

Calamitic Liquid Crystals as Nanoscale Analogues of a Block Copolymer

Makoto Yoneya,^{*,†} Kotaro Araya,[‡] Etsushi Nishikawa,[†] and Hiroshi Yokoyama^{†,§}

Yokoyama Nano-structured Liquid Crystal Project, ERATO, Japan Science and Technology Agency, 5-9-9 Tokodai, Tsukuba 300-2635, Japan, Hitachi Research Laboratory, Hitachi, Ltd., 7-1-1 Omika, Hitachi 319-1292, Japan, and Nanotechnology Research Institute, National Institute of Advanced Industrial Science and Technology, 1-1-4 Umezono, Tsukuba 305-8568, Japan

Received: March 17, 2004; In Final Form: May 6, 2004

The micro-segregation picture of a block copolymer was applied to a low molecular weight liquid crystal (LC) to clarify the similarities between them with respect to structured mesophase formation. Calamitic LC molecules were regarded as block compounds composed of a rigid anisometric core terminated by flexible chains. Then, the incompatibility parameter $\chi_{\text{core-chain}}$ and volume fraction f_{core} were considered analogous to χ_{AB} and f_{A} in A–B diblock copolymers. Fedors's method, which was originally used for polymers, was utilized to estimate $\chi_{\text{core-chain}}$ and f_{core} . We found good correspondence in the χ versus f phase diagram between block copolymers and block LCs.

Liquid crystal (LC) materials that form complex nano-structured mesophases (e.g., cubic phase) have attracted increasing interest recently.¹ In these nonconventional LC materials, some individual molecular characteristics (e.g., hydrogen-bonding, lateral dipole interactions) have been pointed out for the origin of such complex mesophase formations.^{2,3} In addition, nanoscale segregation of incompatible molecular parts are considered to play an important role in their self-assembly.^{4,5}

Calamitic LC molecules can be regarded as block compounds composed of a rigid anisometric (mesogenic) core terminated by flexible chains. Polyphilic block molecules¹ consisting of a chemically incompatible core and chains, e.g., a hydrocarbon mesogenic core with oligo(ethylene oxide) chains,⁶ siloxane chains,⁵ or perfluoroalkyl chains³ etc., have been found to form not only smectic but also columnar, cubic, and other three-dimensionally structured mesophases. Such structured mesophases are popularly found in a block copolymer system, since even minor chemical differences are sufficient for such mesophase formation in large polymer molecules.¹ More precisely the parameters which govern these mesophase formations for A–B diblock copolymers are the total degree of polymerization $N = N_{\text{A}} + N_{\text{B}}$, the Flory–Huggins parameter χ_{AB} , and the volume fraction of the components f_{A} . The Flory–Huggins parameter χ_{AB} is a measure of the incompatibility between components A and B, and an order–disorder transition (e.g., formation of lamellar phase) occurs when $\chi_{\text{AB}}N$ exceeds a critical value (~ 10 at $f = 0.5$).^{7,4} Hence, low molecular weight LC molecules must possess a strong incompatibility between their different parts to form highly structured mesophases.¹ As the volume fraction f governs the interfacial curvature of the micro-segregated system, the phase diagram of the diblock copolymer can be represented in an f versus χN diagram.⁷

In this study, we try to adapt the f – χN diagram approach to a structured mesophase forming a LC molecule to clarify

the similarities to the copolymer. The Flory–Huggins parameter χ_{AB} can be estimated according to the following equation:

$$\chi_{\text{AB}} = V_{\text{R}}(\delta_{\text{A}} - \delta_{\text{B}})^2/RT \quad (1)$$

where δ_{A} and δ_{B} represent the Hildebrand solubility parameter and V_{R} is a reference volume.¹ The solubility parameter δ is defined as the square root of the cohesive energy density and can be written as follows:

$$\delta = (\Delta E/V)^{1/2} \quad (2)$$

where ΔE is the vaporization energy and V is the molar volume. ΔE and V can be estimated by the following simple additive assumption according to Fedors's method⁸

$$\Delta E = \sum \Delta e_i, \quad V = \sum v_i \quad (3)$$

Here Δe_i and v_i are the additive atomic and group contributions for the vaporization energy and molar volume, respectively. Fedors's method was originally used for solubility problems of polymers in organic solvents.⁸ It has also been successfully applied to low molecular weight LC systems by Araya and Iwasaki⁹ assuming δ from eq 2 can be applied to LC phases as well as an isotropic liquid.

In the case of diblock copolymers, χ_{AB} can be estimated from eq 1 using the solubility parameters of each segment, δ_{A} and δ_{B} , which can separately be estimated by Fedors's method. We extend this to a low molecular weight calamitic LC molecule. In this case, we assume the LC molecule is composed of two segments, i.e., a rigid core and flexible chains, and we estimate $\chi_{\text{core-chain}}$ from

$$\chi_{\text{core-chain}} = V_{\text{R}}(\delta_{\text{core}} - \delta_{\text{chain}})^2/RT \quad (4)$$

where we consider V_{R} and T in eq 4 as the total volume $V_{\text{core}} + V_{\text{chain}}$ and melting temperature of the LC compound, respectively. In contrast to the block copolymer, there is no unique definition to distinguish the core and chains in the LC molecule.

* To whom correspondence should be addressed.

† Japan Science and Technology Agency.

‡ Hitachi, Ltd.

§ National Institute of Advanced Industrial Science and Technology.

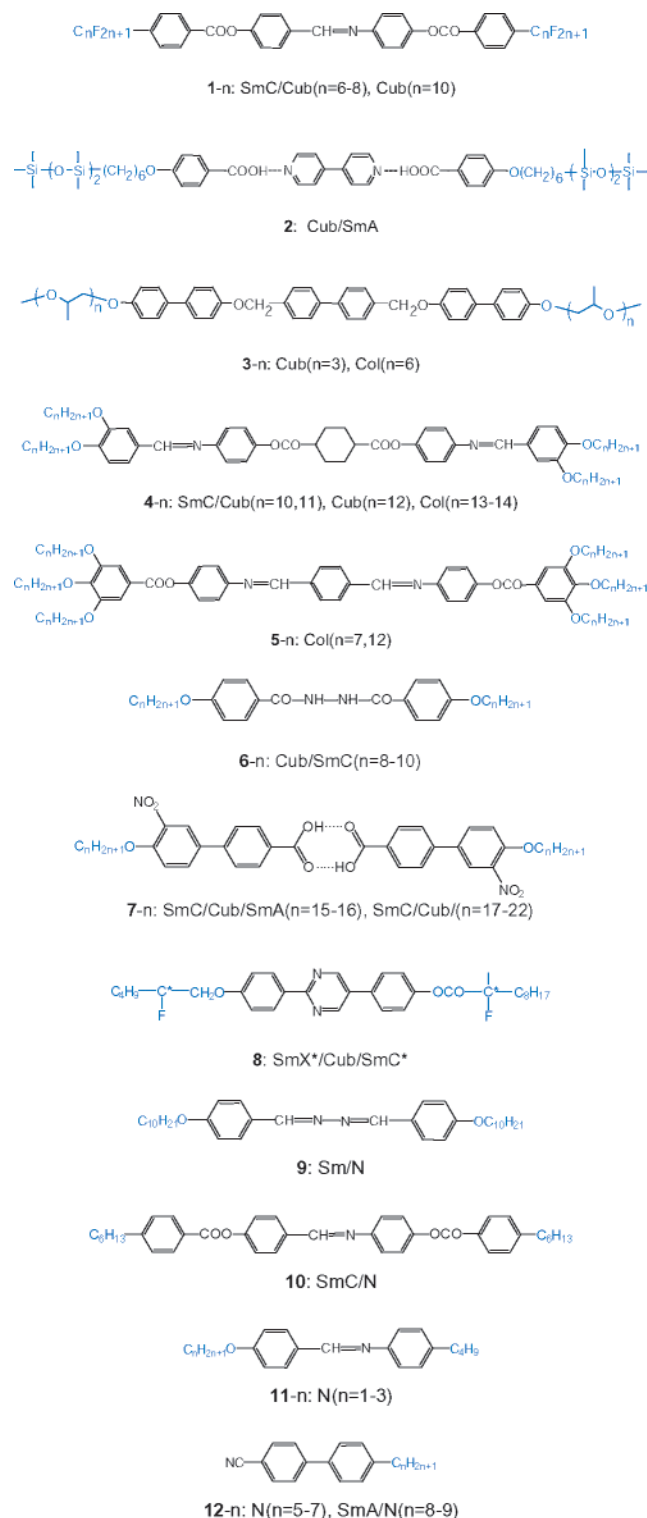


Figure 1. Various LC compounds: polyphilic molecules with perfluoroalkyl,³ siloxane,⁵ oligo(ethylene oxide)⁶ chains, and tetra- and hexa-catenar molecules;¹⁷ classic cubic compounds ANBC,¹⁸ BABH,¹¹ and rather new dichiral molecules.¹² In each molecule, the blue colored parts were assigned to the chain parts.

However, in most LC compounds that appear later in this article, assignment of the core and chains is rather straightforward.

Figure 1 show various LC compounds that we have evaluated $\chi_{\text{core-chain}}$ and f_{core} for.

These LC compounds can be grouped as follows: **1–5**, examples of polyphilic block LCs¹; **6–8**, cubic phase forming LCs (classical and rather new dichiral ones); **9–12**, conventional nematic and/or smectic LCs. In all these LC compounds, the

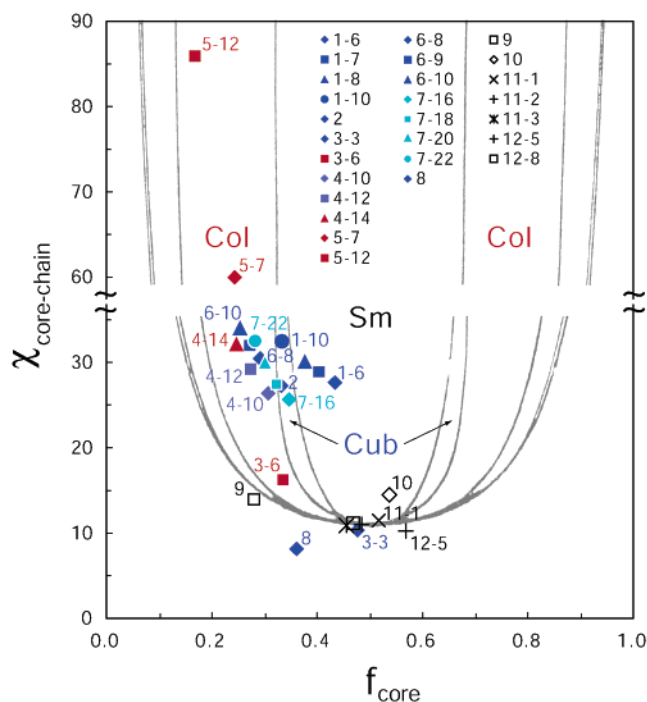


Figure 2. f_{core} versus $\chi_{\text{core-chain}}$ plot for calamitic LCs. Colors are used for the identification of the phase type (blue for cubic and red for columnar). Theoretical phase boundaries for the diblock copolymer⁷ are traced in the background.

rigid core part was defined between the phenyl rings at each side (see Figure 1), except for compound **12** in which the cyano-terminal group is considered to be a part of the core. Some compounds are considered to form a complex (**2**) or dimer (**7**) and $\chi_{\text{core-chain}}$ values were evaluated for those forms.

Calculated f_{core} and $\chi_{\text{core-chain}}$ values for these LC compounds are plotted in Figure 2 as the $f - \chi$ diagram.

When we compare this to the $f - \chi$ diagram for poly-(isoprene- β -styrene) diblock copolymers,¹⁰ the fit to the corresponding theoretical phase diagram⁷ is as good as the latter one. $\chi_{\text{core-chain}}$ values for LC compounds which show cubic and/or columnar phases (**1–8**) are larger (with exceptions **3** and **8**) than those of the compounds without such phases (**9–12**). We found that not only rather nonconventional polyphilic LCs, e.g., **1** and **2**, but also classical cubic LCs such as **6** and **7** show high $\chi_{\text{core-chain}}$ values over 20. The large $\chi_{\text{core-chain}}$ value gap is especially clear when we compare the cubic phase forming perfluoroalkyl terminated compound **1–6** and the corresponding alkyl terminated one, **10**.³ Similar contrast can be found between compounds **6–10** and the comparable compound **9** which has the group $-\text{CH}=\text{N}-\text{N}=\text{CH}-$ instead of the highly polar $-\text{CO}-\text{NH}-\text{NH}-\text{CO}-$ in **6**.¹¹

In this context, compounds **3** and **8** are exceptional among the other cubic LCs as these have rather low $\chi_{\text{core-chain}}$. For compound **3** with oligo(ethylene oxide) chains, the evaluations seems to be underestimated and shows its one aspect of limitation. Since the oligo(ethylene oxide) chains in **3** are highly flexible compare to its aromatic core, and this rigid-flexible incompatibility would be another contribution to phase segregation though the interaction parameter of the segments are rather similar. Therefore, we should take into account this rigid-flexible incompatibility contribution for better estimation. Related to this flexibility of the oligo(ethylene oxide) chains, the importance of the ether linkage $-\text{O}-$ between the core and chain part (which exists in the most of the complex mesophase forming molecules in Figure 1) could be pointed out. This

flexible ether linkage would contribute to enhance the rigid-flexible contrast between the core and chains as their "interface".

For compound **8**, if we include the $-\text{OCO}-$ and $-\text{O}-$ group that is attached to the both ends of the ring system to be a part of core, the $\chi_{\text{core-chain}}$ value increases to 14.1 (from the original value 8.12) but still lower than the values for the other cubic phase forming LCs. Hence, we think the misfit positively shows that the cubic phase formation of **8** is not the same origin (i.e., nanosegregation) as for the other LCs, but for example, chiral recognition that has been suggested.^{12,13} Careful control studies by Yoshizawa's group¹⁴ have shown how important the chirality is to the mesomorphism, in particular formation of the cubic phase. Diele¹⁵ and Fazio et al.¹⁶ also have argued importance of intermolecular association and recognition in the cubic phase formation.

Core fractions f_{core} for the compounds showing the structured LC phases are around 0.2–0.4, more precisely, $f_{\text{core}} \sim 0.2$ –0.3 for columnar phase showing compounds and $f_{\text{core}} \sim 0.3$ –0.4 for cubic phase showing compounds. Regarding the diblock copolymer $f - \chi N$ phase diagram,⁷ we note the latter ($f \sim 0.3$ –0.4) correspond to bicontinuous cubic phase. The identification between discontinuous and bicontinuous structure has not been well established in thermotropic cubic LCs.¹⁵ However, the above comparison suggests a bicontinuous structure at least for the cubic LCs in Figure 1.

In summary, we tried to adapt the $\chi - f$ diagram to structured mesophase forming LC molecules and found good correspondence between that for copolymers (although within a limited number of examples). We hope our result would be a starting point for discussion toward rational molecular design of new nano-structured LCs.

Acknowledgment. We thank Dr. Jun Yamamoto and all of the members of the Yokoyama Nano-structured Liquid Crystal Project for stimulating discussions. We are much indebted to the reviewers for their valuable comments that were reflected as some important parts of this article.

References and Notes

- (1) Tschierske, C. *J. Mater. Chem.* **2001**, *11*, 2467.
- (2) Diele, S.; Göring, P. in *Handbook of Liquid Crystals Vol.2B*; Demus, D., Goodby, J., Gray, G. W., Spiess, H. W., Vill, V., Eds.; Wiley-VCH: Weinheim, 1998; Chapter XIII, p 887.
- (3) GuilleVIC, M.-A.; Gelbrich, T.; Hursthouse, M. B.; Bruce, D. W. *Mol. Cryst. Liq. Cryst.* **2001**, *362*, 147.
- (4) Tschierske, C. *J. Mater. Chem.* **1998**, *8*, 1485.
- (5) Nishikawa, E.; Samulski, E. T. *Liq. Cryst.* **2000**, *27*, 1457.
- (6) Lee, M.; Cho, B.-K.; Yang, Y.-G.; Zin, W.-C. *J. Am. Chem. Soc.* **2000**, *122*, 7449.
- (7) Matsen, M. W.; Bates, F. S. *Macromolecules* **1996**, *29*, 1091.
- (8) Fedors, R. F. *Polym. Eng. Sci.* **1974**, *14*, 147.
- (9) Araya, K.; Iwasaki, K. *Mol. Cryst. Liq. Cryst.* **2003**, *392*, 49.
- (10) Khandpur, A. K.; Förster, S.; Bates, F. S.; Hamley, I. W.; Ryan, A. J.; Bras, W.; Almdal, K.; Mortensen, K. *Macromolecules* **1995**, *28*, 8796.
- (11) Demus, D.; Gloza, A.; Hartung, H.; Hauser, A.; Rapthel, I.; Wiegeleben, A. *Cry. Res. Technol.* **1981**, *16*, 1445.
- (12) Yoshizawa, A.; Umezawa, J.; Ise, N.; Sato, R.; Soeda, Y.; Kusumoto, T.; Sato, K.; Hiyama, T.; Takanishi, Y.; Takezoe, H. *Jpn. J. Appl. Phys.* **1998**, *37*, L942.
- (13) Takanishi, Y.; Ogasawara, T.; Yoshizawa, A.; Umezawa, J.; Kusumoto, T.; Hiyama, T.; Ishikawa, K.; Takezoe, H. *J. Mater. Chem.* **2002**, *12*, 1.
- (14) Yoshizawa, A.; Ise, N.; Kusumoto, T.; Takanishi, Y.; Takezoe, H.; Hiyama, T. *Mol. Cryst. Liq. Cryst.* **2001**, *364*, 271.
- (15) Diele, S. *Curr. Opin. Colloid Interface Sci.* **2002**, *7*, 333.
- (16) Fazio, D.; Mongin, C.; Donnio, B.; Galerne, Y.; Guillon, D.; Bruce, D. W. *J. Mater. Chem.* **2001**, *11*, 2852.
- (17) Nguyen, H.-T.; Destrade, C.; Malthête, J. *Adv. Mater.* **1997**, *9*, 375.
- (18) Gray, G. W.; Jones, B.; Narson, F. *J. Chem. Soc.* **1957**, 393.