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Theoretical Study of Hydrogen-Bonded Supramolecular Liquid Crystals

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ABSTRACT: We propose a new theoretical method to study hydrogen-bonded supramolecular liquid crystals. It is based on our recent theory of associating polymer solutions combined with McMillan's molecular theory of liquid crystallization. We derive phase diagrams of supramolecular liquid crystals consisting of two different species of molecules, such as dimers and trimers. In such phase diagrams, liquid crystallization and two-phase separation coexist. There are two different types of phase separation: one is caused by the first-order transitions of liquid crystals, and the other is demixing by repulsive interaction between the different species of molecules. As a result, multicritical phenomena such as tricritical point, Flory's chimney type two-phase region, etc., appear. Comparison of phase diagrams of dimerized supramolecular liquid crystals with those of corresponding flexible polymers suggests that a new microphase separation transition may occur inside the layers of the smectic A phase.

I. Introduction

Some rigid molecules are known to undergo liquid crystallization when hydrogen-bonded to each other. For example, aromatic acid derivatives with alkoxy or alkyl terminal groups form dimers due to a hydrogen bond between their carboxylic acid groups and show mesomorphism.[1−4] Association between different species of molecules also induces the isotropic/anisotropic phase transition.[5,6] Mesophases of some liquid-crystalline molecules are stabilized by a hydrogen bond with different species of molecules. More markedly, some nonmesogenic molecules form a compound with a mesogenic core when hydrogen bonded. Compounds formed by hydrogen bonds are often called "supramolecules", because molecules assemble into superstructures. A supramolecule with liquid crystallinity is called a "supramolecular liquid crystal". Supramolecular liquid crystals exhibit various new properties and functions. For example, they are easily switched between the isotropic phase and anisotropic one by changing thermodynamic conditions.

Liquid-crystalline molecules are classified into two main categories: thermotropic liquid crystals and lyotropic liquid crystals. Thermotropic liquid crystals change from the isotropic liquid state to a liquid-crystalline one at a certain temperature on cooling. Lyotropic liquid crystals, being dissolved in an appropriate solvent, liquid-crystallize when their concentration reaches a threshold value. Supramolecular liquid crystals have both properties: they change from the isotropic liquid state to a liquid-crystalline one not only by changing temperature but also by changing composition.

Supramolecular liquid crystals reported so far have various molecular architectures. For a mixture of two different species of molecules A and B, each carrying at least one rigid part that form mesogenic core by association, the following types are known:[7,8] dimer type,[9] trimer type,[10] main-chain type,[11,12] side-chain type,[6] combined type,[13] and network type.[14−16]

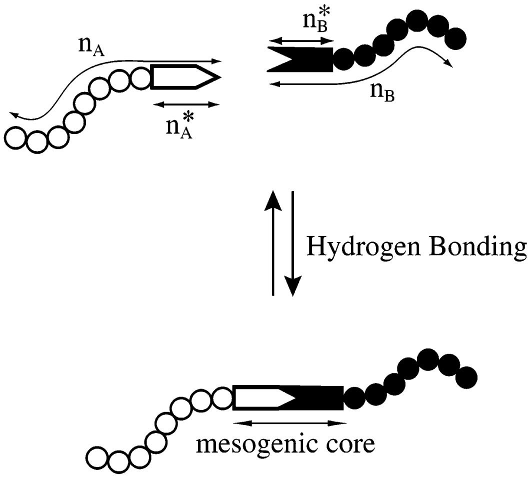

Figure 1. Schematic illustration of a dimer-type hydrogen-bonded supramolecular liquid crystal (A·B).

Dimer Type A·B. An A- and a B-molecule, each carrying one rigid part with one functional group at its free end, associate with each other and form a compound with a longer (or a new) mesogenic core (Figure 1). A typical example is a complex of 4-(hexyloxy)benzoic acid and *trans*-4-alkoxy-4′-stilbazoles with various alkyl chain lengths. Experimental results[9] show that the transition temperature from the isotropic liquid state to a liquid-crystal state depends only little on the alkyl chain length of the stilbazoles. When the number of carbons in the alkyl chain is smaller than 5, both the smectic phase and nematic phase appear. When it is larger than 5, only the smectic phase appears.

Trimer Type A·B·A. Two A molecules associate with one B-molecule, so that a compound with one or two mesogenic cores is formed. An A-molecule has one rigid part and carries a functional group at its free end. A B-molecule has two rigid parts connected by a flexible chain and carries a functional group at its each end. Or, it may be a rigid-rod-like molecule carrying a functional group at its both ends (Figure 2). For example, complexes of 4-alkoxybenzoic acid (or 4-alkylbenzoic acid) and 4,4′-bipyridine (or *trans*-1,2-bis(4-pyridyl)ethylene) are studied.[10] A nematic phase ap-

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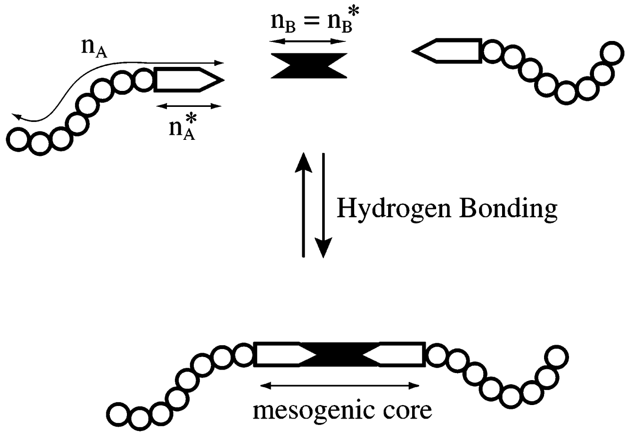

Figure 2. Schematic illustration of a trimer-type hydrogen-bonded supramolecular liquid crystal (A·B·A).

pears when the number of carbons in the alkyl chain of the benzoic acid moiety lies in the range from 1 to 4, whereas only the smectic phase appears when it is larger than 5. The reported experimental phase diagram on the temperature−molarity plane shows that the liquid-crystallization temperature is highest at the stoichiometric composition.

The purpose of our study is to propose a new theoretical method to study these various supramolecular liquid crystals and to derive their phase diagrams and compare them with the experimental data.

Various theoretical methods to deal with liquid crystallization have been proposed so far. Onsager[17] proposed the statistical theory for dilute solutions of very thin rigid-rod-like molecules by taking the excluded-volume effect into account.

Flory[18] extended the lattice theory of polymer solutions to suit solutions of rodlike molecules by taking the orientation of molecular axis into account.[19] Using this extended lattice theory, he derived phase diagrams that show a narrow coexistence region between an isotropic phase (I) and a nematic phase (N), now referred to as a "*chimney*", at higher temperature. At a certain temperature the chimney merges into a wide two-phase coexistence region due to the mixing enthalpy effect between rodlike molecules and solvent molecules. Near this merging temperature, the concentration of the rodlike molecules in the nematic phase sharply changes with temperature.

Another famous molecular field theory using orientational order parameter was proposed by Maier and Saupe.[20−22] It was later extended by McMillan[23] to deal with the smectic A phase (S_m).

As for liquid-crystal phases induced by hydrogen bonding, there have been only a few theoretical studies. Sear et al.[24] studied a mixture consisting of two species of cylindrical molecules that associate with each other and form a cylindrical dimer. On the basis of Onsager's theory, they estimated the free energy of the mixture and derived a phase diagram exhibiting a "*reentrant nematic phase*" between two different species of S_m phase regions. One of these S_m phases is formed by the free cylindrical molecules, and the other is formed by the cylindrical dimers.[24] Such cylindrical dimers are regarded as the supramolecular liquid-crystalline molecules because association induces a new S_m structure. It is, however, difficult to apply their theoretical treatment to other supramolecular liquid-crystalline molecules with complex shapes since their treatment is based on a mathematically complicated calculation of the excluded volume. It is also not suitable to high-concentration solutions because of the virial expansion.

Bladon et al.[25] theoretically studied dimer-type and main-chain-type hydrogen-bonded liquid crystals that associate within the same species by taking only the N phase into account.

To deal with a mixture of polymers and liquid-crystalline molecules or a mixture of two different species of liquid-crystalline molecules, Kyu et al.[26−28] proposed a new theory that combines Flory−Huggins lattice theory with Maier−Saupe−McMillan theory about liquid crystals.[20−23] This treatment uses the partition function regarding the orientational and the translational order given by McMillan[23] instead of the partition function regarding the rigidity of a molecule derived by Flory.[19]

In the present paper, we study binary mixtures of associating nonmesogenic molecules that form liquid-crystalline compounds by association between the different species of molecules. Therefore, we must treat all of the three important factors, i.e., molecular association, phase separation, and liquid crystallization. To satisfy this requirement, we introduce the Maier−Saupe−McMillan theory into our theory of associating polymer solutions.[29−31] The latter is based on Flory−Huggins lattice theory of polymer solutions.[18] The introduction of McMillan's theory enables the consideration of S_m phases. We estimate the free energy of various supramolecular liquid crystals and derive complete phase diagrams. Though Painter, Coleman, and co-workers[32−35] have also studied polymer mixtures forming nonmesogenic hydrogen-bonded complexes experimentally and theoretically, our theory starts from a slightly different viewpoint. By taking the orientational order into our previous free energy,[36,37] we can compare our new results on the supramolecular liquid crystals with our old ones on the corresponding associating flexible polymers. It is well-known that flexible diblock copolymers form mesophases (lamellar phase, hexagonal one, cubic one, etc.) by microphase separation. In our previous studies[36,37] we reported microphase formation in associating binary mixtures in which flexible block copolymers are thermoreversibly formed by hydrogen bonds. Since the lamellar structure is similar to the smectic A structure, we expect the one-to-one correspondence between the lamellar phase of flexible dimers and the S_m phase of mesogenic dimers.

II. Free Energy of Supramolecular Liquid Crystals

We consider model mixtures of A- and B-molecules on the basis of the lattice theory of polymer solutions. An A-molecule and a B-molecule are assumed to consist of r_A and r_B rigid-rod segments connected by flexible chains, respectively. The rigid-rod segment of the A-molecule and that of the B-molecule form a mesogenic core when hydrogen bonded. In this study we assume that hydrogen bonding occurs only between different species of molecules. Let n_A be the number of statistical units on the A-molecule, and let n_B be that on the B-molecule. Let n'_A be the number of statistical units included in the flexible chain part on the A-molecule, and let n'_B be that on the B-molecule. In the present paper, a compound consisting of l A-molecules and m B-molecules is indicated by the symbol (l, m) and called a "(l, m)-cluster". For example, a free A-molecule is given by (1, 0), a free B-molecule is (0, 1), a heterodimer is (1, 1), a trimer consisting of two A-molecules and one B-molecule is (2, 1), and a comblike compound containing f B-molecules bound to the chain side of an A-molecule via flexible spacers is (1, f). Using such symbols, we write the number of the (l, m)-clusters by $N_{l,m}$, its number density by $\nu_{l,m}$, and its volume fraction by $\phi_{l,m}$. Here, the number density, i.e., the number of (l,m)-clusters per lattice cell, is defined by $\nu_{l,m} \equiv N_{l,m}/\Omega$, and the volume fraction is defined by $\phi_{l,m} \equiv (n_A l + n_B m)\nu_{l,m}$, where Ω is the total number of the cells on the hypothetical lattice. If we assume that all statistical units on the A-molecule and the B-molecule have the same volume a^3, and regard also the volume of the lattice cell as a^3, Ω is defined by $\Omega \equiv V/a^3 = \sum_{l,m}(n_A l + n_B m)N_{l,m}$, where V is the volume of the system. The total number density ν of clusters, i.e., the total number of clusters per lattice cell, is given by $\nu = \sum_{l,m}\nu_{l,m}$. In the present paper, we take the total volume fraction ϕ_A of the A-molecule as an independent variable and write it as ϕ: $\phi = \phi_A = \sum_{l,m} n_A l \nu_{l,m}$. Under the incompressibility condition, the total volume fraction ϕ_B of the B-molecule is given by $1 - \phi$: $\phi_B = \sum_{l,m} n_B m \nu_{l,m} = 1 - \phi$.

The free energy of such mixtures consists of three terms:

$$\Delta F = \Delta F_{\text{rea}} + \Delta F_{\text{mix}} + \Delta F_{\text{ori}} \tag{2.1}$$

The first term ΔF_{rea} comes from the free energy change due to forming various clusters by hydrogen bonding between the A-molecule and the B-molecule. It is given by the difference between the chemical potential $\mu°_{l,m}$ of an (l, m)-cluster and those $\mu°_{1,0}$, $\mu°_{0,1}$ of the free molecules in the isolated state in the undiluted system:

$$\beta\Delta F_{\text{rea}} \equiv \sum_{l,m}\beta(\mu°_{l,m} - l\mu°_{1,0} - m\mu°_{0,1})N_{l,m} \tag{2.2}$$

Here β is defined by $\beta \equiv 1/k_B T$, where T is the temperature and k_B the Boltzmann constant. We subdivide this term into three factors

$$\beta\Delta F_{\text{rea}} = \sum_{l,m}(\Delta^{\text{comb}}_{l,m} + \Delta^{\text{conf}}_{l,m} + \Delta^{\text{bond}}_{l,m})N_{l,m} \tag{2.3}$$

and consider each in detail. The first factor $\Delta^{\text{comb}}_{l,m}$ is the combinatorial entropy coming from the number of the ways $w_{l,m}$ to form an (l, m)-cluster and hence $\Delta^{\text{comb}}_{l,m} = -\ln w_{l,m}$. The second one $\Delta^{\text{conf}}_{l,m}$ is the conformational entropy change resulting from the restriction on the possible conformational states due to hydrogen bonding. To estimate it, we employ conventional lattice−theoretical entropy of disorientation,

$$\Delta S^{\text{dis}} = k_B \ln\left(\frac{n\delta_{\max}}{se^{n-1}}\right) \tag{2.4}$$

for a flexible chain consisting of n statistical units. Here $\delta_{\max} \equiv z(z-1)^{n-2}$ is the maximum number of possible internal conformations of the chain, where z is the lattice coordination number. The symbol s represents the symmetry number of the chain, which takes 2 for a symmetric chain and 1 for an asymmetric one. Applying ΔS^{dis} to the flexible-chain parts on the molecules, we find

$$\Delta^{\text{conf}}_{l,m} \equiv \Delta S^{\text{dis}}_{l,m} - l\Delta S^{\text{dis}}_{1,0} - m\Delta S^{\text{dis}}_{0,1} = -\ln\left\{\frac{[n'_A l + n'_B m]}{[n'_A]^l[n'_B]^m}\left[\frac{(z-1)^2 s}{ze}\right]^{l+m-1}\right\} \tag{2.5}$$

The third factor $\Delta^{\text{bond}}_{l,m}$ in eq 2.3 is the free energy change resulting from the reaction between the functional groups on A- and B-molecules. If we assume, for simplicity, that all clusters contain no cyclic structure, an (l, m)-cluster has $l + m - 1$ hydrogen bonds, so that the third factor is given by

$$\Delta^{\text{bond}}_{l,m} \equiv (l + m - 1)\beta\Delta f_0 = (l + m - 1)\beta(\Delta\epsilon_0 - T\Delta s_0) \tag{2.6}$$

where Δf_0 is the free energy change per bond formation between the A-molecule and the B-molecule and consists of the energy change $\Delta\epsilon_0$ (<0) and the entropy change Δs_0 (<0).

The second term ΔF_{mix} in eq 2.1 comes from the free energy change due to mixing all clusters. Introducing the polydispersity due to association into the mixing entropy derived by Flory and Huggins, we write this term by

$$\beta\Delta F_{\text{mix}} = \sum_{l,m} N_{l,m} \ln \phi_{l,m} + \chi\phi(1 - \phi)\Omega \tag{2.7}$$

where χ is Flory's χ-parameter, which defines the strength of interaction between both the statistical units of the A- and B-molecule. Since we deal with binary mixtures consisting only of A- and B-molecules, no term of solvent appears here.

The mixing entropy ΔF_{mix} is not influenced by the rigidity of constituent molecules.[38,39] In the system containing mesogenic molecules, the effect caused by the rigidity of molecules must be taken into account. To include it, Flory[19] adopted the assumption that a rodlike molecule aligning to the orientation axis consists of submolecules that are arranged parallel to the orientation axis and joined to each other laterally near their ends. He evaluated the number of ways to assign rodlike molecules on the lattice. It was, however, difficult to treat S_m phases on the basis of such a method. Therefore, here we employ McMillan's free energy[23] as ΔF_{ori}, because his free energy includes both of the effects due to orientational ordering of mesogenic cores and translational ordering of their center of mass. We then have

$$\beta\Delta F_{\text{ori}} = \left\{(-\ln Z) + \frac{1}{2}\zeta(\eta^2 + \alpha\sigma^2)\nu_M\right\}N_M \tag{2.8}$$

where N_M is the total number of mesogenic cores in the system, and $\nu_M \equiv N_M/\Omega$ is the number of mesogenic cores per lattice cell. These depend on temperature and composition. The symbol η expresses the nematic order parameter, σ smectic order parameter, ζ nematic interaction parameter, and α smectic interaction parameter. The partition function Z refers to each mesogenic core and is defined by

$$Z(\eta,\sigma) \equiv \frac{1}{d}\int_0^d \mathrm{d}z \int_0^1 \mathrm{d}\cos\theta\, \exp\{\zeta[\eta + \alpha\sigma\cos(2\pi z/d)]P_2(\cos\theta)\nu_M\} \tag{2.9}$$

where d is the distance between the neighboring planes in a smectic A structure on which the centers of mass of mesogenic cores are located. In the following it is referred to as layer thickness. The symbol θ expresses the angle between the longitudinal axis of each mesogenic core and the preferential orientational axis. The function $P_2(x) \equiv (3x^2 - 1)/2$ is the Legendre polynomial of degree 2. McMillan obtained this partition function by using the self-consistent one-particle potential derived from the following assumptions: (1) an anisotropic interaction between mesogenic particles has a simple form based on Maier–Saupe model, (2) the molecules are preferentially oriented in the z direction, and (3) their centers of mass sit on planes parallel to the x–y plane and intersecting the z-axis at 0, $\pm d$, $\pm 2d$, etc.

It is scarcely problematic to introduce McMillan's free energy which averages the orientational order of mesogenic core over all continuous angle space as an additional term because the free energy form per lattice cell based on the lattice theory is essentially independent of a selected lattice and consists only of continuous quantities, such as volume fraction and the χ-parameter. The effect of the lattice is implicit in the χ-parameter. However, we usually ignore the effect. The lattice theory can, therefore, allow us to select the hypothetical lattice on which mesogenic cores can orient all directions. Flory stated in his paper[19] that his approximation that molecules incline to all continuous angles from an orientation axis are scarcely more serious than those of the lattice model itself.

The nematic interaction parameter ζ is defined by

$$\zeta \equiv \frac{A}{V_m{}^2 k_B T} \tag{2.10}$$

on the basis of the result derived by Maier and Saupe[20–22] that considered only the dipole–dipole component of the anisotropic dispersion force between two molecules. Here, V_m is the molar volume of rigid-rod particle, and A is taken to be a constant independent of pressure, volume, and temperature. According to their theory, the value of ζ at the nematic/isotropic transition temperature T_{NI} is given by

$$\zeta(T_{NI}) \equiv \frac{A}{V_c{}^2 k_B T_{NI}} = 4.541 \tag{2.11}$$

where V_c is the molar volume of a rigid-rod particle in the nematic phase at T_{NI}.[40] The comparison of the free energy for rigid-rod particles derived by Maier and Saupe with the free energy derived on the basis of the theory of Onsager[17] and Isihara[41] shows that ζ is proportional to the square of the length of particle if it is sufficiently thin; if the particle consists of n statistical units, $\zeta \propto n^2$.

The nematic order parameter η is defined by

$$\eta \equiv \langle P_2(\cos\theta)\rangle \tag{2.12}$$

where the symbol $\langle\cdots\rangle$ means that the average is taken by the use of the weight Z given by eq 2.9. In the isotropic state $\eta = 0$ since the mesogenic cores are randomly oriented. In the nematic state and the smectic state $\eta \neq 0$ since the mesogenic cores are preferentially oriented toward a certain direction.

The smectic order parameter σ is defined by

$$\sigma \equiv \langle P_2(\cos\theta)\cos(2\pi z/d)\rangle \tag{2.13}$$

In the isotropic state and the nematic state $\sigma = 0$ because the center of mass of each mesogenic core is randomly placed. In the smectic state $\sigma \neq 0$ because the center of mass sits on the plane orthogonal to the preferential orientational axis, so that a multilayered structure is constructed of the mesogenic cores.

The smectic interaction parameter α introduced by McMillan determines the strength of the smectic interaction and is defined by

$$\alpha = 2\exp\{-(\pi r_0/d)^2\} \tag{2.14}$$

where r_0 is of the order of the length of the mesogenic core. It is also known from an experimental result that the layer thickness d is of the order of the length of a liquid-crystalline molecule.[40] The parameter α is a dimensionless quantity and can vary between 0 and 2.

Each order parameter η, σ is decided by minimizing the total free energy:

$$\left(\frac{\partial \Delta F}{\partial \eta}\right)_{T,\phi} = 0 \tag{2.15}$$

$$\left(\frac{\partial \Delta F}{\partial \sigma}\right)_{T,\phi} = 0 \tag{2.16}$$

These conditions are equivalent to the coupled eqs 2.12 and 2.13. In supramolecular liquid crystals, the number density ν_M must be determined self-consistently.

In the following we consider two specific models: dimer-type model and trimer-type model.

III. Dimer-Type Model

In this section, we derive phase diagrams of mixtures consisting of two species of associating linear molecules A and B forming hydrogen-bonded liquid-crystalline dimer A·B. Each molecule is assumed to have a nonmesogenic rigid-rod-like part and a flexible tail chain. An A-molecule carries a hydrogen-bond donor at the end of its rodlike part, and a B-molecule carries a hydrogen-bond acceptor at the end of its rodlike part. When forming a dimer A·B, the combined rodlike part becomes sufficiently long to form a mesogenic core (Figure 1).

The number of statistical units n'_i on the flexible tail of the i-molecule (i = A, B) is defined by $n'_i \equiv n_i - n_i^*$, where n_i^* is the number of statistical units on the rigid part. For simplicity, we assume that the size of the rigid part is the same as that of the statistical unit. Hence we have $n_A^* = n_B^* = 1$. The total number of the lattice cells is given by $\Omega = n_A N_{1,0} + n_B N_{0,1} + (n_A + n_B) N_{1,1}$. Since the number of the mesogenic cores is equal to that of the dimers, it is given by $N_M = N_{1,1}$, and hence $\nu_M = \nu_{1,1}$. The free energy of the mixture is then given by

$$\beta\Delta F = N_{1,0}\ln\phi_{1,0} + N_{0,1}\ln\phi_{0,1} + N_{1,1}\ln\phi_{1,1} + \chi\phi(1-\phi)\Omega + \Delta_{1,1}N_{1,1} + \left\{(-\ln Z) + \frac{\zeta}{2}(\eta^2 + \alpha\sigma^2)\nu_{1,1}\right\}N_{1,1} \tag{3.1}$$

Here, the free energy of association is given by

$$\Delta_{1,1} = -\ln(\lambda_0/n') + \beta\Delta\epsilon_0 \tag{3.2}$$

where $n' \equiv n'_A n'_B/(n'_A + n'_B)$ is the reduced molecular weight of the flexible tails, and

$$\lambda_0 \equiv \frac{(z-1)^2 s}{ze} \exp(1 + \Delta s_0/k_B) \tag{3.3}$$

is a constant related to the entropy of bond formation.

From this free energy, we obtain the chemical potential $\Delta\mu_{1,0}$ of the free A-molecule, $\Delta\mu_{0,1}$ of the free B-molecule, and $\Delta\mu_{1,1}$ of the dimer as

$$\beta\Delta\mu_{1,0} = 1 + \ln \phi_{1,0} - n_A\nu + n_A\chi(1-\phi)^2 + n_A\frac{\zeta}{2}(\eta^2 + \alpha\sigma^2)\nu_{1,1}^2 \tag{3.4}$$

$$\beta\Delta\mu_{0,1} = 1 + \ln \phi_{0,1} - n_B\nu + n_B\chi\phi^2 + n_B\frac{\zeta}{2}(\eta^2 + \alpha\sigma^2)\nu_{1,1}^2 \tag{3.5}$$

$$\beta\Delta\mu_{1,1} = 1 + \ln \phi_{1,1} - (n_A + n_B)\nu + n_A\chi(1-\phi)^2 + n_B\chi\phi^2 - \ln(\lambda_0/n') + \beta\Delta\epsilon_0 - \ln Z + (n_A + n_B)\frac{\zeta}{2}(\eta^2 + \alpha\sigma^2)\nu_{1,1}^2 \tag{3.6}$$

The number ν of molecules per lattice cell that have translational degree of freedom is given by $\nu \equiv (N_{1,0} + N_{0,1} + N_{1,1})/\Omega$.

To evaluate the number of dimers, we use the equilibrium condition for dimer formation:

$$\Delta\mu_{1,1} = \Delta\mu_{1,0} + \Delta\mu_{0,1} \tag{3.7}$$

Substituting the chemical potentials into this condition, we find the volume fraction of dimers is given by

$$\phi_{1,1} = \frac{1}{n'}\lambda Z \phi_{1,0}\phi_{0,1} \tag{3.8}$$

Here, the association constant $\lambda(T)$ is given by

$$\lambda \equiv \lambda_0 \exp[C/t] \tag{3.9}$$

by using the reduced temperature $t \equiv T/T_{NI}$ and a material constant C defined by

$$C \equiv -\Delta\epsilon_0/k_B T_{NI} \tag{3.10}$$

By the use of the reduced temperature and eqs 2.10 and 2.11, the nematic interaction parameter ζ can be written as

$$\zeta = 4.541/t \tag{3.11}$$

under the incompressibility condition. At a given temperature t and a given composition ϕ, the volume fraction of the free A-molecule is written by

$$\phi_{1,0} = \phi - n_A\nu_{1,1} \tag{3.12}$$

and that of the free B-molecule by

$$\phi_{0,1} = 1 - \phi - n_B\nu_{1,1} \tag{3.13}$$

On substituting these volume fractions into eq 3.8, we find that the number density $\nu_{1,1}$ of the dimer, i.e., the mesogenic core satisfies

$$\nu_{1,1} = \frac{1}{(n_A + n_B)n'}\lambda Z(\phi - n_A\nu_{1,1})(1 - \phi - n_B\nu_{1,1}) \tag{3.14}$$

where we have used the relationship $\phi_{1,1} = (n_A + n_B)\nu_{1,1}$. By solving this equation for $\nu_{1,1}$ at a given set of t and ϕ, we obtain ν_{11}, η, and σ as a function of the thermodynamic variables. If there are several solutions, the one that makes the free energy lowest is the true solution.

A. Athermal Mixture. First, we consider athermal mixtures for which there is no mixing enthalpy. Hence, we have $\chi = 0$ at all temperatures so that macroscopic phase separation does not occur. Parameters are fixed at $n_A = n_B = 10$, $\lambda_0 = 5.0$, and $C = 0.1$. Figures 3 and 4 show the order parameters as functions of the temperature for three compositions, $\phi = 0.3$, 0.4, and 0.5. We fix the smectic interaction parameter α at 0.2 (Figure 3) and 0.5 (Figure 4). The solid line is the nematic order parameter η (left axis), the broken line is the smectic order parameter σ (left axis), and the dotted line is the number density of the mesogenic core $\nu_M = \nu_{1,1}$ (right axis). The letters "I", "N", and "S_m" express the state in which the mixture has the lowest free energy in each temperature range divided by the vertical dot−dash line. In these mixtures, the volume fraction ϕ is 0.5 at the stoichiometric composition at which the number of the hydrogen-bond donors and that of the hydrogen-bond acceptors are equal to each other. At this stoichiometric composition, N/S_m is the continuous phase transition for $\alpha = 0.2$, while for $\alpha = 0.5$, it is first order. Therefore, the effect of α is the same as in McMillan's result. At a given temperature, a mixture with the stoichiometric composition form a largest number of mesogenic cores, so that both the I/N transition temperature and the N/S_m transition temperature are highest at this composition. It qualitatively agrees with experimental results on the hydrogen-bonded supramolecular liquid crystals reported by Kato et al.[6,10] and Alexander et al.[11]

A smaller value of α gives lower N/S_m transition temperature. The I/N transition temperature is independent of α. Therefore, with decreasing α, the N state is stabilized against the change in temperature.

Figures 5 and 6 show phase diagrams of the mixtures corresponding to Figures 3 and 4. Thin solid line shows the I/N transition line, thick solid line the N/S_m transition line, and dotted line the two-phase coexistence line (binodal). The hatched area bordered by the binodal curve is the metastable region, and the crosshatched area with the symbol "U" is the unstable region. Note that the temperature scales in these figures are different. The I/N line and the binodal surrounding it at $\alpha = 0.2$ completely agree with those at $\alpha = 0.5$ at higher temperature at which no influence of the N/S_m transition appears.

At temperatures above the I/N line (point A in Figure 6) the mixture forms a homogeneous isotropic liquid phase. The reason for the appearance of the two-phase coexistence region surrounding the I/N line is that the I/N transition is a first-order phase transition. This two-phase separation must be therefore distinguished from a conventional macroscopic phase separation caused by the effect of mixing enthalpy. The I/N transition does not lead to a mixture with the stoichiometric composition to two-phase separation, because such a mixture has a lower free energy at a given temperature than that of the mixtures with different composition. As

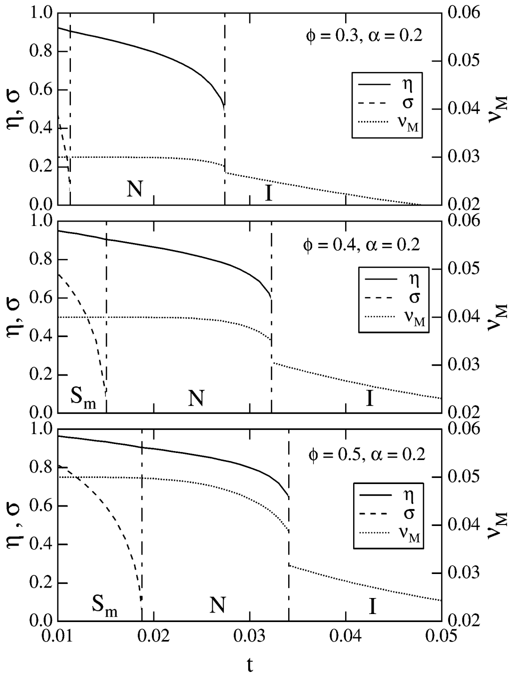

Figure 3. Dependence of three order parameters ν_M (dotted line, right axis), η (solid line, left axis), and σ (broken line, left axis) on temperature at three compositions (top: $\phi = 0.3$; middle: $\phi = 0.4$; bottom: $\phi = 0.5$) in the dimer-type model ($n_A = n_B = 10$, $n^*_A = n^*_B = 1$). The smectic interaction parameter is fixed at $\alpha = 0.2$.

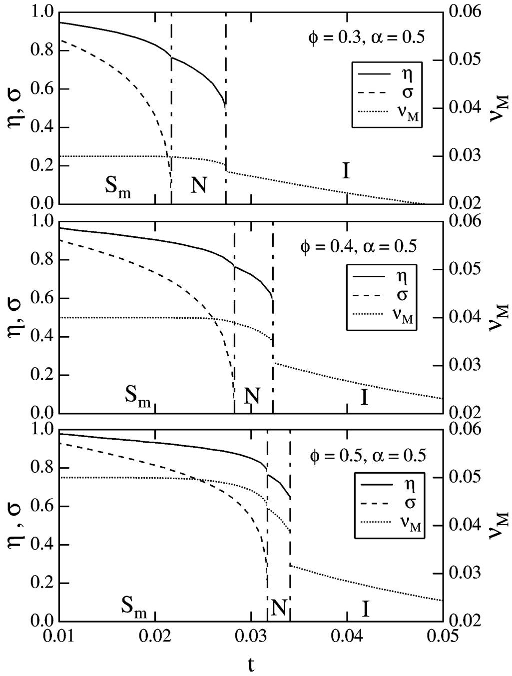

Figure 4. Dependence of three order parameters ν_M, η, and σ on temperature at three compositions $\phi = 0.3$, 0.4, and 0.5 at $\alpha = 0.5$.

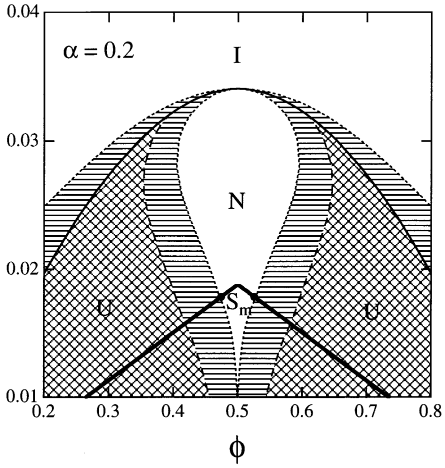

Figure 5. Phase diagram of the athermal mixture corresponding to Figure 3. The thin solid line is the I/N transition line, the thick solid line is the N/S_m transition line, and the dotted line is the binodal due to the I/N transition. The hatched area is the metastable region, and the crosshatched area with "U" is the unstable region. Filled circle represents a critical end point.

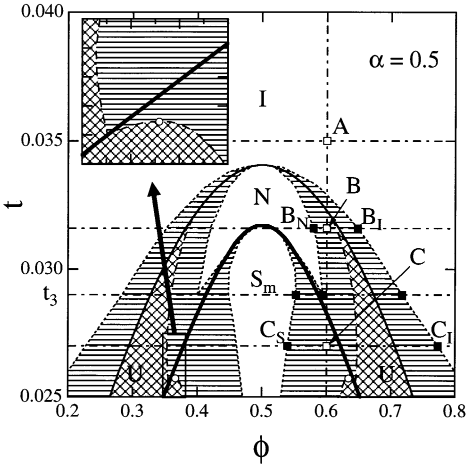

Figure 6. Phase diagram of the athermal mixture corresponding to Figure 4. The white circle represents a critical solution point.

Figures 3 and 4 show, the extent of association between the A-molecules and the B-molecules suddenly increases at the I/N transition temperature on cooling, so that a sufficient number of mesogenic cores to form an N structure are formed. The formation of an N structure with the stoichiometric composition at the I/N transition temperature reduces the free energy enough to turn into a stable homogeneous N phase. The free energy curve in the N state at a given temperature has a minimum at the stoichiometric composition. The mixtures with another composition may also construct a homogeneous N structure at I/N transition temperature, but it should be a temporary structure since its free energy is not low enough to realize a stable homogeneous N phase. Thus, such mixtures must eventually separate into two phases, an I phase and an N phase here. Resultant phases have different composition from each other and from the whole mixture. This phase separation obeys the following mechanism: at a given temperature, the mixture with the stoichiometric composition has the greatest number of mesogenic cores, so that it forms the highest ordered structure and is lowest in the free energy. Therefore, a homogeneous N phase with another composition formed temporarily at the I/N transition temperature prefers its N structure to get closer to the N structure with the stoichiometric composition. To bring the composition close to the stoichiometric composition and to realize this preference, the excess free molecules are expelled from the temporary homogeneous N phase. Such expelled free molecules gather and form another phase. Since the phase separation accompanying the I/N transition is caused by the crossing with a finite angle of the free energy of I state and of N state at the

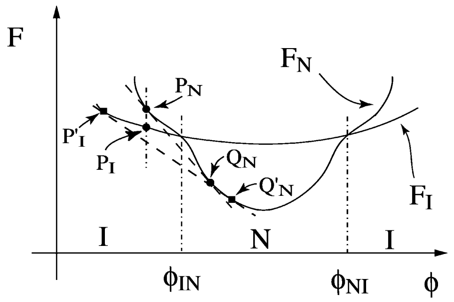

Figure 7. Sketch of the free energy curve of the I state F_I and that of the N state F_N at a given temperature. At the compositions ϕ_{IN} and ϕ_{NI} the phase transition between an I phase and an N phase occurs.

transition point, the phase formed by the expelled free molecules becomes a stable I phase. Consequently, the temporary N phase separates into the stable I phase with a distant composition from the stoichiometric one and the stable N phase with a closer composition. When the mixture is quenched from point A to point B in Figure 6, it separates into the I phase indicated by point B_I and the N phase indicated by point B_N.

When temperature is lowered, the influence of entropy on the free energy becomes small, so that a regular structure with low enthalpy is stabilized. When the composition approaches closer to the stoichiometric composition, the nematic order becomes higher. Thus, at low temperature, there is a wider coexistence region accompanying the I/N transition.

We should notice that there is an unstable region hidden in the coexistence region. The I/N line lies on the one boundary of this unstable region. Such an unstable region appears since the free energy curve F_I in the isotropic state with positive second derivative and the free energy curve F_N in the nematic state with negative second derivative intersect with each other at the I/N transition composition ϕ_{IN}, ϕ_{NI} (Figure 7). It does not result from the first-order nature of the I/N transition but from the difference of entropy between two N structures with different composition. A mixture quenched into this unstable region tends to phase separate into a N phase with a low order parameter (P_N in Figure 7) and a N phase with a high order parameter (Q_N). The free energy of N state at P_N is higher than that of the corresponding I state at P_I. Therefore, phase separation into two N phases (P_N and Q_N) does not lower the total free energy. Instead, the mixture separates eventually into an I phase (P'_I) and a higher-ordered N phase (Q'_N).

An unstable region hidden in a two-phase coexistence region due to the first-order nature is well-known in metallurgy.[42] Recently, the existence of the spinodal curve hidden in a metastable region has been a focus of study on crystallization of polymers.[43,44] All these hidden unstable regions accompany first-order phase transitions and lie in the region where the liquid state has the lowest free energy. The unstable regions shown in Figures 5 and 6 are the same except that they appear in the region where N state has the lowest free energy.

Next, we pay attention to the N/S_m line. Figure 5 shows that the N/S_m line exists inside the homogeneous N phase region in the vicinity of $\phi = 0.5$. This N/S_m transition is not a first-order phase transition but a continuous one. Figure 3 shows that dimer formation is almost complete at the N/S_m transition temperature. The curve of nematic order parameter η shows that the orientation of the mesogenic cores progresses sufficiently to form an S_m structure. Thus, the curves of ν_M and η are continuous across the N/S_m transition temperature. The smectic order parameter σ is zero at this transition temperature and increases continuously on cooling. These behaviors suggest that the N/S_m transition is not a first-order phase transition, but a continuous phase transition. If we heat up the mixture from the S_m phase to the N phase, the spatial distribution of the centers of mass of the mesogenic cores in the direction of the preferential orientational axis in the S_m layer, and the orientational distribution of the longitudinal axis of the mesogenic cores become gradually broad. Once the N/S_m transition temperature is reached, the spatial distribution of the cores becomes uniform at the N/S_m transition point. No phase separation occurs. It should be noted that the two-phase coexistence region into which the N/S_m line comes in Figure 5 is not caused by the N/S_m transition but caused by the I/N transition. The continuous phase transition line (N/S_m line) crosses into the first-order phase separation region and disappears. The intersection represented by the filled circle should be therefore regarded as a "critical end point". A phase separation between an I phase and an S_m phase occurs below this point. The I phase essentially consists of free A-molecules or of free B-molecules, and the S_m phase essentially consists of A·B-dimers. Figure 5 shows that only the S_m phase with the stoichiometric composition appears at lower temperature than $t = 0.01$.

Figure 6 shows the phase diagram in which narrow two-phase coexistence region accompanies both the N/I line and the N/S_m line. The N/S_m transition in this figure is therefore a first-order phase transition similar to the I/N transition. From Figure 4, we see dimer formation is incomplete at the N/S_m transition temperature since this N/S_m transition occurs at high temperature. Therefore, even if the mixture has a composition that is closer to the stoichiometric one, the S_m structure temporarily formed has many free molecules, so that such a temporary S_m phase must expel excess free molecules to be stabilized. As a result, the mixture separates into an S_m phase and an N phase or into an S_m phase and an I phase.

At about the temperature $t = 0.03$, the mixture can take five types of state depending on its composition: S_m, S_m−N coexistence, N, N−I coexistence, and I. As the composition lies farther from the stoichiometric one, the N state becomes more stable than the S_m state, because the N structure has more degrees of freedom to accommodate more free molecules than the S_m structure.

The temperature t_3 is a special temperature which separates the system into different phase behaviors. Above t_3, the S_m−N phase separation occurs, whereas below t_3 the S_m−I phase separation occurs. At t_3, the mixture has three different states depending on the composition: I, I−N−S_m three-phase coexistence, and S_m.

If the mixture is quenched deep into the point C, it separates into the S_m phase with the composition corresponding to the point C_S and the I phase with the composition corresponding to the point C_I. At this temperature S_m−N phase separation no longer occurs, because the orientational order of N structure becomes so high that no stable N structure can accommodate free molecules expelled from a S_m (or N) structure formed

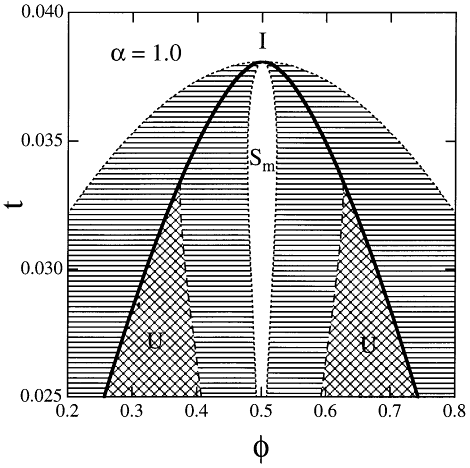

Figure 8. Phase diagram of the athermal mixture with parameters corresponding to those of Figures 5 and 6, except $\alpha = 1.0$. Here, the thick solid line is the I/S transition line.

temporarily. Therefore, the expelled free molecules must form an I phase.

In the magnified part in Figure 6, we see that the spinodal does not lie on the N/S_m line, and the unstable region has a critical solution point (open circle). It suggests that the unstable region appears independently of the N/S_m transition; the unstableness essentially results from the difference of entropy beween S_m structures that are different from each other in composition.

To examine the dependence of phase behavior on the strength of the smectic interaction in detail, we calculate phase diagrams at larger α. Figure 8 shows the phase diagram at $\alpha = 1$. Other parameters are the same as those of Figures 5 and 6. The S_m phase occurrence temperature (thick solid line) rises much higher than at $\alpha = 0.5$, so that a direct transition between an I phase and an S_m phase occurs. A larger α increases the influence of the enthalpy on the free energy relative to that of the entropy, so that an S_m structure with lower entropy and lower enthalpy is more stable than an N structure. Let us consider what happens when we heat the mixture from the S_m phase. By definition, the increase of α means the increase of the layer thickness d since the size of mesogenic core is a constant. If d, and hence α, are small, a small fluctuation of mesogenic cores along the direction of the preferential orientational axis can destroy the layered S_m structure, so that the transition to the N phase requires less energy. Such a small fluctuation can be caused by thermal motion. If d, and hence α, are large, a large fluctuation of mesogenic cores is needed to destroy the layered S_m structure. There is therefore a high-energy barrier between an S_m phase and an N phase. Thermal energy cannot overcome this energy barrier until temperature become higher. The large thermal motion enough to destroy an S_m structure also destroys an N structure simultaneously. Consequently, the direct transition from an S_m phase to an I phase occurs. A liquid-crystalline phase is stable only in a narrower composition area at $\alpha = 1.0$ than at $\alpha = 0.2$ and 0.5, because many free molecules remain in a liquid-crystalline structure formed temporarily at the I/S_m transition temperature even if the composition is near the stoichiometric composition.

Next, we study the relationship between the length n'_A, n'_B of the flexible part of each molecule and the layer thickness d of an S_m structure. Figure 9 shows the transition temperature t_N for the N phase and t_S for the S_m phase as functions of the length of the flexible part in the molecules. We consider the symmetric case with $n'_A = n'_B$. We assume two different relationships $d \propto n_A + n_B$ (filled circle) and $d \propto (n_A + n_B)^{1/2}$ (filled square). With increasing n'_A and n'_B, the N phase occurrence temperature t_N (white triangle) falls monotonically faster than t_S. By definition, t_N is independent of α and hence of the ratio $d/(n_A + n_B)$. Since, in this study, we assume that the nematic interaction parameter ζ is independent of the shape and the size of the mesogenic core, the dependence of t_N on n'_A and n'_B comes from the entropy of disorientation.

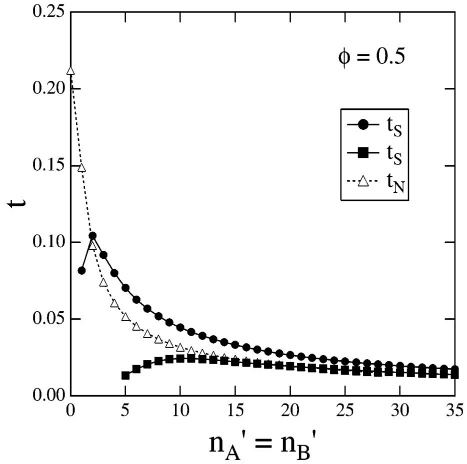

Figure 9. Dependence of the nematic transition temperature t_N (white triangle) and the smectic A phase transition temperature t_S (filled circle and filled square) on the number of statistical units in the flexible tails of the A- and the B-molecule, n'_A and n'_B, in the athermal mixture with parameters corresponding to those of Figures 3 and 4, except n_A, n_B, and α. Here $n'_A = n'_B$, and hence $n_A = n_B$. The composition of the mixture is fixed at the stoichiometric composition $\phi = 0.5$. When the layer thickness d of the smectic A structure is assumed to be proportional to the length of the dimer ($d = n_A + n_B$), t_S is given by a filled circle. When the layer thikness is assumed to be proportional to the square root of the length of the dimer ($d = (n_A + n_B)^{1/2}$), t_S is given by a filled square.

If d is of the order of the length of a dimer, t_S becomes lower with increasing n'_A and n'_B from 2.0. No N phase occurs. When $n'_A = n'_B < 2.0$, an N phase occurs. If d is proportional to the square root of the dimer length, t_S becomes higher with increasing n'_A until n'_A reaches a certain value. Once n'_A exceeds this value, t_S becomes lower gradually. The t_N curve and t_S curve intersect at about $n'_A = n'_B = 21$, so that no nematic phase occurs for $n'_A = n'_B > 21$. These results qualitatively agree with the experimental relationship between the transition temperatures and the number of carbons in the alkyl chain in nonassociating liquid-crystalline molecules.[45]

In Figure 10, the length of the flexible tail of the B-molecule is fixed at $n'_B = 5$, so that we have $n_B = 6$. Other parameters are fixed at the same value as those in Figure 9. Each curve agrees with that of the example shown in Figure 9 qualitatively. All curves in Figure 10 change slower than those in Figure 9, because only one of the flexible ends of dimers changes its length. Kato et al.[9] experimentally investigated such a case. They measured the transition temperature in the mixtures of *trans*-4-alkoxy-4′-stilbazole with the different lengths of the alkyl chain and 4-(hexyloxy)benzoic acid. Their result shows that an N phase appears when

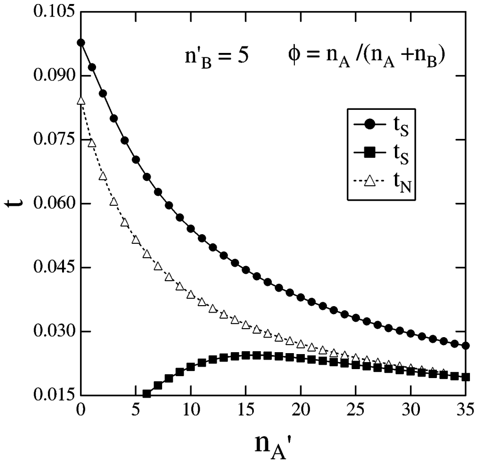

Figure 10. Dependence of t_N and t_S on the number of the statistical units n'_A. Here n'_B is fixed at 5, and hence $n_B = 6$. The composition of the mixture is fixed at the stoichiometric composition $\phi = n_A/(n_A + n_B)$. Others correspond to those of Figure 9.

the number of carbons in the alkyl chain lies between 1 and 5, but it does not appear for chains longer than 5. Our theoretical result agrees with this experimental result except that the I/N transition temperature in a theoretical model monotonically rises with decreasing n'_A, while experimental result shows that the isotropic/anisotropic transition temperature depends only little on the number of the carbons.

B. Effect of Mixing Enthalpy. In this section, we consider the effect of mixing enthalpy. For numerical calculation we assume that Flory's χ-parameter takes the form $\chi \equiv C_1 + C_2/t$ using the reduced temperature $t = T/T_{NI}$ with C_1 and C_2 constants specific to the combination of molecular species. This is equivalent to the Schultz−Flory form.

Figure 11a shows a phase diagram of a symmetric mixture with $n_A = n_B = 10$ and $n_A^* = n_B^* = 1$. Other parameters are given by $\lambda_0 = 30.0$, $C = 0.3$, $C_1 = -0.5$, and $C_2 = 0.05$. Figure 11b magnifies the important part in Figure 11a. The thin solid line is the I/N transition line, and the thick solid line the N/S$_m$ transition line. Letters "I", "N", and "S$_m$" represent the state whose free energy is lowest in each area. Dotted lines limiting the hatched metastable region are binodals. The crosshatched area with "U" is the unstable region due to the new mechanism described in the preceding section, whereas the crosshatched area with "U′" is the conventional unstable region due to demixing. White circles represent critical solution points.

At high temperatures, both the two-phase coexistence region caused by the I/N phase transition and that by repulsive interaction between the two different species of molecules appear. The mixture separates either into two I phases by the effect of mixing enthalpy or into I phase and N phase by the I/N transition depending upon the composition.

At intermediate temperature, the two coexistence regions merge, but the U region and the U′ region remain separate. From such a structure of the phase diagram, two-step phase separation is possible; the mixture first separates into two metastable I phases or metastable I and N phase and then into stable I and N phase. For example, when the mixture is quenched to black triangle point in Figure 11b, it separates temporarily into the metastable I and N phase (white square) by the driving force based on the I/N transition and eventually into the stable I and N phase (black square) by cooperative driving force due to the I/N transition and the demixing. It is, however, also possible that larger fluctuation in spinodal decomposition leads to a direct separation into the stable I and N phase.

At lower temperature, two unstable regions U and U′ also merge, so that the mixture separates directly into the stable I and N phase or into the stable I and S$_m$ phase by the cooperative driving force.

If we divide the phase diagram into two at the middle and see the left half, it is similar to a theoretical phase diagram of a lyotropic liquid crystal first derived by Flory[19] and later confirmed by an experiment by Miller et al.[46] The narrow I/N coexisting region extending from the macroscopic phase separation region is called a "chimney". In lyotropic liquid crystals, the chimney goes straight up to high temperature, but our results show that in supramolecular liquid crystals there is a limiting temperature of chimney, because the number of mesogenic cores decreases with increasing temperature.

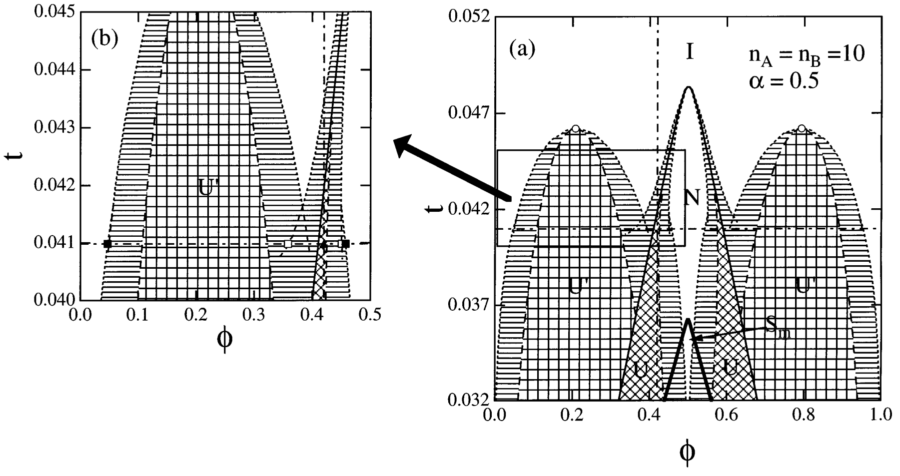

Figure 11. (a) Phase diagram of a thermal mixture forming a dimer-type hydrogen-bonded supramolecular liquid crystal. The thin solid line is the I/N transition line, the thick solid line is the N/S transition line, and the dotted line is the binodal. The hatched area is the metastable region. The crosshatched area with "U" is the unstable region due to entropy difference between two different species of N structures. The crosshatched area with "U′" is the unstable region due to mixing two different species of molecules. White circle represents the critical solution point. Parameters are fixed at $n_A = n_B = 10$, $n^*_A = n^*_B = 1$, $\lambda_0 = 30.0$, $C = 0.3$, $C_1 = -0.5$, $C_2 = 0.05$, and $\alpha = 0.5$. (b) Magnification of the part in (a).

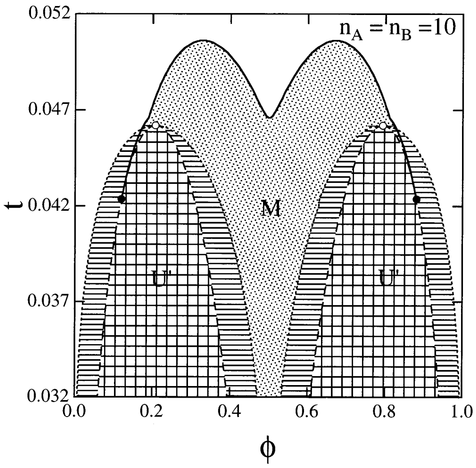

Figure 12. Phase diagram of a hydrogen-bonded flexible dimer. The dotted line is the binodal, and the solid line is the microphase separation transition line. In the dotted area with the capital letter "M", the mixture forms a mesophase. The hatched area is the metastable region, and the crosshatched area with "U′ is the unstable region. Parameters are $n_A = n_B = 10$, $n^*_A = n^*_B = 0$, $\lambda_0 = 30.0$, $C = 0.3$, $C_1 = -0.5$, and $C_2 = 0.05$.

For comparison, we show in Figure 12 a corresponding phase diagram of dimer forming associating flexible polymer mixtures without rigid segments ($n^*_A = n^*_B = 0$). All other parameters are the same. The mixture separates into a free A (or B) polymer-rich phase and a dimer-rich phase since association energy between different species of molecules decrease the free energy. The dimer-rich phase forms mesoscopic morphology (lamellar structure, cylindrical one, cubic one, and so forth) by microscopic phase separation. Such a microphase separated region corresponds to the liquid-crystalline phase in the case of hydrogen-bonded liquid crystals. By comparing Figure 11 with Figure 12, we see that the smectic region "S_m" in Figure 11 gives the mesophase region "M" in Figure 12. Therefore, it suggests that the microphase separation transition may occur within the smectic layer; the mixture with a given composition may undergo a transition from an ordinary S_m phase to a new S_m phase in which each smectic layer separates into a sublayer of A-molecule and of B-molecule.

IV. Trimer-Type Model

Let us move onto the trimers. Consider a mixture of A- and B-molecules which form mesogenic hydrogen-bonded trimers A·B·A. An A-molecule contains a nonmesogenic rigid-rod-like part with n^*_A statistical units and a flexible tail chain with $n'_A = n_A - n^*_A$ statistical units. The rigid part carries a hydrogen-bond donor at its free end. A B-molecule is a nonmesogenic rigid-rod-like molecule with $n_B = n^*_B$ statistical units (i.e., $n'_B = 0$). This rigid molecule carries a hydrogen-bond acceptor at its both ends. We assume that the number of statistical units in the rigid part of both molecules is equal to unity, $n^*_A = n^*_B = 1$, for simplicity. The total number Ω of the lattice cells is given by $\Omega = n_AN_{1,0} + n_BN_{0,1} + (n_A + n_B)N_{1,1} + (2n_A + n_B)N_{2,1}$. Once two A-molecules and one B-molecule form a trimer A·B·A by a hydrogen bond, three connected nonmesogenic rigid parts are assumed to form one mesogenic core (Figure 2). The connected rigid parts in a dimer A·B is assumed to be too short to form a liquid-crystalline state. Therefore, the number of mesogenic cores agrees with the number of trimers:

$$N_M = N_{2,1} \tag{4.1}$$

and hence $\nu_M = \nu_{2,1}$.

The free energy of the whole mixture measured from the reference state is given by

$$\beta\Delta F = N_{1,0} \ln \phi_{1,0} + N_{0,1} \ln \phi_{0,1} + N_{1,1} \ln \phi_{1,1} + N_{2,1} \ln \phi_{2,1} + \chi\phi(1 - \phi)\Omega + \{-\ln 2 + \beta\Delta f_0\}N_{1,1} + \{-\ln[\lambda_1/n'_A] + 2\beta\Delta f_0\}N_{2,1} + \left\{(-\ln Z) + \frac{\zeta}{2}(\eta^2 + \alpha\sigma^2)\nu_{2,1}\right\}N_{2,1} \tag{4.2}$$

We then have

$$\beta\Delta\mu_{1,0} = 1 + \ln \phi_{1,0} - n_A\nu + n_A\chi(1 - \phi)^2 + n_A\frac{\zeta}{2}(\eta^2 + \alpha\sigma^2)\nu_{2,1}^2 \tag{4.3}$$

$$\beta\Delta\mu_{0,1} = 1 + \ln \phi_{0,1} - n_B\nu + n_B\chi\phi^2 + n_B\frac{\zeta}{2}(\eta^2 + \alpha\sigma^2)\nu_{2,1}^2 \tag{4.4}$$

$$\beta\Delta\mu_{1,1} = 1 + \ln \phi_{1,1} - (n_A + n_B)\nu + n_A\chi(1 - \phi)^2 + n_B\chi\phi^2 - \ln 2 + \beta\Delta f_0 + (n_A + n_B)\frac{\zeta}{2}(\eta^2 + \alpha\sigma^2)\nu_{2,1}^2 \tag{4.5}$$

$$\beta\Delta\mu_{2,1} = 1 + \ln \phi_{2,1} - (2n_A + n_B)\nu + 2n_A\chi(1 - \phi)^2 + n_B\chi\phi^2 - \ln\{\lambda_1/n'_A\} + 2\beta\Delta f_0 - \ln Z + (2n_A + n_B)\frac{\zeta}{2}(\eta^2 + \alpha\sigma^2)\nu_{2,1}^2 \tag{4.6}$$

for the chemical potential of each cluster, where a new material constant λ_1 is defined by

$$\lambda_1 \equiv \frac{2(z - 1)^2 s}{ze} \tag{4.7}$$

The total number density ν of clusters is given by

$$\nu \equiv (N_{1,0} + N_{0,1} + N_{1,1} + N_{2,1})/\Omega \tag{4.8}$$

Using the multiple-equilibrium condition, now taking the form

$$\Delta\mu_{1,1} = \Delta\mu_{1,0} + \Delta\mu_{0,1} \tag{4.9}$$

$$\Delta\mu_{2,1} = 2\Delta\mu_{1,0} + \Delta\mu_{0,1} \tag{4.10}$$

we derive the cluster-size distribution functions as

$$\phi_{1,1} = 2\lambda\phi_{1,0}\phi_{0,1} \tag{4.11}$$

$$\phi_{2,1} = \frac{\lambda_1}{n'_A}Z(\lambda\phi_{1,0})^2\phi_{0,1} \tag{4.12}$$

Here, the association constant $\lambda(T)$ is defined by

$$\lambda \equiv \exp(1 + \Delta s_0/k_B) \exp[-\beta\Delta\epsilon_0] \equiv \lambda_0 \exp[C/t] \tag{4.13}$$

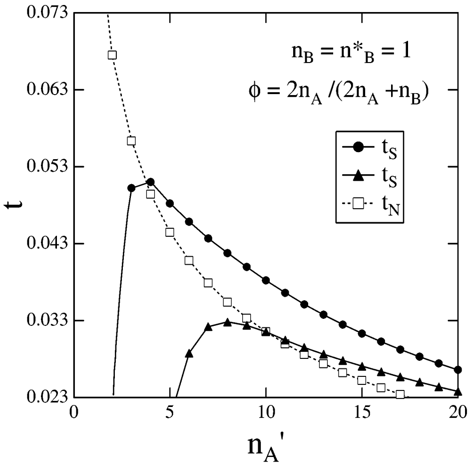

Figure 13. Dependence of t_N (white square) and t_S (filled circle and filled triangle) on n'_A in an athermal mixture forming a trimer-type hydrogen-bonded supramolecular liquid crystal: $n^*_A = n_B = n^*_B = 1$, $\lambda_0 = 1.0$, $\lambda_1 = 1.0$, $C = 0.2$, and $\chi = 0$. The composition of the mixture is fixed at the stoichiometric composition $\phi = 2n_A/(2n_A + n_B)$. When the layer thickness d is assumed to be proportional to the length of the trimer ($d = 2n_A + n_B$), t_S is given by filled circle. When the layer thickness is assumed to be proportional to the 0.8th power of the length of the trimer ($d = (2n_A + n_B)^{0.8}$), t_S is given by a filled triangle.

by the use of the reduced temperature t, where $\lambda_0 \equiv \exp(1 + \Delta s_0/k_B)$.

Figure 13 shows the transition temperatures t_N (white square) and t_S (black marks) on the length n'_A of the flexible tail of the A-molecule at the stoichiometric composition $\phi = 2n_A/(2n_A + n_B)$. A change in the length of the flexible tail influences t_N via the disorientational entropy in the free energy. The temperature t_N is independent of the ratio between the layer thickness d of a smectic A structure and the length $2n_A + n_B$ of the trimer. The t_N points that lie below t_S in Figure 13 is physically meaningless. When n'_A is larger than the value at the crossing point, the direct I/S transition occurs. The temperature t_S decreases with increasing n'_A. On the other hand, when n'_A is smaller than the crossing value, both the N phase and S_m phase appear. Reducing n'_A makes an N phase region wider. Though t_S depends on the smectic interaction parameter α, the relationship between t_S and α is independent of the ratio $d/(2n_A + n_B)$. Thus, with increasing n'_A the temperature t_S rises at first, but once n'_A exceeds a certain number (4 or 8 in this example), t_S monotonically falls. The experimental result for about a 2:1 molar ratio mixtures of 4-alkoxy- or 4-alkylbenzoic acid and 4,4′-bipyridine or *trans*-1,2-bis(4-pyridyl)ethylene[10] shows that the direct transition between the I phase and the S_m phase

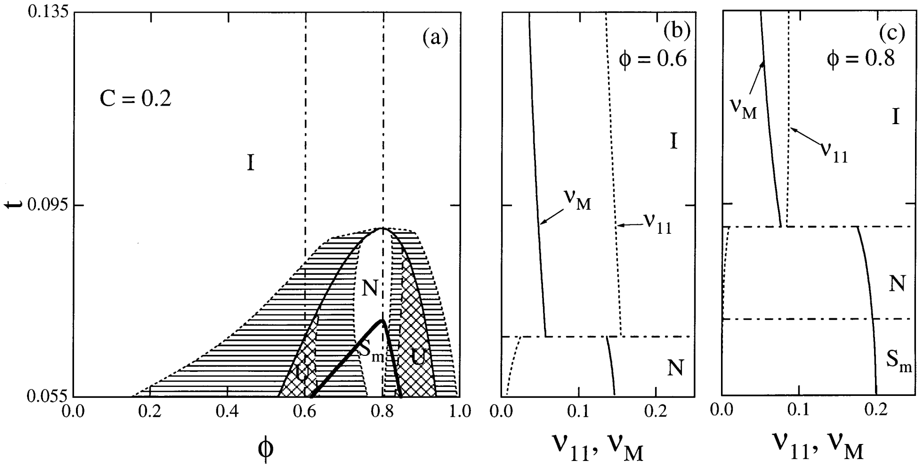

Figure 14. (a) Phase diagram of a trimer-type hydrogen-bonded supramolecular liquid crystal with lower association strength, $C = 0.2$. Other parameters are $n_A = 2$, $n^*_A = 1$, $n_B = n^*_B = 1$, $\lambda_0 = 1.0$, $\lambda_1 = 1.0$, $C_1 = -0.5$, $C_2 = 0.1$, and $\alpha = 0.2$. (b) Cluster size distribution at $\phi = 0.6$. (c) Cluster size distribution at $\phi = 0.8$. Vertical axis represents the reduced temperature t.

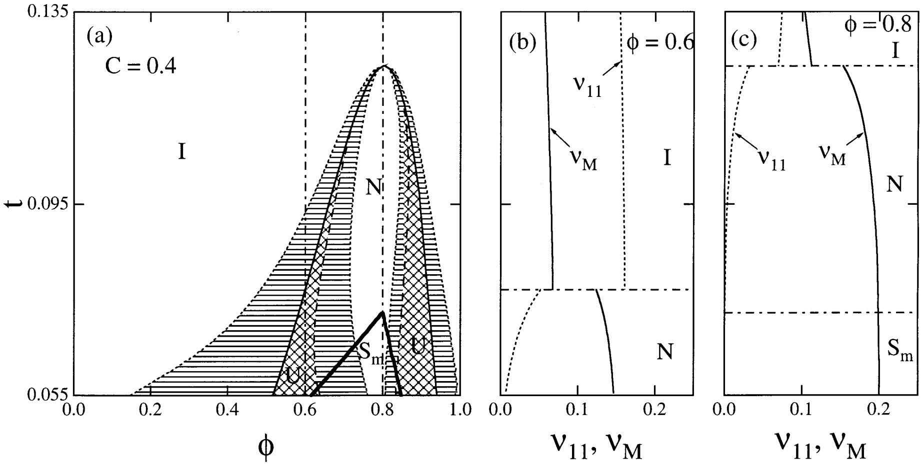

Figure 15. (a) Phase diagram of a trimer-type hydrogen-bonded supramolecular liquid crystal with higher association strength, $C = 0.4$. Other parameters are equal to those in Figure 14. (b) Cluster size distribution at $\phi = 0.6$. (c) Cluster size distribution at $\phi = 0.8$. The vertical axis represents the reduced temperature t.

occurs when the number of carbons on the alkyl chain is higher than a certain threshold value. It also shows that, for the number of the carbons smaller than the threshold, an N phase appears. Our theoretical result gives the same tendency as this experimental result.

Figures 14a and 15a show two phase diagrams of a trimer-type model. Parameters are fixed at $n_A = 2$, $\lambda_0 = 1.0$, $\lambda_1 = 1.0$, $C_1 = -0.5$, and $C_2 = 0.1$. The smectic interaction parameter α is fixed at $\alpha = 0.2$. In Figure 14 the material parameter C corresponding to the strength of hydrogen bond is $C = 0.2$, whereas in Figure 15 $C = 0.4$. The A-molecule and the B-molecule of the mixture shown in Figure 15 tend to associate with each other stronger than those in Figure 14. In these cases, the liquid-crystallization temperature is much higher than that of the ordinary phase separation, so that the latter cannot be seen in these figures. At the stoichiometric composition $\phi = 2n_A/(2n_A + n_B) = 0.8$, not only the I/N transition but also the N/S transition become easiest due to the complete association. This result agrees with the experimental one.[10]

In Figure 14a, the two-phase coexistence region due to the I/N transition has a wide range in composition just below the peak of the I/N transition line. As Figure 14b,c shows, when the value of the association strength C is small, only the small number of mesogenic cores can be formed on cooling in the I phase. Once the I/N transition temperature is reached, the number of the mesogenic cores increases discontinuously. The number of dimers (1,1), on the other hand, decreases remarkably at the I/N transition temperature. Even if the mixture separates into an I phase and an N phase just below the highest I/N transition temperature, the N phase can contain only a few dimers. Thus, the I phase must accept a large number of dimers, so that its composition becomes closer to $\phi = 0.5$. As Figure 15b,c shows, the number of mesogenic cores and that of dimers have a small jump at the I/N transition temperature when a strong hydrogen bond is formed. Thus, when the mixture is quenched just below the highest I/N transition temperature, I−N phase separation does not require expelling so many dimers from the N phase, so that the composition of the I phase lies far from $\phi = 0.5$.

V. Conclusion and Discussion

We have derived phase diagrams of hydrogen-bonded supramolecular liquid crystals by using our new theoretical method. Those phase diagrams show that liquid crystallization, the so-called “chimney” type of phase separation accompanying it, and ordinary macroscopic phase separation caused by repulsive interaction between the different species of molecules all coexist. Both the nematic transition temperature and the smectic A transition temperature become highest at the stoichiometric composition. Total structures of the theoretical phase diagrams agree with the reported experimental results.[6,10,11] Our phase diagrams also resemble those of a nematic liquid-crystal mixture derived by Hwang et al.[47] experimentally and Kyu et al.[48] theoretically and of polymer dispersed liquid crystals derived by Matsuyama et al.[49] theoretically.

By determining the smectic interaction parameter α and the architecture of constituent molecules arbitrarily, we have found that transition temperatures depend on α similarly to that obtained by McMillan.[23] The dependence of transition temperatures on the length of the flexible tails of constituent molecules qualitatively agrees with the reported experimental results.[9,10] However, it turned out impossible to find the unique relationship between the smectic interaction parameter α and molecular architectures within our theoretical framework.

The phase diagrams derived here show two chimneys which extend to the high temperature along liquid-crystallization lines and meet at one point with stoichiometric composition. This is one of the characteristic features of supramolecular liquid crystals.

Comparing the phase diagrams of dimer-forming supramolecular liquid crystals with those of corresponding flexible polymers suggests that a new microphase separation transition inside each smectic A layer may occur after the smectic A transition.

We have not considered the effect of external fields, magnetic and electric fields, on the phase behavior of supramolecular liquid crystals. Controlling association and dissociation of molecules by the external fields is an important subject, and results of the study by our theory will be reported in a forthcoming paper.

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