Notes

Effect of Chain Length and Degree of Substitution on the Cholesteric Pitch: Theoretical Considerations

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I. Introduction

Recently a microscopic theory was proposed to calculate the temperature and concentration dependence of the cholesteric pitch.[1] In the present paper we apply this model to experimental results on the pitch of cellulose derivatives. The properties of the cholesteric mesophases in these polymer liquid crystals have been examined in detail, and the effect of the temperature, solvent, and chemical nature of the substituents has been explored. The degree of polymerization is a parameter of importance in polymeric liquid crystals, and measurements of the pitch of thermotropic cholesteric polymers show a decrease with an increase in the degree of polymerization.[2,3] The handedness of the helicoidal arrangement has been measured and shown to depend on the type[4,5] and quantity of the solvent[4,6] in lyotropic systems and on the temperature in thermotropic systems[3,7] and can be changed by modifying the chemical structure of the substituent.[5]

Many types of microscopic interactions have been proposed to explain these effects.[8–17] The theory used here has the advantage that it does not specify the type of potential present in a given system but simply uses an expansion in nematic and chiral parts valid for any interactions present in a cholesteric system (dispersion, steric, H bonds, dipoles, ...).

II. Theory

We study the interaction between two rodlike molecules at positions $\mathbf{r}_1$ and $\mathbf{r}_2$ of respective orientations Ω_1 and Ω_2. We use a form for the chiral interaction first proposed for induced dipole–dipole and dipole–quadrupole interactions[10] and extended to higher order multipoles.[12] Similar forms have been shown to occur for chiral dispersion forces,[13] dipoles in a helicoidal arrangement,[16] and rods with an asymmetric structure[11] and have been used as an attractive perturbation to calculations on hard-rod systems.[8,9]

$$V(\mathbf{r}_1,\mathbf{r}_2,\Omega_1,\Omega_2) = V_{\mathrm{N}}(\mathbf{r}_{12},\Omega_1\Omega_2) + (\Omega_1\ \Omega_2\cdot\mathbf{r}_{12})\ V_{\kappa}(\mathbf{r}_{12},\Omega_1\Omega_2) \tag{1}$$

with

$$V_{\mathrm{N}}(\mathbf{r}_{12},\Omega_1\Omega_2) = V_2(\mathbf{r}_{12})\ P_2(\Omega_1\Omega_2) \tag{2}$$

$$V_{\kappa}(\mathbf{r}_{12},\Omega_1\Omega_2) = V_1(\mathbf{r}_{12})\ P_1(\Omega_1\Omega_2) + V_3(\mathbf{r}_{12})\ P_3(\Omega_1\Omega_2)$$

$$P_L\ (L = 1\text{–}4) = \text{Legendre functions}$$

Using the method developed in ref 18 and extended to include contributions of orientational entropy,[1] the pitch p was found to be given by

$$Q = dq = \frac{2\pi d}{p} = \frac{n_0 + \dfrac{\hat{x}n_1 + \hat{x}^2 n_2}{n}}{\dfrac{\lambda_2}{\gamma_2} + \dfrac{\hat{x}d_1 + \hat{x}^2 d_2}{n}} \tag{3}$$

with the symbols defined as follows:

$$n_0 = m_1 + m_2 S^2(T)$$

$$n_1 = \frac{4}{5}m_1$$

$$n_2 = -\frac{8\sigma_2(T)}{35}(m_1 + m_2 S(T))$$

$$d_1 = 2\left[\frac{2}{5}\left(\frac{\lambda_2}{\gamma_2} + 3{m_1}^2\right) + \frac{2}{3}{m_2}^2 S(T)^2\right]$$

$$d_1 = -2\sigma_2(T)\left[\frac{4}{35}\left(\frac{\lambda_2}{\gamma_2} + 6{m_1}^2\right) + \frac{48}{35}S(T)\ m_1 m_2 + \frac{80}{231}{m_2}^2 S(T)^2\right]$$

$$n = 2 + \frac{\hat{x}^2}{5}{\sigma_2}^2(T)$$

$$\hat{x} = x\frac{L\gamma_2}{kT_{\mathrm{c}}}\frac{T_{\mathrm{c}}}{T}, \quad S(T) = \left(\frac{\sigma_4(T)}{\sigma_2(T)}\right),$$

$$m_1 = \left(\frac{\mu_1}{3} - \frac{\mu_3}{7}\right)\frac{1}{\gamma_2}, \quad m_2 = \frac{10}{21}\frac{\mu_3}{\gamma_2}$$

$$\gamma_2 = \int V_2(\eta)\ \mathrm{d}\vec{\eta}$$

$$\lambda_2 = -\int \xi^2 V_2(\eta)\ \mathrm{d}\vec{\eta}, \quad \mu_m = \int \frac{\xi^2}{\eta}V_m(\eta)\ \mathrm{d}\vec{\eta}, \quad \vec{\eta} = \vec{r}/d, \quad \xi = z/d \tag{4}$$

We have defined the z-axis as the optical axis.

The parameters of importance are found to be a reduced concentration $\hat{x}$, a ratio $S(T)$ of second order $\sigma_2(T)$ and fourth order $\sigma_4(T)$ order parameters, a ratio of an average nematic field γ_2, and the nematic and chiral interactions λ_2, μ_1, and μ_3 of second, first, and third order in the expansion of the intermolecular potential in spherical harmonics. Normalization of length is made with respect to an intermolecular distance d and of temperatures with respect to the isotropic–anisotropic transition temperature of the pure melt T_{c}. In a simple solvent the concentration x of the cholesteric can also be varied and dilutes the anisotropic interactions. The degree of polymerization is given by L.

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Table I
Chiral Interaction Parameters μ_1 and μ_2 Normalized with Respect to the Nematic Interaction γ_2[a]

		$S(T_c) = 0.1$				$S(T_c) = 0$:	$S(T_c) = -0.1$
		solution 1	solution 2	solution 3	solution 4	solution 1	solution 1
$T_c = 140$ °C, DP = 29	μ_1/γ_2	−0.0775	12.932	7.2857	31.227	−0.08283	−0.09899
	μ_3/γ_2	−0.2383	49.864	−113.15	−107.01	−0.25785	−0.28882
$T_c = 173$ °C, DP = 140	μ_1/γ_2	−0.149					
	μ_3/γ_2	−0.6047					

[a] Solutions 2–4 represent nonphysical solutions. $S(T_c)$ is the ratio of the order parameters at the transition temperature T_c; DP denotes the degree of polymerization. The nematic interaction parameters are $\lambda_2/\gamma_2 = -2$.

III. Numerical Applications

As in the previous paper,[1] the internal parameters γ_2, λ_2, σ_2, and σ_4 are fixed using representative values and we concentrate on variations of the chiral interactions μ_1 and μ_3.

We use $S(T) = S(T_c) + 0.42 \exp(-7.31/(T_c - T))$; $S(T_c)$ is the value at the transition.

$$\sigma_2(T) = 0.28(T_c - T)^{0.26}(1.15^{1/(T_c-T)}), \quad T < T_c - 0.65$$

The mean-field value for $kTc/-L\gamma_2 = 0.22$.

III.1. Effect of the Degree of Polymerization.[2] (Acetoxypropyl)cellulose (APC) polymers were shown to be thermotropic cholesterics. The isotropization temperature was studied as a function of the degree of polymerization (DP) and shown to increase with an increase in DP until a plateau is reached in samples of high molar mass. The temperature dependence of the cholesteric pitch was also measured, and the pitch was shown to increase with an increase in the temperature. At a given temperature the cholesteric pitch decreases with an increase in DP. We will use these results to compare with theoretical predictions. The method is as follows. A test value of DP is chosen, here the smallest, as ln (DP) = 3.5. Two points are chosen on the selective reflection curve versus temperature for this value of DP. Using the measured value of T_c for this value of DP, we can then determine μ_1 and μ_3 from eq 3. This requires solution of a set of two coupled quadratic equations in μ_1 and μ_3 equivalent to calculating the possible intersection points of two ellipses. Only one set of μ_1/γ_2 and μ_3/γ_2 fulfills the condition of being smaller than 1 (see Table I) and is retained. These values also give the most reasonable temperature dependence beyond the measured range (Figure 1). The influence of the control parameter $S(T_c)$ was also investigated and appears to affect the results for the pitch only in the vicinity of the transition temperature. This justifies the use of the small positive value, more realistic than that obtained in a self-consistent, mean-field calculation.[19] Using the calculated values of μ_1/γ_2 and μ_3/γ_2 and the experimental transition temperatures, the pitch as a function of molecular weight can be obtained (Figure 2). Qualitative agreement is found. The calculated slope of the pitch as a function of temperature does not vary as rapidly with the DP as the experimental value. This can also be seen by calculating the values of μ_1/γ_2 and μ_3/γ_2 for DP = 140. An increase of over a factor of 2 relative to the low molar mass (Table I) is necessary to fit the experimental curve. This may be due to the simplifications inherent in the theory: use of the rigid-rod model and mean-field theory and neglect of higher order parameters. It may also be due to a variation of the interaction parameters with DP and/or temperature, as has already been concluded in the nematic systems.[20]

We conclude that the variation of the pitch with DP can be related to the similar variation of the transition temperature. Whether this variation is caused by steric hard-rod interactions as suggested elsewhere[8,9] is a question which remains to be explored.

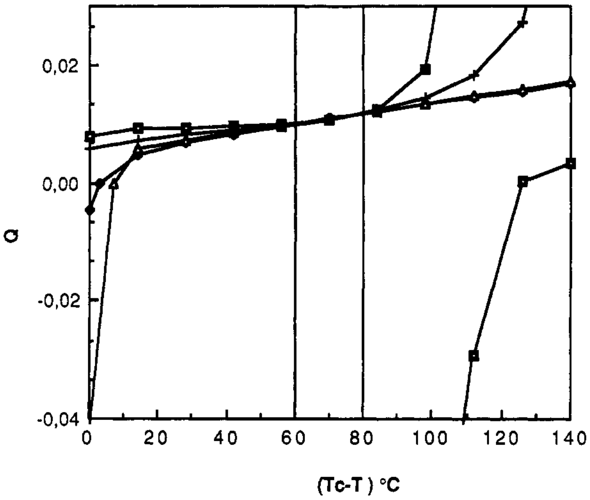

Figure 1. Inverse pitch Q in units of interatomic distance as a function of relative temperature $T_c - T$ for the four solutions of Table I; DP = 29, $S(T_c) = 0.1$. Note the difference in behavior outside the experimental region 60 °C < $T_c - T$ < 80 °C and the divergence for solution 3: (◆) solution 1, (△) solution 2, (□) solution 3, (+) solution 4.

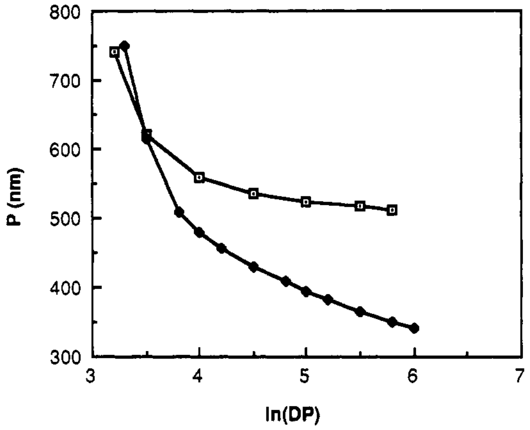

Figure 2. Variation of the pitch p with degree of polymerization DP at 100 °C for (acetoxypropyl)cellulose. The theoretical curve (□) is calculated using Table I, solution 1, for DP = 29, $S(T_c) = 0.1$, and the experimental values of the transition temperature of ref 2. Comparison is made to the experiments of ref 2 (◆). The interatomic distance $d = 7$ Å, and the mean refractive index is taken as 1.3.

III.2. Effect of Substitution.[5] Ethylcellulose (EC) is a cholesteric liquid crystal which can change its handedness in different solvents. Acetylation of EC gives a new cholesteric liquid crystal, acetylethylcellulose (AEC), whose physical properties vary with the degree of substitution. In a 45% solution of AEC in chloroform it was shown that the helicoidal structure changes from left-handed to right-handed at a critical degree of acetylation DA* around 0.18–0.2. The slope of the absolute value of the pitch as a function of temperature also changes from negative to positive at DA*.

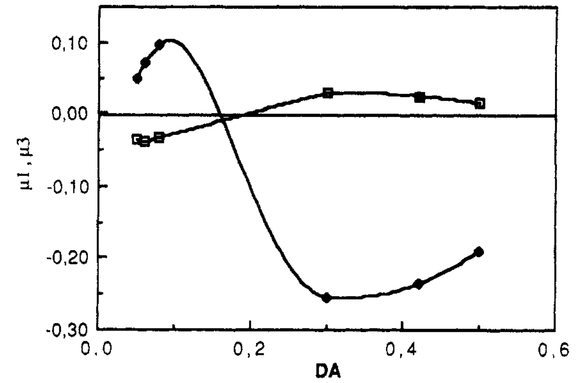

Figure 3. Values of the ratio of the chiral interaction parameters μ_1 (□) and μ_3 (◆) and the nematic interaction γ_2 as a function of the acetyl content DA deduced from the experiments on acetylethylcellulose in ref 5. We use $\lambda_2/\gamma_2 = -2$, $d = 7$ Å, $S(T_c) = 0.1$, and a mean refractive index of 1.6. The transition temperatures are taken from ref 5. The full curves are an extrapolation to fourth order in DA.

As discussed in section III.2, we can use these results to calculate μ_1 and μ_3 as a function of the acetyl content. We approximate the transition temperature T_c by the measured fusion temperatures, the anisotropic–isotropic transition being ill-defined. The dependence of the pitch on the temperature and on the acetyl content is well described using the chiral interaction parameters given in Figure 3. We find a profound modification of these parameters with a change of sign in the vicinity of the critical acetyl content DA*.

The results of the fit of μ_1 and μ_3 as a function of degree of substitution DA show a continuous transition from the values for the left-handed cholesteric EC to the values for the right-handed cholesteric in the fully substituted AEC. An excellent fit to the numerical results is given by a fourth-order polynomial in DA. Besides an effect of dilution, second order in DA, it would therefore appear that the interaction of importance itself is also dependent on the degree of substitution. One possibility is related to the disappearance of hydrogen bonds occurring in EC but replaced by substitution in AEC. The hydrogen bonds could also be blocked by certain solvents such as dichloroacetic acid, also leading to a change of handedness.

IV. Discussion of Results

Although the qualitative variation of the pitch as a function of molecular weight is well reproduced, a better fit may be obtained by use of the elastic chain model. A characteristic change for a DP in the vicinity of the persistence length can be expected, and calculations are currently in progress.

All theories which predict a change of handedness of the pitch[1,9,18] are based on a cancellation of repulsive and attractive interactions, for example, at a certain critical temperature. For example, in ref 9, repulsive steric interactions are balanced by attractive polar interactions corresponding to the vanishing of m_1 in the present work. A change of handedness with DA could therefore be obtained on the assumption of a change in geometry and/or a change in optical activity, which does not seem to be in agreement with experimental results.[5] These theories all use an expansion of the free energy with respect to the pitch. From our numerical results we find that the higher order terms in the expansion of the potential (eq 2, Table I, and Figure 3) and in the expansion of the pitch (eq 3) are of the same order of magnitude as the lower order terms and may therefore lie outside the range of validity of this method.

It would be of interest to relate the chiral parameters either to specific molecular interactions (which seems difficult in view of the complex chemical structure) or to other physical properties. Thermodynamic properties have been calculated, but the biaxiality and the contribution of chirality to the order parameters or the transition temperature appear to be small.[21] The values of the nematic interaction parameters are also not well-known and could possibly be orders of magnitude larger than the values used here.

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