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Liquid−Liquid Equilibria of Dendrimer in Polar Solvent

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We present the liquid−liquid equilibria of a homogeneous dendrimer solution using a lattice cluster theory and a specific interaction model. We examined the phase behavior of dendrimer solutions by varying the dendrimer generation number, the number of bonds between two consecutive branch points along a chain, and the strength of specific interaction among end-groups of dendrimer and solvent molecules. There was only a slight change in the liquid−liquid coexistence curve of dendrimer solutions for various generation numbers. The critical temperature increases with decreasing generation number and increasing separator length. Our results show that the coexistence curve shows a great dependence on specific interactions and structure factors.

Introduction

In recent years, many researchers have taken an interest in exploring and developing a variety of uses for dendritic macromolecules, which are highly branched, tree-like molecules (dendrimers and hyperbranched polymers).[1] Many applications[2] for dendritic polymers have been proposed. These include nanoscale catalysts and reaction vessels, micelle mimic, magnetic resonance imaging agent, immunodiagnostics, agents for delivering drugs into cells, chemical sensors, information-processing materials, high-performance polymer, adhesive and coating, separation media, and molecular antennae for absorbing light energy. These applications are due to the highly branched chain architecture and numerous chain ends that can be functionalized.

The standard lattice model of polymers was solved in the simple mean field approximation independently by Flory[3] and Huggins,[4] and the treatment of the former is customarily termed the Flory−Huggins theory. Lattice theories have contributed much to the understanding of polymer solutions. In addition, much work has been done to improve the mathematical solution of the lattice model, including chain connectivity and nonrandom mixing.[5] However, the mean field approximation has been found to be quantitatively deficient in some aspects.

The lattice models are supplemented by an entropic contribution to interaction energies. Barker and Fock[6] developed a quasi-chemical method to account for the specific interaction. ten Brinke and Karasz[7] have developed an incompressible model of a binary mixture with a specific interaction. Using a quasi-chemical approach to treat the nonrandom character of the polymer solution, Panayiotou and Vera[8] and Renuncio and Prausnitz[9] have developed an improved Flory-Orwoll-Vrij-Eichinger (FOVE) equation of state model, and Panayiotou[10] and Sanchez and Balazs[11] have generalized the lattice fluid model to account for the specific interaction. In 1990, Veytsman[12] proposed an expression for the contribution of the hydrogen bonds to the free energy of fluid that is valid for the general case. Furthermore, Freed et al.[13−15] reported a complicated lattice field theory for polymer solutions, which is formally an exact mathematical solution of the Flory−Huggins lattice. However, most of these lattice theories fail to yield a dependence of solution properties on the polymer architecture. Recently, Freed et al.[16−21] developed a systematic expansion of the partition function of 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[22] employed the LCT to obtain solvent activities and liquid−liquid equilibria for homogeneous dendrimer polymers.

In this study, we investigate the effects of specific interactions among end group sites of dendrimer and solvent molecules for the liquid−liquid equilibria (LLE) of dendrimer that has a specific molecular structure. We also present hypothetical results for LLE of dendrimer/polar solvent systems that have specific interactions.

Theoretical Consideration

In the model development of the dendrimer solutions, we used the standard lattice model scheme. We placed the polymer solution on a lattice with N total sites. Each monomer or a solvent molecule occupies one lattice site and each polymer molecule is assumed to occupy M lattice sites. The lattice is assumed to be fully occupied.

Volume fractions of polymer (ϕ_2) and solvent (ϕ_1) in solution are

$$\phi_1 = N_s/N \tag{1}$$

$$\phi_2 = N_pM/N \tag{2}$$

where, N_p and N_s are the number of polymer molecules and the number of solvent molecules in solution, respectively. Each site

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has z nearest neighboring sites. Attractive interactions in this system are characterized by three parameters ϵ, F_{11}^{S}, and F_{12}^{S}, given by

$$\epsilon = \epsilon_{11} + \epsilon_{22} - 2\epsilon_{12} \tag{3}$$

where ϵ_{11} is the energy of a solvent−solvent contact, ϵ_{22} is the energy of a nonbonded polymer segment−segment contact, and ϵ_{12} is the energy of a polymer segment−solvent contact. Subscript 1 refers to 1-component (the solvent) and subscript 2 refers to 2-component (the polymer). F_{11}^{S} is the free energy of solvent−solvent specific interaction formation and F_{12}^{S} is the free energy of specific interaction formation between the polymer end-group and the solvent.

We assume that the intermolecular forces are divided into physical and chemical forces. This assumption implies that the Helmholtz energy of mixing can be added as follows:

$$A = A^{\mathrm{LCT}} + A^{\mathrm{S}} \tag{4}$$

where A^{LCT} and A^{S} are physical and chemical contributions to the Helmholtz energy, respectively. This decoupling of the intermolecular interaction is clearly an approximation. We employ LCT to calculate the physical contribution of chemical potential. We reduce the detailed description of LCT model.

Lattice Cluster Theory. Freed et al.[16−21] have proposed an LCT for homogeneous dendrimers. In their model, the free energy is given by a double expansion series in $1/z$ and $\epsilon/k_{\mathrm{B}}T$, where k_{B} is the Boltzmann constant and T is the absolute temperature in Kelvin. We use the truncated form of the series at the fourth order in $1/z$ and the second order in $\epsilon/k_{\mathrm{B}}T$. Details of our calculations are given in the literature.[12−21]

Specific Interaction Contribution to the Free Energy. Veytsman[12] proposed an expression for the contribution of hydrogen bonds to the free energy of fluid that is valid for the general case. We applied this model to the specific interaction contribution.

Consider a volume V divided into N equal cells. The system contains molecules of k species, and N_i is the number of i^{th} kind of molecules. Any molecule of the i^{th} kind has d_i donor sites and a_i acceptor sites. For simplicity, we assume that all donor sites are only one type of donating and acceptor sites are only one type of accepting. We assume that association bonds are formed as a specific interaction occurs. A donor site of an i^{th} kind molecule can form a specific interaction with an acceptor site of a j^{th} kind molecule if the sites are located in the adjacent cells. Such a bond is referred to as (i,j) bond and the free energy of an (i,j) bond formation is F_{ij}^{S}.

The total specific interaction energy is given by

$$E_{\mathrm{S}} = \sum_{i}^{k}\sum_{j}^{k} M_{ij}E_{ij}^{\mathrm{S}} \tag{5}$$

where E_{ij}^{S} is the favorable energy change on the specific interaction formation between a donor group i and an acceptor group j. M_{ij} is the number of (i,j) pair-specific interaction formations. The number of way Ω_{S} of distributing M_{ij} bonds among the functional groups of the system is proposed for the general case.[12]

$$\Omega_{\mathrm{S}} = \prod_{i=1}^{k}\frac{(N_id_i)!}{(N_id_i - \sum_{m=1}^{k}M_{im})!}\prod_{j=1}^{k}\frac{(N_ja_i)!}{(N_ja_j - \sum_{n=1}^{k}M_{nj})!}\prod_{i=1}^{k}\prod_{j=1}^{k}\frac{P_{ij}^{M_{ij}}}{(M_{ij})!} \tag{6}$$

The mean field probability[23] that a specific acceptor j will be proximate to a given donor i is proportional to the volume of the acceptor group divided by the total system volume;

$$P_{ij} \sim \frac{1}{N} \tag{7}$$

Furthermore, the bond formation requires that a donor and an acceptor adopt a unique spatial orientation with respect to one another. Formation of the bond is accompanied by a loss of orientational degree of freedom. In general, for a donor i−acceptor j pair, the probability is given by[23]

$$p_{ij} = \frac{e^{S_{ij}^{\mathrm{S}}/R}}{N} \tag{8}$$

where S_{ij}^{S} is the entropy loss associated with the specific interaction formation of an (i,j) pair.

In the mean-field approximation, we obtain

$$\begin{aligned}A^{\mathrm{S}} = {} & \sum_{i=1}^{k}\sum_{j=1}^{k}M_{ij}F_{ij}^{\mathrm{S}} + \\ & k_{\mathrm{B}}T\sum_{i=1}^{k}\sum_{j=1}^{k}M_{ij}\ln\frac{eNM_{ij}}{(N_id_i - \sum_{m=1}^{k}M_{im})(N_ja_j - \sum_{n=1}^{k}M_{nj})} + \\ & k_{\mathrm{B}}T\sum_{i=1}^{k}N_id_i\ln\left(1 - \sum_{j=1}^{k}\frac{M_{ij}}{N_id_i}\right) + k_{\mathrm{B}}T\sum_{j=1}^{k}N_ja_j\ln\left(1 - \sum_{i=1}^{k}\frac{M_{ij}}{N_ja_j}\right)\end{aligned} \tag{9}$$

In equilibrium, the free energy A^{S} at a given M_{ij} is obtained by minimizing with respect to M_{ij}

$$\begin{aligned}A^{\mathrm{S}} = {} & k_{\mathrm{B}}T\sum_{i=1}^{k}\sum_{j=1}^{k}M_{ij} + k_{\mathrm{B}}T\sum_{i=1}^{k}N_id_i\ln\left(1 - \sum_{j=1}^{k}\frac{M_{ij}}{N_id_i}\right) + \\ & k_{\mathrm{B}}T\sum_{j=1}^{k}N_ja_j\ln\left(1 - \sum_{i=1}^{k}\frac{M_{ij}}{N_ja_j}\right)\end{aligned} \tag{10}$$

where M_{ij} values are determined by the set of quadratic equations

$$NM_{ij} = (N_id_i - \sum_{m=1}^{k}M_{im})(N_ja_j - \sum_{n=1}^{k}M_{nj})\exp\left(-\frac{F_{ij}^{\mathrm{S}}}{k_{\mathrm{B}}T}\right) \tag{11}$$

where $F_{ij}^{\mathrm{S}} = E_{ij}^{\mathrm{S}} - TS_{ij}^{\mathrm{S}}$.

Equations 10 and 11 give the excess free energy due to the specific interaction formation. To apply this model to a dendrimer solution, we consider the binary mixture of dendrimer and solvent. Solvent has both a donor site ($d_1 = 2$) and an acceptor site($a_1 = 1$). The dendrimer has only acceptor sites: a_2 is equal to the number of end groups of dendrimer molecule.

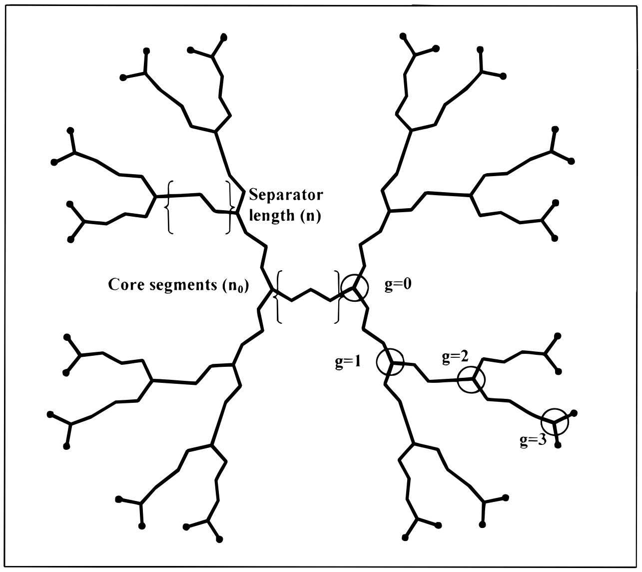

Figure 1. Schematic description of dendrimer. Key: (●) end-groups that can be functionalized.

For this system, the chemical contribution to the free energy is

$$A^{\mathrm{S}} = k_{\mathrm{B}}T(M_{11} + M_{12}) + k_{\mathrm{B}}T\left[N_{\mathrm{s}}d_1 \ln\left(\frac{N_{\mathrm{s}}d_1 - (M_{11} + M_{12})}{N_{\mathrm{s}}d_1}\right)\right] + k_{\mathrm{B}}T\left[N_{\mathrm{s}}a_1 \ln\left(\frac{N_{\mathrm{s}}a_1 - M_{11}}{N_{\mathrm{s}}a_1}\right) + N_{\mathrm{p}}a_2 \ln\left(\frac{N_{p}a_2 - M_{12}}{N_{\mathrm{p}}a_2}\right)\right] \quad (12)$$

$$NM_{11} = (N_{\mathrm{s}}d_1 - M_{11} - M_{12})(N_{\mathrm{s}}a_1 - M_{11}) \exp\left(-\frac{F_{11}^{\mathrm{S}}}{k_{\mathrm{B}}T}\right) \quad (13\text{-}1)$$

$$NM_{12} = (N_{\mathrm{s}}d_1 - M_{11} - M_{12})(N_{\mathrm{p}}a_2 - M_{12}) \exp\left(-\frac{F_{12}^{\mathrm{S}}}{k_{\mathrm{B}}T}\right) \quad (13\text{-}2)$$

Details of derivation steps are omitted.

Results and Discussion

We examined liquid–liquid equilibria of dendritic polymer solutions. Figure 1 shows a schematic of a dendrimer structure. The dendrimers are characterized by three parameters: the generation number (g), the number of bonds (n) between branch points, and the number of segments (n_0) between 0th generation points (the nodes).

Figure 2 represents hypothetical liquid–liquid coexistence curves with and without specific interactions. The dotted line is from the model with specific interactions. The change of free energy for a solvent–solvent specific interaction formation ($F_{11}^{\mathrm{S}}/k_{\mathrm{B}}$) is −10.0 Kelvin (K) and that of the polymer–solvent specific interaction formation is ($F_{12}^{\mathrm{S}}/k_{\mathrm{B}}$) is −4.0 K. The solid line is computed from the model without specific interactions; it reduces to the original LCT model and gives much higher critical temperature and lower critical composition for the dendrimer–solvent system than that of the model with specific interactions. This result probably means that the dendrimer, when in a polar solvent, would be more soluble if its chain-ends would present some specific interaction sites. Figure 3 shows the effect of $F_{12}^{\mathrm{S}}/k_{\mathrm{B}}$ in liquid–liquid equilibria of a dendrimer with $g = 5$, $n = 10$, and $n_0 = 3$. Figure 3 shows the change of coexistence curves of dendrimer solutions for different polymer–solvent specific interaction free energy at fixed $F_{11}^{\mathrm{S}}/k_{\mathrm{B}} = -20.0$ K. Increase of the polymer–solvent specific interaction induces the miscibility of the system. This result implies that we could control the miscibility of the given system by changing properties of end-groups.

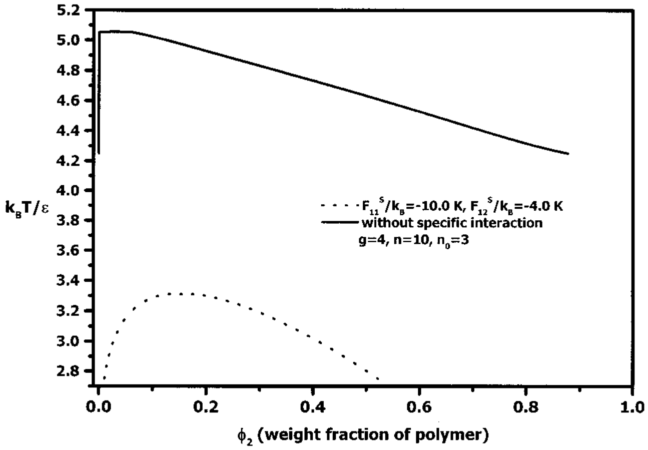

Figure 2. Coexistence curves for the dendrimer/solvent system. Generation number (g) is 4, separator length (n) is 10, and core segment length is 3. The solid line is from the model without specific interaction formations. The dotted line is from this work ($F_{11}^{\mathrm{S}}/k_{\mathrm{B}}. = -10$ K, $F_{12}^{\mathrm{S}}/k_{\mathrm{B}} = -4$ K).

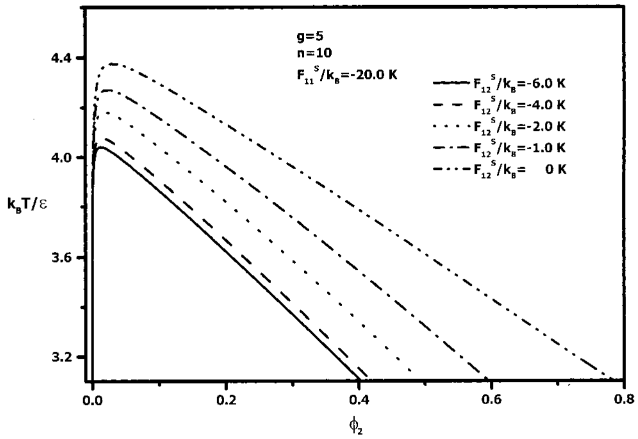

Figure 3. Phase behaviors of dendrimer/solvent systems for change of end-group–solvent specific interaction free energy ($F_{12}^{\mathrm{S}}/k_{\mathrm{B}}$) at fixed solvent–solvent specific interaction free energy ($F_{11}^{\mathrm{S}}/k_{\mathrm{B}} = -20.0$ K). The generation number is 5 and the separator length is 10. Lines are calculated from this work.

We present LLEs for various generation numbers in Figure 4. The miscibility of the dendrimer solution decreases with the generation number because the molecular weight of dendrimer increases with the generation number. However, more end-groups are associated with the solvent molecule for higher generation numbers than those of lower generation numbers, which makes the system miscible. In this figure, we found that there is only slight change in the LLE coexistence curve compared with hydrogen bonding energy change. Figure 4 also shows the competing effect between the molecular weight dependence and the hydrogen bonding effect on LLE of dendrimer solutions.

Figure 5 shows the phase change with different separator lengths (n) at a fixed number of hydrogen bonding. The miscibility region decreases with the separator length. Critical

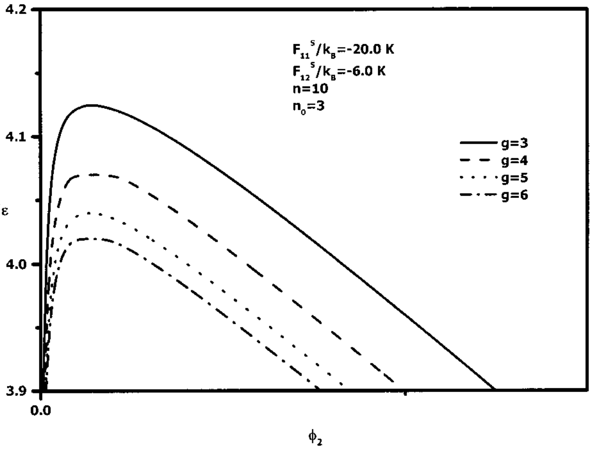

Figure 4. Phase behaviors of dendrimer/solvent systems for different generation numbers (3–6) at fixed specific interaction free energies (F_{11}^S, F_{12}^S). The separator length is 10 and core segment length is 3.

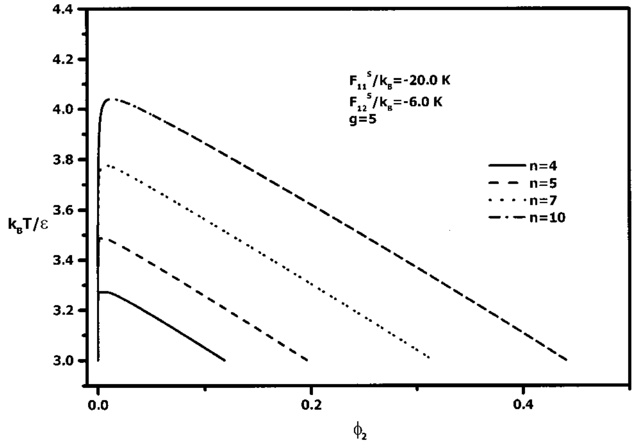

Figure 5. Phase behavior of dendrimer/solvent system for different separator length (4–10) at fixed specific interaction free energies (F_{11}^S, F_{12}^S). The generation number is 4 and the core segment length is 3.

temperature increases with the separator length and with decreasing the generation number. However, the critical concentration depends slightly on structure factors (*g*, *n*). We expect that it is possible to maintain miscibility for the higher molecular weight of dendrimer.

Conclusion

We examined the effects of polymer structure and the specific interactions for the homogeneous dendrimer solutions. This work shows that liquid–liquid coexistence curve for a homogeneous dendrimer solution with specific interactions is much lower than that of systems without specific interactions.

Calculations for different free energies of dendrimer end-group/solvent specific interactions (F_{12}^S) show enhanced miscibility with increasing F_{12}^S. In calculations for different free energies of specific interaction, the strength of F_{12}^S makes the system miscible. Phase behaviors of dendrimer solutions greatly depend on the specific interaction. For the effect of structure factors, critical temperature increases with the separator length and with decreasing the generation number. However, the critical concentration depends slightly on structure factors.

In this study, we show the change of phase behavior for chemically different segments at the periphery of a dendrimer. The miscibility of dendrimer solutions depends greatly on the properties of the end-groups and structure factors. A new model presented in this study serves as a useful approach to understanding dendrimer solutions with specific interactions among end-groups of dendrimer and solvent molecules.

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