius of DODAC vesicles.[25] In the present context this would not be the key parameter, however: similar data are obtained with CaCl$_2$, the addition of which does not alter the DODAC vesicle radius.[25]

Conclusions

The present results emphasize the complexity and variability of different surfactant aggregate properties. The permeability of the interface, very different in Mi and Ve, plays a determinant role in the reactivity of species moving across the Ve interface. The viscosity is also an important parameter: in Ve, charged species can be anchored between the surfactant molecules. As well recognized the chemical nature of the solubilizate, its location, and possibly a strained geometry in the aggregate may also be quite critical.

Nevertheless, beside such specific features, some quantitative relationships can be disclosed which relate some characteristics of a particular reaction to a particularly pertinent parameter. Such is the case for electron-transfer processes vs. the interfacial electric potential $\Delta\psi$.

Similar laws, linear for φ_{ion} vs. $\Delta\psi$[1] and exponential for TMB$^+$ decay rate constant vs. $\Delta\psi$,[2] have been obtained previously for negatively charged micelles. Such findings illustrate the analogous influence of the water–lipid charged interface in both types of aggregates. However, the decay mechanism appears more complex in Ve systems where much higher solute concentration lead to intravesicular solute–solute derivative reactions.

Obviously, Mi or Ve assemblies affect the electron-transfer yield and rates not only through the existence of surface electric potentials. Even electrically neutral surfactant assemblies may increase the lifetime of transient species by several orders of magnitude when the reaction partners are solubilized in two separate phases. Reaction pathways other than mutual recombination are thus favored.

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Pitch of a Polymer Cholesteric

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The pitch of a cholesteric solution of semiflexible macromolecules is calculated in the second virial approximation. The predicted concentration dependence is very close to that determined for poly(γ-benzyl L-glutamate) solutions by DuPré and Duke (*J. Chem. Phys.* **1975**, *63*, 143).

Most calculations of the pitch in cholesteric solutions have focused on details involving chiral dispersion forces.[1-5] A general theory based on the virial expansion of the free energy was set up by Straley.[6] However, this work has been taken up by few others, probably because his prediction for the twist modulus K_2 and pitch p were in stark disagreement with experiment. Here, it is pointed out that proper evaluation of Straley's integrals together with adequate consideration of chain flexibility lead to concentration dependences of K_2 and p closely matching those found for poly(γ-benzyl L-glutamate) solutions.[7] Our analysis

using scaling arguments is straightforward although it gives only qualitative insight.

For the moment we model the macromolecules by rods of length L and number density ρ_L. To simulate chiral interactions, each rod is enveloped by a thin helical thread of thickness Δ. All the

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helices have the same handedness. If Δ is much smaller than the rod diameter D, the chiral interaction between two rods is a perturbation in comparison with the usual excluded-volume effect. If we let Δ tend to zero formally, the solution would be nematic with a free energy described as in ref 8. The chiral perturbation, switched on when Δ is nonzero, induces a cholesteric organization of the director with an attendant change in the free energy density δF expressed by[6]

$$\delta F = \tfrac{1}{2}k_B T\rho_L^2 \int \int dm_1 \ dm_2 \ f(m_1 \cdot n)C(m_1,m_2) \cdot \nabla f(m_2 \cdot n) -$$
$$\tfrac{1}{4}k_B T\rho_L^2 \int \int dm_1 \ dm_2 \ \nabla f(m_1 \cdot n) \cdot D(m_1,m_2) \cdot \nabla f(m_2 \cdot n) \quad (1)$$

Here, k_B is the Boltzmann constant, T is the temperature, and f is the orientational distribution function depending on the director n, which itself is a function of the spatial coordinate r. Thus, f depends implicitly on r; its gradient with respect to r is denoted by ∇f. The unit vectors m_1 and m_2 are aligned along the axes of the test rods 1 and 2. Equation 1 represents the first two terms of a Taylor expansion of the excluded-volume effect in the second virial approximation. Hence, the vector C and tensor D are defined in terms of the Mayer function $\Phi(m_1,m_2,\xi)$ where ξ is the vector distance between the centers of the test rods[6]

$$C(m_1,m_2) \equiv -\int d\xi \ \xi\Phi(m_1,m_2,\xi) \quad (2)$$

$$D(m_1,m_2) \equiv -\int d\xi \ \xi\xi\Phi(m_1,m_2,\xi) \quad (3)$$

subject to the following symmetry relations

$$\Phi(m_1,m_2,\xi) = \Phi(m_2,m_1,-\xi) \quad (4)$$
$$C(m_1,m_2) = -C(m_2,m_1)$$
$$D(m_1,m_2) = D(m_2,m_1)$$

Whenever a cholesteric solution is not influenced by external forces, the director adopts a pure twist deformation; i.e., $\nabla \cdot n = 0$ and $\nabla \times \nabla \times n = 0$ but the pseudoscalar $n \cdot \nabla \times n$ is nonzero. The pitch of this helicoidal structure is determined by balancing the chiral forces inducing twist ($\sim C$) against elastic forces favoring the nematic state ($\sim D$). The latter are also proportional to the twist modulus K_2:

$$\tfrac{1}{2}k_B T\rho_L^2 \int \int dm_1 \ dm_2 \ \nabla f(m_1 \cdot n) \cdot D(m_1,m_2) \cdot \nabla f(m_2 \cdot n) =$$
$$-K_2(n \cdot \nabla \times n)^2 \quad (5)$$

Similarly, we introduce a coefficient K_t pertaining to the chiral interaction C:

$$\tfrac{1}{2}k_B T\rho_L^2 \int \int dm_1 \ dm_2 \ f(m_1 \cdot n)C(m_1,m_2) \cdot \nabla f(m_2 \cdot n) =$$
$$-K_t(n \cdot \nabla \times n) \quad (6)$$

We infer the configuration of the director by minimizing δF given by eq 1, 5, and 6 with respect to the quantity $n \cdot \nabla \times n$.[9] Accordingly, $n \cdot \nabla \times n$ must be a constant:

$$n \cdot \nabla \times n = K_t/K_2 \equiv -q \quad (7)$$

A solution of eq 7 in terms of the coordinates $r = (x,y,z)$ is

$$n_x = \cos qz, \quad n_y = \sin qz, \quad n_z = 0$$

Hence, q signifies the magnitude of the wave vector of the cholesteric so the pitch $p \equiv |2\pi/q|$ becomes

$$p = |2\pi K_2/K_t| \quad (8)$$

Our objective is to calculate p for chiral rods and chains in the Gaussian approximation:

$$f(\theta) \simeq (\alpha/4\pi) \exp(-\tfrac{1}{2}\alpha\theta^2) \quad (\alpha \gg 1; 0 \le \theta \le \tfrac{1}{2}\pi) \quad (9)$$
$$f(\theta) = f(\pi - \theta)$$

where $\cos \theta = m \cdot n$ and α is a variational parameter ultimately linked to the number density.

Grosberg and Zhestkov[10] and Odijk[11] have independently calculated K_2 for rods or chains interacting via excluded-volume interactions. If we delete numerical coefficients, we have for rodlike nematics (neglecting slight cholesteric perturbations)

$$\alpha \simeq (L^2 D\rho_L)^2 \quad (10)$$

$$K_2 \simeq k_B TL^2\rho_L \quad (11)$$

For long semiflexible chains the scaling recipe[11-13] consists of replacing L by $\lambda = P/\alpha$ and ρ_L by $\rho_\lambda = \alpha\rho_P$, where λ is the deflection length, P is the persistence length, and ρ_l is the number density of effective segments of length l ($l = L, P,$ or λ). Equations 10 and 11 yield[10,11]

$$\alpha \simeq (P^2 D\rho_P)^{2/3} \quad (L \gg \lambda) \quad (12)$$

$$K_2 \simeq (k_B T/D)(P^2 D\rho_P)^{1/3} \quad (L \gg \lambda) \quad (13)$$

In order to derive K_t, we postulate that C has the form proposed by Straley[6]

$$C(m_1,m_2) = hL^2 D\Delta(m_1 \times m_2)(m_1 \cdot m_2) \quad (14)$$

Because C scales as a length to the fourth power, it can only be proportional to Δ and the excluded-volume $L^2 D$. In addition, its angular dependence must be such that $C(m_1,m_2) = -C(m_2,m_1)$ and $C(m_1,m_2) = C(m_1,-m_2) = C(-m_1,m_2)$. The factor h, a function of the macromolecular pitch divided by Δ, was not taken into consideration in ref 6, but if these two scales are of the same order of magnitude, h is of order unity. When inserting eq 9 and 14 into eq 6, we can estimate various terms by observing that $|m_1 \times m_2| = \sin \gamma \simeq \gamma \simeq \langle\theta^2\rangle^{1/2} \simeq \alpha^{-1/2}$ with γ the angle between rods 1 and 2, and $|\nabla f(n)| \simeq |\partial f/\partial\theta|n \cdot \nabla \times n| \simeq \theta\alpha f|n \cdot \nabla \times n|$. In this way we can show that the leading behavior of K_t is

$$|K_t| \simeq k_B TL^2 D\Delta\rho_L^2 \quad (15)$$

Hence, the pitch of a solution of rigid chiral rods is given by eq 8, 11, and 15:

$$p \simeq (\Delta D\rho_L)^{-1} \quad (16)$$

For a solution of long semiflexible chiral chains, eq 15 and 16 become eq 17 and 18 in view of the scaling prescription

$$L \rightarrow \lambda, \quad \rho_L \rightarrow \rho_\lambda$$

$$|K_t| \simeq k_B TP^2\Delta D\rho_P^2 \quad (L \gg \lambda) \quad (17)$$

$$p \simeq \Delta^{-1}P^{-4/3}D^{-5/3}\rho_P^{-5/3} \quad (L \gg \lambda) \quad (18)$$

The condition for the validity of the second virial approximation is $D/L \ll \alpha^{-1/2}$ for rods ($L \ll \lambda$) and $D/\lambda \ll \alpha^{-1/2}$ for long chains ($L \gg \lambda$). The estimates $P \simeq 800$ Å, $D \simeq 16$ Å, and $\alpha = O(10)$ used in ref 13 show that PBLG is stiff enough to be a good model polymer for testing eq 13 and 18. DuPré and Duke[7] determined the pitch of dioxane solutions of PBLG as a function of PBLG concentration by measuring the distance between regular striations under a polarization microscope. The twist modulus K_2 was gleaned from the values of the critical magnetic field H_c causing the cholesteric structure to unwind. According to macroscopic theory[14,15]

$$H_c \sim K_2^{1/2}/p \quad (19)$$

The theoretical exponents $\tfrac{1}{3}$, $-\tfrac{5}{3}$, and $\tfrac{11}{6}$ for the concentration dependence of K_2 (eq 13), p (eq 18), and H_c (eq 19), respectively, are rather close to 0.36, -1.8, and 2 deduced by DuPré and Duke[7] (actually they plot K_2 versus the concentration in their Figure 5

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but log K_2 would also be linear in log ρ because the concentration range is narrow; the exponent would be about 0.36). However, the molecular weight dependence[7] of p cannot be quantitatively explained. In ref 13 we derived an expression for α as a function of the contour length L (see eq IX.10 with $X_a = 0$, corrected for a misprint[13]):

$$\alpha^{1/2}[(L/6\lambda)[1 + \tfrac{1}{2}\tanh(L/5\lambda)] + 1] = \tfrac{1}{2}\pi^{1/2}L^2 D\rho_L \quad (20)$$

This predicts a decrease of $p \sim \alpha^{-1}$ by about 4% when the molecular weight of PBLG increases from 310 000 to 550 000; this is to be contrasted with the 10–20% decrease shown in Figure 3 of ref 7. However, the molecular weight dependence is probably sensitive to the model and approximations employed. We remark that the approximation involved in using Straley's C (eq 14) is probably not that crucial in evaluating the exponents pertaining to the concentration dependence of K_2 and p. Indeed, similar expressions have been proposed for other types of interaction.[4] To a certain extent the above-mentioned exponents might be universal and independent of whether the chiral interactions are repulsive or attractive.

Analysis of Some Equations of State in Relation to Microscopic Interpretations of Mechanically Significant Entropy for Polymeric Glasses and Melts

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The ratio of the entropic part to the total value of the bulk modulus, denoted Υ, is evaluated for seven equations of state. The ideal gas and van der Waals equations provide a conceptual reference. Under all conditions the ideal gas has $\Upsilon = -1$. Other equations of state of particular relevance to macromolecular liquids and glasses are considered. The simple microscopic models built with impenetrable molecules, free volume, and interaction energies that scale with reciprocal volume are shown to be too simplistic for even the equilibrium melts. Polymeric glasses cannot be treated even qualitatively with any but the empirical Tait equation. It is suggested that this results from neglect of the intrinsically polymeric nature of the condensed phases of interest. The Υ criterion is shown to be related to the so-called Anderson–Gruneisen parameter.

I. Introduction

Two broad, thermodynamic classes of polymeric solids are familiar to us. In one class, there are the wholly amorphous elastomers under conditions where the temperature exceeds the glass transition temperature, $T \gg T_g$. These are essentially liquids that are given solid form by virtue of their chemical cross-links. Under most conditions (excluding, for example, inordinately high cross-link densities, extremes of extension, or $T \lesssim T_g$) this class is in true thermodynamic equilibrium. In the second class are all other polymer solids: glasses, semicrystalline polymers, and extreme exemplifications of elastomers. These materials are not in thermodynamic equilibrium; consequently, their volume is not a function of state variables only and a unique equation of state cannot be written. Nevertheless, the deformation behavior of materials in this second class is of obvious practical concern, and this has encouraged many researchers over the years to attempt to determine at least the proper form(s) for their equations of state.

Recently[1-3] attention has been focused on the entropic contributions to the bulk moduli of amorphous polymers. That contribution is not always negligible, and it is natural to ask about the microscopic sources of the mechanically important entropy. As an initial attempt to answer that question, the present contribution will analyze some of the consequences of supposing that various forms for equations of state are applicable. The microscopic models used to generate the different equations of state, or at least their a posteriori interpretation, provide insights into the important physical processes that influence the mechanical deformation of polymer solids in either class.

Specifically, consider the ratio of the entropic part of the bulk modulus, $B \equiv [-1/V(\partial V/\partial P)_T]^{-1}$ to the total.[4] V and P denote volume and pressure, respectively. This quantitative measure was introduced by Theodorou and Suter[1] and has been subsequently rederived and christened Υ.[2] The formulation of choice for study of equations of state is[2]

$$\Upsilon = T\left[\frac{1}{k}\left(\frac{\partial k}{\partial T}\right)_P + \frac{\alpha}{k^2}\left(\frac{\partial k}{\partial P}\right)_T\right] \quad (1)$$

where T is the absolute temperature, α is the isobaric thermal expansion coefficient $[\alpha \equiv (1/V)(\partial V/\partial T)_P]$, and k is the isothermal compressibility, the reciprocal of B previously introduced. Υ is dimensionless. Once given an equation of state, Υ can be obtained by partial differentiation. Limited data available to date[2,3] indicates that Υ can be either positive or negative for macromolecular solids. The absolute value is characteristically less than unity.

II. Special Cases

A. The Ideal Gas. As is well-known, the equation of state for the ideal gas is

$$P\bar{V} = RT \quad (2)$$

where R is the gas constant and the overbar denotes a molar quantity, here, volume. It is a simple matter to show that the Υ corresponding to the behavior described in eq 2 is

$$\Upsilon_i = -1 \quad (3)$$

for all conditions.

Therefore, the bulk modulus of the ideal gas is wholly entropic. This conclusion is inescapable on physical grounds, since the microscopic model of an ideal gas possesses no characteristic beyond positional entropy and its resulting kinetic pressure. This makes the ideal gas a useful conceptual reference, which will prove to be more formally accessible if Υ values are reported as their negative reciprocals. Thus from eq 3 we have

$$-1/\Upsilon_i = 1 \quad (4)$$

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(4) Recall that $B = -V(\partial^2 A/\partial V^2)_T$ where A is the Helmholtz free energy. Of course, A has both an energy and an entropy contribution.