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## Liquid Crystals

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713926090>

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Online publication date: 06 August 2010

**To cite this Article** Yoon, Dong Kyu and Bae, Young Chan(2010) 'Phase behaviour of nematic liquid crystal/hyperbranched polymer systems', *Liquid Crystals*, 28: 10, 1539 – 1545

**To link to this Article:** DOI: 10.1080/02678290110071510

**URL:** <http://dx.doi.org/10.1080/02678290110071510>

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# Phase behaviour of nematic liquid crystal/hyperbranched polymer systems

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(Received 18 January 2001; accepted 15 May 2001)

The phase behaviours of the nematic liquid crystal EBBA (4-ethoxybenzylidene-4'-*n*-butylaniline) in hyperbranched polymers are investigated by thermo-optical analysis. We adopt Freed's lattice cluster theory to describe the structures of the hyperbranched polymers. To account for highly oriented interactions between segments, our proposed model requires an additional parameter ( $\delta\epsilon/k$ ) related to the energy of the orientated interaction. Calculated values using the proposed model show a remarkably good agreement with experimental data for the given system.

## 1. Introduction

Mixtures of polymers and nematic liquid crystals (LCs) are subjects of intensive investigation in many laboratories around the world. The interest is motivated by their potential use in many fields of high technology involving electronic equipment, display systems, commutable windows, etc [1, 2]. In particular, PDLC (polymer dispersed liquid crystal) systems are multi-component mixtures and can be switched electrically from a light scattering 'off' state to a highly transparent 'on' state.

A distinctive feature of the phase behaviour of such mixtures is the presence of a nematic–isotropic biphasic region in the temperature–composition phase diagram [3, 4]. Some mixtures containing liquid crystals also exhibit liquid–liquid phase separation [5, 6] as seen in mixtures of normal fluids and polymer solutions. In conjunction with experimental work to obtain temperature–composition phase diagrams [3–5], several molecular-thermodynamic models have also been proposed to calculate phase diagrams for mixtures containing liquid crystals. In particular, reports on the first liquid crystalline polymers [7], followed by the early patents describing the use of mesophases for producing solids with ultra high orientation and properties [8], stimulated hopes that reproduction of the complex molecular organization typical of biological assemblies had finally been discovered.

Many statistical theories of nematic phases have been presented. The best known among these are those

suggested by Onsager [9] and by Maier and Saupe [10–12]. The Onsager treatment has proven successful for the description of systems of rigid molecules of high axial ratio which display lyotropic behaviour, while the Maier–Saupe treatment has found application in the case of lower axial ratio molecules displaying thermotropic LC behaviour. Maier and Saupe [11, 12] postulated that the orientation-dependent interaction between nematogenic molecules arises from the anisotropy of their dispersion interactions. Flory and Ronca [13, 14] extended the original Flory lattice model to include anisotropic molecular forces, and created a theoretical frame work which was particularly well suited for the description of mixtures containing nematogens [6, 8, 15]. They combined an orientation-dependent energy with a partition function derived for a system of 'hard' rod-like molecules in which the intermolecular energy is the same for all configurations that are devoid of overlaps. Their treatment of a mixture consisting of rods, coils and a solvent met with gratifying success in a comparison with experimental data. Brochard *et al.* [15] then developed a conceptually simple incompressible model by combining the Flory–Huggins theory [14] for polymer solutions and blends and the Maier–Saupe theory [10–12] for nematic liquid crystals. The Flory–Ronca treatment was extended by Ballauff [16] to binary mixtures of a thermotropic nematogen and a coiled species consisting of isodiametric segments linked together flexibly. The free volume which is known to be of utmost importance in describing thermotropic systems is introduced by methods devised previously [17, 18]. In their work, the comparison of the model with experimental results was made only for polymers of relatively low

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molecular mass. Dorgan and Soane [19] later reported on nematic liquid crystal/wide range molecular mass polymer systems.

Further, the lattice models are supplemented by an entropic contribution to the interaction energies, and Barker and Fock [20] originally developed a quasi-chemical method to take account of such specific interactions. Ten Brinke and Karasz [21] later extended an incompressible model of a binary mixture with the specific interaction, and using a quasi-chemical approach to treat the non-random character of the polymer solution, Panayiotou and Vera [22] and Renucio and Prausnitz [23] proposed an improved FOVE equation of state model. Later, Panayiotou [24] and Sanchez and Balazs [25] generalized the lattice fluid model to account for the specific interaction for the compressible model.

Freed *et al.* [26, 27] reported a complicated lattice field theory for polymer solutions, which is formally an exact mathematical solution of the Flory–Huggins lattice. However, most existing lattice theories fail to explain the polymer architecture. Freed *et al.* [26, 27] proposed a systematic expansion of the partition function of the lattice polymer using well known lattice cluster theory (LCT). This model takes into account the effect of branching on the thermodynamic properties of polymer solutions. Lue and Prausnitz [28] applied the LCT to obtain solvent activities and liquid–liquid equilibria for homogeneous-dendrimer polymers.

In this work, we develop the model to describe the phase behaviours of nematic liquid crystal/hyperbranched polymer systems. We also modify the LCT to account for strongly interacting components by employing the concept of the generalized lattice fluid (LF) model [21, 25]. The experimental technique to determine the cloud points of the given systems involved thermo-optical analysis (TOA).

## 2. Experimental

### 2.1. Materials

The liquid crystal material used in this study was EBBA (4-ethoxybenzylidene-4'-*n*-butylaniline) obtained from the Sigma Aldrich Co. Nematic–isotropic transition temperatures were measured by TOA.

The hyperbranched polyols, generation 2 ( $M_w = 1750$ ,  $M_w/M_n = 1.44$ ), 3 ( $M_w = 3600$ ,  $M_w/M_n = 1.30$ ), and 4 ( $M_w = 7300$ ,  $M_w/M_n = 1.18$ ) were purchased from the Aldrich Chemical Co. (44706-4, 44707-2, 44708-0). All polymer samples were used without further purification.

### 2.2. Sample preparation

Samples were prepared by the solvent casting method with various compositions. The materials were weighed into clean sample vials. EBBA/hyperbranched polyol

samples were dissolved in methanol and stirred at 60°C for 10 h until samples became homogeneous. The samples were then dried in a vacuum oven at 60°C for 30 h.

### 2.3. TOA technique

The thermo-optical analysis (TOA) apparatus consists of a heating–cooling stage, a photodiode (Mettler FP82) and a microprocessor (Mettler FP90). An IBM PC was used as a data acquisition system.

A sample was placed in the microscope heating stage and heated to 100°C to achieve homogenization. The sample was repeatedly heated and cooled over a temperature range near the clearing temperature (76.4°C) of the pure nematogen while the light intensity was monitored. If the measured transition points upon heating and cooling agreed, the point was taken as the equilibrium transition temperature. If these temperatures were different, slower heating and cooling rates were employed. In the case of a slight discrepancy, the transition temperature upon cooling, corresponding to the traditional cloud point, was taken as the equilibrium temperature.

## 3. Theoretical considerations

We consider a binary system consisting of a rod-like nematogen and a hyperbranched polymer. The diameters of the components are assumed to be equal to the size of the lattice cell. The axial ratio of the rod-like particle is  $x_1$  and the contour length of the polymer chain is  $x_p$ . The combinatorial analysis along the lines given by Flory [29] and Freed [26, 27] may be readily adopted for the system under consideration. As usual [11, 17, 18], the mixing partition function  $Z_M$  is subdivided into a liquid crystal part, a polymer part, an orientational part, and an attractive interaction part:

$$Z_M = Z_{LC} Z_{orient} Z_{polymer} Z_{int}. \quad (1)$$

$Z_{LC}$  and  $Z_{polymer}$  are partition functions representing the method of packing the lattice with LC and polymer, respectively. First, lattice sites are occupied by hyperbranched polymer and then the liquid crystal is packed. The quantity  $y$  below specifies the disorientation of the rod-like particles. For a molecule with the long axis at an angle  $\psi$  with respect to the domain axis [11],

$$y = \frac{4}{\pi} x_1 \sin \psi \quad (2)$$

with the orientational distribution function for the rod-like component being given by the ratio  $n_{1y}/n_1$  of the number of molecules with disorientation  $y$  to the total number  $n_1$ ; the mean value  $\bar{y}$  follows as

$$\bar{y} = \sum_y \frac{n_{1y}}{n_1} y. \quad (3)$$

$Z_{LC}$  is given by

$$Z_{LC} = \frac{(n_0 - n_p x_p - n_1(x_1 - \bar{y}))!}{(n_0 - n_p x_p - n_1 x_1)! n_1! (n_0 - n_p x_p) n_p (\bar{y} - 1)}. \quad (4)$$

The reader is referred to the Appendix for a definition of some terms. The orientational partition function  $Z_{orient}$  is expressed as [11, 18]:

$$Z_{orient} = \prod_y \left[ \left( \frac{\omega_y n_1}{n_{1y}} \right) \exp(-x_1 \varepsilon_y / 2k_B T) \right]^{n_{1y}} \quad (5)$$

where

$$\omega_y = \sin \psi \quad (6)$$

is the *a priori* probability of disorientation  $y$  for a rod-like solute [10],  $\varepsilon_y$  is the orientation dependent interaction energy and  $k_B$  is a Boltzmann constant.

Equation (4) expresses the expected number of configurations for the rod-like species in the empty lattice after the polymer is packed. The inclusion of the anisotropic molecular dispersion forces is accomplished by introducing the mean energy of a rod-like segment expressed as [10, 29]

$$\varepsilon_y = -k_B T^* \phi_1 s \left( 1 - \frac{3}{2} \sin^2 \psi \right). \quad (7)$$

For the entire system, this energy is summed over all segment pairs,

$$E_{orient} = -\frac{1}{2} n_1 x_1 \phi_1 s^2 k_B T^* \quad (8)$$

where  $T^*$  is the characteristic temperature of a given nematic species [10]. The order parameter  $s$  is expressed as [16]

$$s = 1 - \frac{2}{3} \langle \sin^2 \psi \rangle. \quad (9)$$

The total number of lattice sites  $n_0$  is expressed as

$$n_0 = n_1 x_1 + n_p x_p \quad (10)$$

hence, the volume fraction  $\phi_1$  and  $\phi_p$  of the liquid crystal and the hyperbranched polymer, respectively, are:

$$\phi_1 = \frac{n_1 x_1}{n_1 x_1 + n_p x_p} \quad (11)$$

$$\phi_p = \frac{n_p x_p}{n_1 x_1 + n_p x_p}. \quad (12)$$

Combining equations (3), (4), (5), and (6), employing Stirling's approximation for the factorials, the free

energies for the LC and the orientation part are obtained [30]

$$-\ln Z_{LC} = -n_1 \bar{y} \ln \bar{y} + \bar{y} + \ln n_1 \quad (13)$$

$$-\ln Z_{orient} = -n_1 \sum_y \frac{n_{1y}}{n_1} \ln \frac{n_{1y}}{n_1 w_y} - \frac{n_1 x_1}{2\theta} s^2. \quad (14)$$

Freed *et al.* [26, 27] proposed a lattice cluster theory (LCT) for homogeneous dendrimers. LCT is useful for describing polymers (dendrimer, hyperbranched polymer and star polymer), which have complex structures. In this study, we adopt LCT to consider the structure of hyperbranched polymers. The lattice is incompressible; that is, the lattice is assumed to be fully occupied.

Lattice sites have  $z$  nearest neighbours, giving  $z$  possible directions for the bonds emanating from a given lattice.  $\varepsilon_{pl}$  is the attractive interaction energy. The free energy is given in double expansion series with  $1/z$  and  $\beta\varepsilon_{pl}$  ( $\beta = 1/k_B T$ ). We truncate the series at the fourth order in  $1/z$  and the second order in  $\beta\varepsilon_{pl}$ . The free energies for a polymer and an attractive interaction energy part are given by

$$\begin{aligned} \frac{\beta \Delta A^{int}}{n_0} = & A^{(1)} \phi_1 (1 - \phi_1) + (A^{(2)} + A^{(3)}) \phi_1^2 (1 - \phi_1)^2 \\ & + A^{(3)} \phi_1^2 (1 - \phi_1)^2 (2\phi_1 - 1)^2 + A^{(4)} \phi_1^2 (1 - \phi_1)^2 \\ & \times [1 - 6\phi_1 (1 - \phi_1) (3\phi_1^2 - 3\phi_1 + 2)] \\ & + (B^{(1)} + B^{(2)}) \phi_1^2 (1 - \phi_1) + B^{(4)} \phi_1^2 (1 - \phi_1)^3 \\ & + C^{(1)} \phi_1^2 (1 - \phi_1) (2\phi_1 - 1)^2 + C^{(2)} (1 - \phi_1) \phi_1^3 \\ & + C^{(3)} \phi_1^3 (1 - \phi_1)^2 (3\phi_1 - 1) + C^{(4)} \phi_1^4 (1 - \phi_1) \end{aligned} \quad (15)$$

where

$$A^{(1)} = \frac{\beta \varepsilon z}{2} \quad (16)$$

$$A^{(2)} = -\frac{(\beta \varepsilon)^2 z}{4} \quad (17)$$

$$A^{(3)} = -\frac{(\beta \varepsilon)^3 z}{12} \quad (18)$$

$$A^{(4)} = -\frac{(\beta \varepsilon)^4 z}{48} \quad (19)$$

$$B^{(1)} = -\beta \varepsilon N(1) \quad (20)$$

$$\begin{aligned} B^{(2)} = & \frac{\beta \varepsilon}{z} (2N(2) + N(3) + N(\perp) + N(1, 2) \\ & - N(1)N(2)K) \end{aligned} \quad (21)$$

$$B^{(3)} = -\frac{2\beta\epsilon}{z}N(1)(2N(1) + N(1, 1) - [N(1)]^2 M) \tag{22}$$

$$B^{(4)} = -\frac{4\beta\epsilon}{z}[N(1)]^3 \tag{23}$$

$$C^{(1)} = -\frac{(\beta\epsilon)^2}{z}[N(1)]^3 \tag{24}$$

$$C^{(2)} = -(\beta\epsilon)^2 N(2) \tag{25}$$

$$C^{(3)} = -(\beta\epsilon)^3 [N(1)]^2 \tag{26}$$

$$C^{(4)} = -\frac{(\beta\epsilon)^2}{2}(N(1, 1) - [N(1)]^2 M) \tag{27}$$

$$\frac{\beta\Delta A^{\text{polymer}}}{n_0} = \frac{(1 - \phi_1)}{M} \ln(1 - \phi_1) + \phi_1 \ln \phi_1 + a^{(0)}\phi_1(1 - \phi_1) + a^{(1)}\phi_1(1 - \phi_1)^2 + a^{(2)}\phi_1(1 - \phi_1)^3. \tag{28}$$

In equation (28):

$$a^{(0)} = \frac{1}{z}[N(1)]^2 + \frac{1}{z^2} \left\{ -4N(1)N(2) + \frac{8}{3}[N(1)]^3 - 2N(1)N(3) + [N(2)]^2 - 2N(1)(N(1, 2) - N(1)N(2)M) + 2[N(1)]^4 + 2[N(1)]^2 \times (N(1, 1) - [N(1)]^2 M) - 6N(1)N(\perp) \right\} \tag{29}$$

$$a^{(1)} = \frac{1}{z^2} \left[ \frac{8}{3}[N(1)]^3 + 2[N(1)]^4 + 2[N(1)]^2(N(1, 1) - [N(1)]^2 M) \right] \tag{30}$$

$$a^{(2)} = \frac{1}{z^2} 2[N(1)]^4 \tag{31}$$

where  $N(\alpha) = N_\alpha/M$  ( $\alpha = 1, 2, 3$  or  $\perp$ ) and  $N(\alpha\beta) = N_{\alpha,\beta}/M$  ( $\alpha = 1$  or  $2$ ).

The combinatorial numbers,  $N_\alpha$  and  $N_{\alpha\beta}$ , describe the architecture of a polymer. In LCT, the polymer architecture is characterized by a set of seven parameters, known as counting indices:  $M$  is the number of segments in each polymer molecule;  $N_1$  is the number of bonds in each polymer molecule;  $N_2$  is the number of consecutive bonds;  $N_3$  is the number of ways in which three consecutive bonds can be chosen;  $N_\perp$  is the number of ways in which three bonds meet at a lattice site for the polymer chain;  $N_\perp$  is the number of ways in which three bonds meet at a lattice site for the polymer chain;  $N_{1,1}$  is the number of distinct ways of selecting two non-sequential bonds on the same chain;  $N_{1,2}$  is the number of distinct ways of selecting one bond and two sequential bonds on the same chain.

In the LCT model, the linear polymers are characterized by a single parameter,  $n$ , the total number of bonds,  $M = n + 1$ , and dendritic polymers are considered to consist of a central core with three arms; the dendrimer structure is characterized by two parameters, the generation number ( $g$ ) and the separator length ( $n$ ), that is the number of bonds between branch points. The combinatorial numbers,  $N_\alpha$  and  $N_{\alpha\beta}$ , are calculated by counting indices for these types of polymer. Geometric parameters for linear and dendritic polymers are listed in table 1.

In LCT, van der Waals attractive energies ( $\epsilon_{22}$ ,  $\epsilon_{11}$  and  $\epsilon_{12}$ ) are present between nearest neighbour monomers, LC molecules, and polymer-LC pairs. The attractive interaction in the system is characterized by a parameter  $\epsilon$ ,

$$\epsilon = \epsilon_{22} + \epsilon_{11} - 2\epsilon_{12}. \tag{32}$$

Sanchez and Balaz [25] have developed their generalized lattice fluid model to account for strongly interacting components. The basic idea is that for two components to interact strongly, they must be in a

Table 1. Geometric parameters for linear and star polymers.

Parameter	Linear	Dendritic polymer
$M$	$n + 1$	
$N_1$	$n$	$3(2^{g-1} - 1)n + 1$
$N_2$	$n - 1$	$3(2^{g-1} - 1)n$
$N_3$	$n - 2$	$3(2^{g-1} - 1)(n - 1) + 3N_\perp$
$N_\perp$	0	$3(2^{g-1} - 1)(n - 2) + 6N_\perp$
$N_{1,1}$	$(n - 1)(n - 2)/2$	$3(2^{g-2} - 1) + 1$
$N_{1,2}$	$(n - 2)(n - 3)$	$3(2^{g-1} - 1)(n - 1)(n - 2)/2 + 3(2^{g-1} - 1)[3(2^{g-1} - 1) - 1]n^2/2 - 3N_\perp + 3(2^{g-1} - 1)[3(2^{g-1} - 1) - 1]n(n - 1) - 6N_\perp$

proper orientation with respect to one another, i.e. there is a specific spatial or geometric constraint in the interaction (specific interaction). Other mutual orientations of the interacting pairs are energetically less favourable, but many more of them may exist. Thus an entropic contribution must be paid to form a specific interaction. Sanchez and Bolaz [25] have adopted a similar approach to that of ten Brinke and Karasz [21], who developed an incompressible model for a binary mixture with specific interaction. To consider the entropic contribution by the specific interaction between the polymer-LC pair, we adapt this approach to the LCT. A detailed description of this procedure is reported elsewhere [25].

The polymer-LC interaction can be weak (non-specific) with energy  $\varepsilon_{12} + \delta\varepsilon$ . The new energy parameter  $f_{12}$ , which accounts for the specific interaction, is given by

$$f_{12} = \varepsilon_{12} + \delta\varepsilon - kT \ln \left[ \frac{1+q}{1+q \exp(-\beta\delta\varepsilon)} \right] \quad (33)$$

where  $\beta = 1/k_B T$ , and  $q$  is the number of ways that the non-specific 1-2 interaction occurs. In this approach, the purely energetic parameter has been replaced by the free energy parameter  $f_{12}$ . Thus equation (33) is rewritten as follows:

$$\begin{aligned} \varepsilon_{p1} &= \varepsilon_{11} + \varepsilon_{22} - 2f_{12} \\ &= \varepsilon - 2\delta\varepsilon + 2k_B T \ln \left[ \frac{1+q}{1+q \exp(-\beta\delta\varepsilon)} \right] \end{aligned} \quad (34)$$

where  $\varepsilon = \varepsilon_{22} + \varepsilon_{11} - 2\varepsilon_{12}$ .

The chemical potential for the anisotropic phase of mixtures of a liquid crystal can be determined from the free energy,

$$\beta\Delta\mu_1 = \beta(\Delta\mu_1^{\text{LC}} + \Delta\mu_1^{\text{orient}} + \Delta\mu_1^{\text{polymer}} + \Delta\mu_1^{\text{int}}) \quad (35)$$

where

$$\beta\Delta\mu_1^{\text{LC}} = -\bar{y} \ln \bar{y} + \bar{y} + \ln n_1 \quad (36)$$

$$\beta\Delta\mu_1^{\text{orient}} = -\ln f_1 - \frac{x_1 s}{\theta} \left( 1 - \frac{1}{2}s - \frac{1}{2}s\phi_1 \right) \quad (37)$$

$$\begin{aligned} \beta\Delta\mu_1^{\text{polymer}} &= \ln \phi_1 + \left( 1 - \frac{1}{x_p} \right) (1 - \phi_1) \\ &+ a^{(0)} (1 - \phi_1)^2 (2\phi_1 - 1) \\ &- a^{(2)} (1 - \phi_1)^3 (3\phi_1 - 1) \end{aligned} \quad (38)$$

$$\begin{aligned} \beta\Delta\mu_1^{\text{int}} &= A^{(1)} (1 - \phi_1)^2 - (A^{(2)} + A^{(3)}) \phi_1 (3\phi_1 - 2) \\ &\times (1 - \phi_1)^2 - A^{(3)} (1 - \phi_1)^2 \phi_1 (2\phi_1 - 1) \\ &\times [1 - 9(1 - \phi_1) + 10(1 - \phi_1)^2] \\ &- A^{(4)} (1 - \phi_1)^2 \phi_1 \\ &\times [1 - 27(1 - \phi_1) + 138(1 - \phi_1)^2 \\ &- 294(1 - \phi_1)^3 + 306(1 - \phi_1)^4 - 126(1 - \phi_1)^5] \\ &+ (B^{(1)} + B^{(2)}) 2\phi_1 (1 - \phi_1)^2 \\ &- B^{(4)} 2\phi_1 (1 - \phi_1)^2 (2\phi_1 - 1) \\ &- C^{(1)} 2\phi_1 (1 - \phi_1)^2 (2\phi_1 - 1) (4\phi_1 - 1). \end{aligned} \quad (39)$$

The order parameter  $s$  and disorientation index  $\bar{y}$  are defined as follows:

$$\bar{y} = \frac{4}{\pi} x_1 \left( \frac{f_2}{f_1} \right) \quad (40)$$

$$s = 1 - \frac{3}{2} \left( \frac{f_3}{f_1} \right) \quad (41)$$

where

$$\begin{aligned} f_p &= \int_0^{\pi/2} \sin^p \psi \exp \left\{ -\frac{4}{\pi} x_1 a \sin \psi \right. \\ &\left. - \frac{3}{2} \left( \frac{x_1 \phi_1 s}{\theta} \right) \sin^2 \psi \right\} d\psi \end{aligned} \quad (42)$$

and  $a$  is defined as

$$a = -\ln \left[ 1 - \phi_1 \left( 1 - \frac{\bar{y}}{x_1} \right) \right]. \quad (43)$$

#### 4. Results and conclusion

To consider the specific interaction in LC/hyperbranched polymer systems, two parameters are introduced: the coordination number ( $z$ ) and the energy parameters ( $\delta\varepsilon_{12}$ ) associated with the specific interactions. The coordination number also appears only as a scale factor in the original LF model. However, Sanchez *et al.* [25] have generalized this factor so that it scales not only the energies, but also an entropy term. Although it must have been specified in the previous work, it can be assigned any reasonable value ( $z = 6$  in our calculation). The energy parameter,  $\delta\varepsilon_{12}$ , is really not an independent parameter: its value depends on the value of the non-specific interaction energy,  $\varepsilon$ .

In the liquid crystal/hyperbranched polymer system, generally speaking, the two-phase sample scatters light more than the homogeneous phase. It causes a jump in the measured light intensity at the transition temperature when polarizers are used. In an isotropic one-phase region, no light is transmitted and the intensity is very low. If a nematic phase is present in the two-phase

Table 2. The structures of the polymers.

Generation no.	Structure
2	$O[CH_2C(CH_2H_5)(CH_2O^-)]_2A_4B_8$
3	$O[CH_2C(CH_2H_5)(CH_2O^-)]_2A_4A_8B_{16}$
4	$O[CH_2C(CH_2H_5)(CH_2O^-)]_2A_4A_8A_{16}B_{32}$

$$A = [COC(CH_3)(CH_2O^-)]_2, B = [COC(CH_3)(CH_2OH)]_2$$

Table 3. Equation of state data for EBBA.

$\rho$ (40°C) = 0.9881 g cm <sup>-3</sup>	$\alpha = 8.22 \times 10^{-4} K^{-1}$
$T_{ni} = 76.4^\circ C$	$x_1 = 3.7$

regime, light is transmitted through the crossed polarizers due to the birefringent nature of this phase.

We employ Flory's lattice model and Freed's lattice cluster theory to describe the phase behaviour of our liquid crystal/hyperbranched polymer systems. Structures of the polymers used are in table 2 and the thermodynamic properties of EBBA are summarized in table 3. Figure 1–3 show how the theoretical coexistence curves calculated by the proposed model compare with the experimental data for EBBA as 4-ethoxybenzylidene-4'-butylaniline/hyperbranched polyol systems—generation 2 ( $M_w = 1750$ ,  $M_w/M_n = 1.44$ ), 3 ( $M_w = 3600$ ,  $M_w/M_n = 1.30$ ), and 4 ( $M_w = 7300$ ,  $M_w/M_n = 1.18$ ).

To account for the polydispersity of a separator length ( $n$ ) for the hyperbranched polymer, one can correlate the experimental distribution data for  $n$  with a proper algebraic expression of a distribution function. However, it is very difficult to obtain the experimental distribution curve for  $n$ . In this study, we set  $n$  as an adjustable model parameter so that our  $n$  values are mean separator lengths for the given systems.

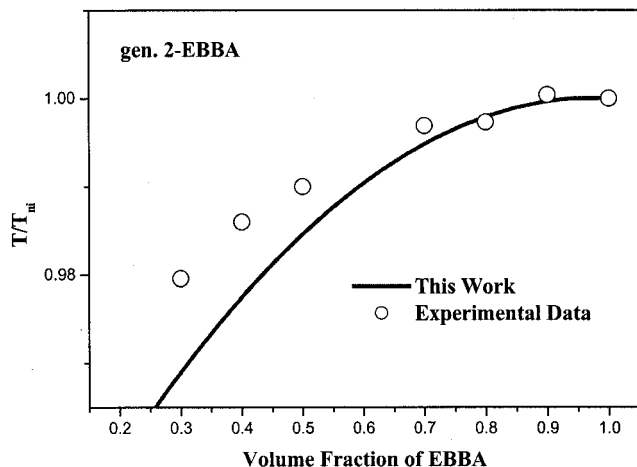


Figure 1. Phase diagram for the EBBA/hyperbranched polyol (generation 2:  $M_w = 1750$ ,  $M_w/M_n = 1.44$ ) system. Solid line is the proposed model; interaction parameters are  $\varepsilon/k = 159.55$  K and  $\delta\varepsilon_{12}/k = -467.57$  K.

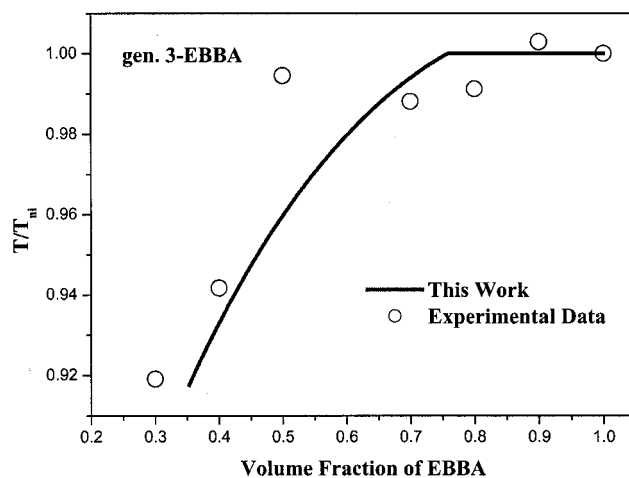


Figure 2. Phase diagram for the EBBA/hyperbranched polyol (generation 3:  $M_w = 3600$ ,  $M_w/M_n = 1.30$ ) system. Solid line is the proposed model; interaction parameters are  $\varepsilon/k = 161.55$  K and  $\delta\varepsilon_{12}/k = -473.40$  K.

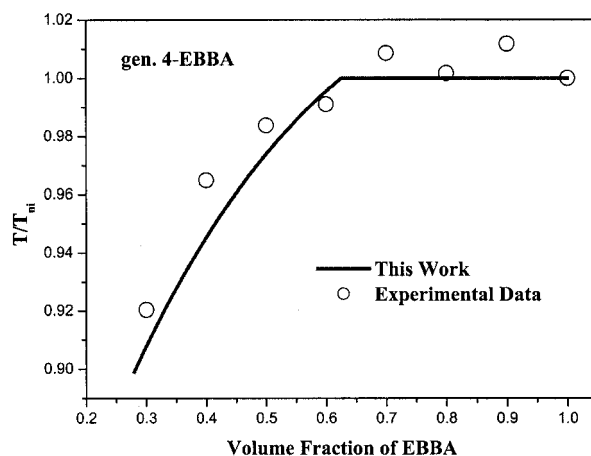


Figure 3. Phase diagram for the EBBA/hyperbranched polyol (generation 4:  $M_w = 7300$ ,  $M_w/M_n = 1.18$ ) system. Solid line is the proposed model; interaction parameters are  $\varepsilon/k = 163.52$  K and  $\delta\varepsilon_{12}/k = -484.62$  K.

In the figures, open circles indicate experimental data and solid lines are calculated values from the proposed model. As shown in these figures, the model gives good agreement with the experimental data. However, in figure 1, there are some deviations between the calculated values and the experimental data in the low concentration region of EBBA. Values of a separator length  $n$  in each system are 6.0 (gen. 2), 6.0 (gen. 3), and 4.0 (gen. 4). Table 4 gives values of the interaction parameters  $\varepsilon/k$  and  $\delta\varepsilon_{12}/k$ ; the effect of the specific interaction between the liquid crystal and the hyperbranched polymer increases with the generation number of the polymer.

Specific interactions are assumed to be formed with equal probability at any contact points of the molecule.

Table 4. Values of energy parameters for EBBA/hyperbranched polyol systems.

Generation no.	$M_w$	$\varepsilon/k$	$\delta\varepsilon_{12}/k$
2	1750	158.53	-443.92
3	3600	162.24	-476.45
4	7300	170.64	-486.55

It is not correct if specific interactions can be formed only at particular parts of a molecule. It appears that this parameter may play an important role in accounting for some deviations of real systems from those described by the lattice model.

International cooperation in Korea Science and Engineering Foundation supported this article.

### Appendix

#### Nomenclature

- $E_{\text{orient}}$  = orientational energy of the system as a whole,  
 $n_0$  = total number of lattice sites,  
 $n_p$  = number of polymer molecules,  
 $n_l$  = number of liquid crystal molecules,  
 $R$  = gas constant,  
 $T$  = absolute temperature,  
 $T_{ni}$  = nematic-isotropic transition temperature,  
 $\phi_p$  = volume fraction of polymer molecules,  
 $\phi_l$  = volume fraction of liquid crystal molecules,  
 $x_p$  = contour length of the polymer chain,  
 $x_l$  = aspect ratio of rod-like component,  
 $\psi$  = angle between rod axis and preferred axis,  
 $T^*$  = characteristic temperature,  
 $\theta$  = reduced temperature ( $T/T^*$ ),  
 $n$  = separator length,  
 $g$  = generation number.

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