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## Liquid Crystals

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## On the relationship of the nematic-isotropic transition temperature of an oligomer to that of its constituent units

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We consider the nematic-isotropic transition temperature for a rigid oligomer formed by linking identical mesogenic units together. In particular, we seek to relate the transition temperature for the oligomer to that of the constituent units, within the framework of the Maier-Saupe molecular field theory and its various parameterizations.

Molecular association can take many forms in liquid-crystalline materials. For lyotropic systems the solvent-induced aggregation of amphiphilic molecules to yield anisotropic micelles is a prime requisite for the formation of a mesophase. Such physical association can also be important for thermotropic liquid crystals, ranging from the relatively weak dimers postulated for the 4-*n*-alkyl-4'-cyanobiphenyls [1] to the stronger dimers formed by the 4-*n*-alkoxybenzoic acids [2]. In addition, mesogenic units may also be linked chemically, for example, through a flexible alkyl chain [3] or a transition metal [4]. As with liquid crystal polymers, this chemical binding results in important modifications to the liquid-crystalline properties in comparison with those of the monomer. Here we are concerned with a single property, namely the nematic-isotropic transition temperature and its relationship to that of the constituent mesogenic units. We shall take these units to be cylindrically symmetric and link them together to form a rigid oligomer which also has cylindrical symmetry. The relationship between the transition temperatures is explored within the framework of the Maier-Saupe molecular field theory of nematogens [5] and the various parameterizations proposed for the theory.

At the heart of this theory is the expression

$$U = -\varepsilon \bar{P}_2 P_2(\cos \beta) \quad (1)$$

for the potential of mean torque experienced by a molecule with its symmetry axis at an angle  $\beta$  to the director.  $\bar{P}_2$  is the second rank order parameter obtained by averaging the second Legendre polynomial  $P_2(\cos \beta)$  and  $\varepsilon$  is a positive coefficient related to the anisotropic pair potential, averaged over the molecular separations. The form of the potential in equation (1) has been derived in several ways and we shall encounter some of these later. The Maier-Saupe theory predicts the nematic-isotropic transition temperature to be

$$T_{NI} = 0.22019\varepsilon/k \quad (2)$$

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and so to solve the problem we have set ourselves we need to relate  $\varepsilon$  for the oligomer to that for its constituent parts which, for the sake of simplicity, we take to be identical. However before we attempt this it is important to realize that the strength parameter  $\varepsilon$  is volume dependent because it is determined by an average over the intermolecular separations. In Maier and Saupe's original derivation it was proposed that  $\varepsilon$  varied as  $V^{-2}$  because the anisotropic potential was assumed to result from London dispersion forces, with their  $r^{-6}$  dependence. Subsequently, however, Cotter has shown that for the molecular field theory to be statistically mechanically consistent  $\varepsilon$  must be linear in the number density  $\varrho$  [6]. The transition temperature should therefore be given by

$$T_{\text{NI}} = 0.22019\varepsilon\varrho/k, \quad (3)$$

where we have not distinguished between the  $\varepsilon$  in the two equations, because there is no risk of confusion.

The change from a monomer to a rigid, cylindrically symmetric oligomer containing  $n$  units alters both the number density and the interaction parameter. The variation in  $\varrho$  is straightforward provided any change in the volume of the system is negligible for then the only alteration is in the number of particles and so

$$\varrho_n = \varrho_1/n; \quad (4)$$

here the subscript 1 denotes the monomer and  $n$  the oligomer. This effect, on its own, would result in a reduction in the transition temperature because of the increase in the average molecular separation. In order to appreciate this result it may be helpful to recall that within the Maier–Saupe theory the molecules are equivalent to spherical particles with an embedded anisotropic interaction centre.

Any increase in  $T_{\text{NI}}$  for the oligomer must therefore be produced by an increase in the strength parameter for the anisotropic centre; however the more recent derivations of the Maier–Saupe theory [5] do not provide a relationship between  $\varepsilon_1$  for the monomer and  $\varepsilon_n$  for the oligomer. To establish this we require an additional assumption, for example the nature of the anisotropic interactions responsible for the nematic phase. In the original derivation these interactions were assumed to be dispersion forces and so  $\varepsilon$  is proportional to the square of the anisotropy in the polarizability  $\Delta\alpha$  ( $\equiv \alpha_{\parallel} - \alpha_{\perp}$ ). For the oligomer

$$\Delta\alpha_n = n\Delta\alpha_1 \quad (5)$$

and so

$$\varepsilon_n = n^2\varepsilon_1 \quad (6)$$

which means that the transition temperature for the oligomer is just  $n$  times that for the monomer. An identical result would be obtained if the interaction parameter could be written as the square of some molecular anisotropy [7] which was itself additive.

Although certain predictions of the Maier–Saupe theory are quite successful the assumption concerning dispersion forces is recognized to be inaccurate. Thus the transition temperatures, calculated from the theory for particular nematogens for which the polarizability anisotropy is known, are found to be far too small [8]. Given this failure of the theory we need to employ an alternative approach to relate the strength parameters  $\varepsilon_1$  and  $\varepsilon_n$ . The approach we shall adopt is that contained in Marcelja's extension of the Maier–Saupe theory to nematogens composed of flexible

molecules [9]. Within the theory it is necessary to relate the interaction parameters for different conformations and this is achieved by assuming group additivity for the fundamental units of the molecule. In general, a conformation is not uniaxial and so the potential of mean torque for this is written as

$$U = - \sum_q (-)^q X_{2,q}^T C_{2,-q}(\omega), \tag{7}$$

where  $\omega$  denotes the director orientation in the molecular frame and  $C_{2,-q}(\omega)$  is a modified spherical harmonic [10].

The total interaction tensor  $X_{2,q}^T$  depends on the orientational order of the various molecular fragments, as well as the number density. The conformation of the oligomer with which we are concerned is cylindrically symmetric and so the potential of mean torque reduces to

$$U = -X_{2,0}^T P_2(\cos \beta); \tag{8}$$

thus  $X_{2,0}^T$  is equivalent to  $\epsilon Q \bar{P}_2$  in the Maier–Saupe theory. To construct the total interaction tensor from those of the individual segments we use [10]

$$X_{2,q}^T = \sum_{r,j} D_{rq}^2(\Omega^j) X_{2,r}^j. \tag{9}$$

Here  $D_{rq}^2$  is a Wigner rotation matrix,  $\Omega^j$  denotes the Euler angles relating the molecular reference frame to that set in the  $j$ th fragment, with its local interaction tensor  $X_{2,r}^j$ . This expression is simplified considerably for our problem because the units are identical and collinear; in consequence

$$X_{2,0}^T = nX_{2,0}. \tag{10}$$

The local interaction tensor  $X_{2,0}$  is related to the orientational order and segmental interaction coefficients by the general result [10]

$$X_j = \epsilon_{ij} \phi_j v_j^{-1} \bar{P}_2^j + \sum_{i \neq j} \epsilon_{ij} \phi_i v_i^{-1} \bar{P}_2^i. \tag{11}$$

Here  $\epsilon_{ij}$  is the strength coefficient resulting from interactions of segment  $i$  with segment  $j$ ,  $\bar{P}_2^j$  is the second rank order parameter for the  $j$ th segment,  $\phi_j$  is the volume fraction of segment  $j$  in the molecule and  $v_j$  is its volume. For  $n$  identical segments the expression for  $X_j$  is simplified to

$$X_j = n\epsilon_{jj} \phi_j v_j^{-1} \bar{P}_2, \tag{12}$$

but the volume fraction also depends on the number of fragments and is just  $n^{-1}$  and so

$$X_j = (\epsilon_{jj}/v_j) \bar{P}_2. \tag{13}$$

Reverting to our original notation gives

$$X_{2,0}^T = n(\epsilon_1/v_1) \bar{P}_2 \tag{14}$$

which means that the transition temperature of the rigid, cylindrically symmetric oligomer is again predicted to be  $n$  times that of the constituent nematogenic units.

An alternative parameterization of the Maier–Saupe theory, designed to reflect the anisotropy in the molecular shape and hence the short range forces has been proposed, implicitly, by Straley [11]. He was concerned with developing a molecular field theory for biaxial particles and these were taken to be rectangular parallelepipeds. When

the width and breadth of these are equal the particles are effectively rod-like and the strength parameter  $\varepsilon$  is given by

$$\varepsilon = (4D^3/3)\{(L/D) - 1\}^2, \quad (15)$$

where  $L$  is the length of the oligomer and  $D$  is its width; this differs slightly from that obtained from the expression given by Straley, which appears to be in error [12]. Since the monomeric units have the same width the length of the oligomer is just  $nL_1$ . If we now allow for the change in the number density on forming the oligomer (cf. equation (4)) then the ratio of nematic-isotropic transition temperatures is

$$T_{NI}^{(n)}/T_{NI}^{(1)} = n^{-1}\{(nL_1 - D)/(L_1 - D)\}^2. \quad (16)$$

We see that only in the limit of very long monomers ( $L_1 \gg D$ ) does this parameterization give our previous result, that the transition temperature of the oligomer is just  $n$  times that of the monomer. In fact this limiting condition is not satisfied by normal mesogenic molecules for which  $L_1/D$  is typically 3. To illustrate the importance of this we have calculated the difference in  $T_{NI}$  for a dimer and a monomer, predicted by equation (16); for  $L_1/D$  of 3 we find the ratio  $T_{NI}^{(2)}/T_{NI}^{(1)}$  equal 3.1 which is significantly greater than the value of 2 given by the other parameterizations.

At present there is very little experimental data which might be used to test these predictions for the transition temperature of a rigid, cylindrically symmetric oligomer and even this may be ambiguous. For example, the dimer formed by linking two 4-*n*-pentyl-4'-cyanobiphenyl ( $T_{NI} = 308$  K) molecules by platinum dichloride has a nematic-isotropic transition of 447 K [4] which is 1.5 times that of the monomer. In contrast, when palladium dichloride is the linking group the nematic-isotropic transition is monotropic and occurs at a temperature of only 365 K [4] which is just 1.2 times that for the monomer. It may well be that these linked dimers undergo fluctuations of differing amplitude, which destroys their linearity. Such fluctuations certainly occur for dimers in which the linking unit is an alkyl chain, as for the  $\alpha,\omega$ -bis(4,4'-cyanobiphenyloxy)alkanes [10]. The non-linear conformations are expected to be significantly reduced, but not absent, for the short, ethane linkage. Even so the nematic-isotropic transition temperature of 518 K [3] is only 1.4 times that for 4-methoxy-4'-cyanobiphenyl which might be considered to be the relevant monomer unit.

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