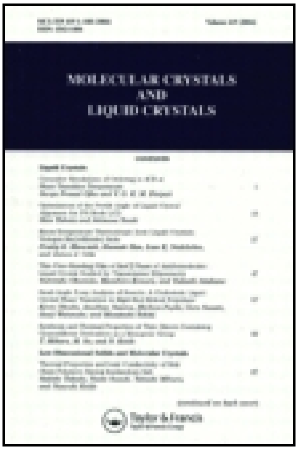


Molecular Crystals and Liquid Crystals

Phase Transition Behaviour of Amphiphilic Supermolecules Possessing a Semiperfluorinated Alkyl Chain

Akihisa Yamaguchi [a] & Atsushi Yoshizawa [a]

[a] Department of Frontier Materials Chemistry, Faculty of Science and Technology, Hirosaki University, Bunkyo-cho, Hirosaki, Japan

Version of record first published: 22 Sep 2010

To cite this article: Akihisa Yamaguchi & Atsushi Yoshizawa (2007): Phase Transition Behaviour of Amphiphilic Supermolecules Possessing a Semiperfluorinated Alkyl Chain, Molecular Crystals and Liquid Crystals, 479:1, 181/[1219]-189/[1227]

To link to this article: http://dx.doi.org/10.1080/15421400701732423

Mol. Cryst. Liq. Cryst., Vol. 479, pp. 181/[1219]–189/[1227], 2007
Copyright © Taylor & Francis Group, LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400701732423

Phase Transition Behaviour of Amphiphilic Supermolecules Possessing a Semiperfluorinated Alkyl Chain

Akihisa Yamaguchi
Atsushi Yoshizawa
Department of Frontier Materials Chemistry, Faculty of Science
and Technology, Hirosaki University, Bunkyo-cho, Hirosaki, Japan

Recently we have found that a novel amphiphilic compound, 1H, 1H, 2H, 2H-heptadecafluoro-1-decyl 3, 4, 5- tris[6-(4′-cyanobiphenyl-4-yloxy)hexyloxy]benzoate, exhibited the phase sequence of isotropic liquid -smectic A-bicontinuous cubic-crystal. In this study, we have prepared compounds possessing biphenyl groups or alkyl chains instead of the cyanobiphenyl groups of the amphiphilic compound and investigated their liquid-crystalline properties using optical microscopy and differential scanning calorimetry. The compound possessing the biphenyl groups was found to exhibit a columnar phase, however, the compound possessing the alkyl chains did not show any liquid-crystalline phase. We discuss the structure-property relationship in the amphiphilic oligomers.

Keywords: cubic phase; liquid crystals; oligomers; phase transition

1. INTRODUCTION

Supermolecular assemblies with well-defined morphologies (e.g., layers, interpenetrating networks, columns, and spheroids) are fundamental components for structure formation in biological systems, as well as for application to production of novel functional materials. For those reasons, investigation of the driving forces of this self assembly process is an important contemporary research topic [1,2].

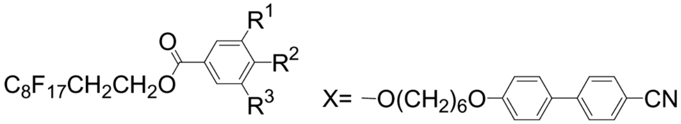
This work was partially supported by Aomori Prefecture Collaboration of Regional Entities for the Advancement of Technological Excellence, JST and A Grant for Priority Research Designated by the President of Hirosaki University.

Address correspondence to Atsushi Yoshizawa, Department of Frontier Materials Chemistry, Faculty of Science and Technology, Hirosaki University, 3, Bunkyo-cho, Hirosaki, 036-8561, Japan. E-mail: ayoshiza@cc.hirosaki-u.ac.jp

In particular, cubic liquid-crystalline phases, which represent three-dimensional ordered supermolecular arrangements such as interpenetrating networks and spheroids, have recently attracted much attention [3,4]. Cubic mesophases are common in lyotropic systems, such as surfactant-solvent systems. The mesophase morphologies of these amphiphilic systems are governed mainly by the volume fraction of the two incompatible segments combined in such molecules. The phase sequence of lamellar (smectic, SmA)-bicontinuous cubic ($\mathrm{Cub_v}$)-hexagonal columnar ($\mathrm{Col_h}$)-micellar cubic ($\mathrm{Cub_I}$), upon increasing the interface curvature between hydrophilic regions and lipophilic regions [1,5]. In contrast to lyotropic cubic systems, few thermotropic compounds with cubic phase are known. They have been found for nitro-substituted and cyano-substituted biphenyl carboxylic acids [6,7], dibenzoylhydrazides [8], polycatenar compounds [9,10], metal complexes [11], amphiphilic polyhydroxy compounds [12,13] and carbohydrate derivatives [14]. In most cases, bicontinuous cubic mesophases have been found for these cubic phases. In tetracatenar mesogens which comprise an extended, rigid core and four terminal chains, the phase sequence of SmC-$\mathrm{Cub_V}$-Col as increasing terminal chains is apparent. This phase sequence is explained in terms of the curvature in the interface between the aromatic core and the terminal chains, and the formation of aggregates of molecules [10e,11f]. In the case of polyhydroxy derivatives, the same sequence of SmA-$\mathrm{Cub_V}$-$\mathrm{Col_h}$-$\mathrm{Cub_I}$ as that reported for lyotropic systems was obtained. The mesophase morphologies are dominated by the interface curvature between hydrophilic regions and lipophilic regions [2c,d].

Pre-organization [15] or a 'bottom-up' approach, is an important concept in the design of mesogenic molecules [2a–b,16,17]. We have reported novel pre-organized systems, e.g., U-shaped molecules [18], binaphthyl derivatives [19] and λ-shaped molecules [20]; the pre-organized compounds were found to induce unusual ordering in the supramolecular liquid-crystalline phase. Therefore, the introduction of amphiphilic properties into the oligomeric molecules is expected to realize a novel type of phase transitions.

Recently, we prepared amphiphilic liquid-crystalline oligomers that comprise cyanobiphenyl mesogenic moieties and a semiperfluorinated alkyl chain (Fig. 1) [21]. The amphiphilic liquid-crystalline oligomers **1–3** were found to show a different phase sequence of SmC-Col-$\mathrm{Cub_V}$ on increasing the cyanobiphenyl mesogenic moieties; the sequence of Col-$\mathrm{Cub_V}$ is opposite that of the ordinary sequence. In this study, we have prepared the related compounds possessing biphenyl groups or alkyl chains instead of the cyanobiphenyl groups of compound **3** and investigated the structure-property relationships.



1: R^1=R^3=H, R^2=X; Iso 143 °C SmC 90 Cr mp 115
2: R^3=H, R^1=R^2=X; Iso 170 °C SmA 116 Col 12 Glassy mp 62
3: R^1=R^2=R^3=X; Iso 155 °C SmA 136 Cub 9 Glassy mp 83

FIGURE 1 Molecular structures and transition temperatures of the amphiphilic oligomers **1**–**3**.

2. EXPERIMENTAL

2.1. Preparation of Materials

The structures of the final products were elucidated using infrared (IR) spectroscopy (FTS-30; Bio-Rad Laboratories, Inc.) and proton nuclear magnetic resonance (1H NMR) spectroscopy (JNM-A400; JEOL).

2.1.1. 1H, 1H, 2H, 2H-Heptadecafluoro-1-decyl 3, 4, 5-tris[6-(biphenyl-4-yloxy)hexyloxy]benzoate, 4

4-Hydroxybiphenyl (0.68 g, 4 mmol) and 1, 6-dibromohexane (1.64 g, 6 mmol) were dissolved in cyclohexanone (4 ml). Potassium carbonate (0.83 g, 6 mmol) was added and the resulting mixture stirred at 70°C for 8 h. The reaction mixture was filtered and the solvent removed by evaporation under reduced pressure. The residue was purified using column chromatography on silica gel using a dichloromethane-hexane (1:1) mixture as the eluent. Recrystallization from hexane gave 4-(6-bromohexyloxy)biphenyl: yield: 0.84 g (63%).

4-(6-Bromohexyloxy)biphenyl (0.80 g, 2.4 mmol) and ethyl 3, 4, 5-trihydroxybenzoate (0.14 g, 0.7 mmol) were dissolved in cyclohexanone (4.5 ml). Then, K_2CO_3 (0.50 g, 3.6 mmol) and KI (0.06 g, 0.36 mmol) were added and the resulting mixture was stirred at 140°C for 25 h. The reaction mixture was filtered and the solvent removed by evaporation under reduced pressure. The residue was purified using column chromatography on silica gel using dichloromethane as the eluent and recrystallization from a hexane/chloroform roform (4/1) mixture, giving ethyl 3, 4, 5-tris[6-(biphenyl-4-yloxy)-hexyloxy]benzoate: yield: 0.42 g (63%).

Ethyl 3, 4, 5-tris[6-(biphenyl-4-yloxy)hexyloxy]benzoate (0.38 g, 0.4 mmol) obtained was refluxed in ethanol/THF (10 ml/10 ml) and KOH (0.16 g, 2.9 mmol) for 2 h. The solution was cooled to room temperature and acidified using aq. HCl. Water (20 ml) was added to the mixture and the aqueous phase was extracted with dichloromethane (2 × 20 ml). The organic extracts were combined, dried over Na_2SO_4, filtered and evaporated, giving 3, 4, 5-tris[6-(biphenyl-4-yloxy)hexyloxy]benzoic acid: yield: 0.36 g (99%).

A mixture of 3, 4, 5-tris[6-(biphenyl-4-yloxy)hexyloxy]benzoic acid (0.3 g, 0.32 mmol) and thionyl chloride (2 ml) was stirred at room temperature for 4 h. Thionyl chloride was then removed by evaporation under reduced pressure, leaving an off-white solid. The product was dissolved 1, 4-dioxane (2 ml). DMAP (0.06 g, 0.5 mmol) and 1H, 1H, 2H, 2H-heptadecafluoro-1-decanol dissolved in 1, 4-dioxane (3 ml) were added and the resulting mixture was stirred at 80°C for 4 h. The reaction mixture was filtered and the solvent removed by evaporation under reduced pressure. The residue was purified using column chromatography on silica gel using a dichloromethane-hexane (4:1) mixture as the eluent and reprecipitated with chloroform/methanol (1/10), giving the desired product: yield: 0.30 g (69%). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.55$–7.45 (m, 15H, Ar-H), 7.40–7.36 (m, 6H, Ar-H), 7.27 (s, 2H, Ar-H), 6.95–6.91 (m, 6H, Ar-H), 4.58 (t, J = 6.4 Hz, Hz, 2H, CH_2OCO), 4.05–3.93 (m, 12H, OCH_2), 2.65–2.51 (m, 2H, CF_2CH_2), 1.87–1.74 (m, 12H, CH_2), 1.56–1.50 (m, 12H, CH_2); IR (KBr): 2942, 2867, 1718, 1600, 1250, 1211, 819 cm^{-1}.

2.1.2. 1H, 1H, 2H, 2H-Heptadecafluoro-1-decyl 3, 4, 5- tridodecyloxybenzoate, 5

1-Bromododecane (1.5 g, 6 mmol) and ethyl 3, 4, 5-trihydroxybenzoate (0.4 g, 2 mmol) were dissolved in cyclohexanone (15 ml). Then, K_2CO_3 (0.83 g, 6 mmol) and KI (0.1 g, 0.6 mmol) were added and the resulting mixture was stirred at 140°C for 7 h. The reaction mixture was filtered and the solvent removed by evaporation under reduced pressure. The residue was purified using column chromatography on silica gel using a toluene-ethyl acetate (29:1) mixture as the eluent, giving ethyl 3, 4, 5-tridodecyloxybenzoate: yield: 0.57 g (41%).

Ethyl 3, 4, 5-tridodecyloxybenzoate (0.5 g, 0.7 mmol) was refluxed in ethanol (95%, 15 ml) and KOH (0.16 g, 2.9 mmol) for 2 h. The solution was cooled to room temperature and acidified using aq. HCl. Water (20 ml) was added to the mixture and the aqueous phase was extracted with dichloromethane (3 × 20 ml). The organic extracts were combined, dried over Na_2SO_4, filtered and evaporated. Recrystallization from ethanol gave 3, 4, 5-tridodecyloxybenzoic acid: yield: 0.46 g (96%).

A mixture of 3, 4, 5-tridodecyloxybenzoic acid (0.2 g, 0.3 mmol) and thionyl chloride (2.5 ml) was stirred at room temperature for 4 h.

Thionyl chloride was then removed by evaporation under reduced pressure, leaving an off-white solid. The product was dissolved 1, 4-dioxane (2 ml). DMAP (0.06 g, 0.5 mmol) and 1H, 1H, 2H, 2H-heptadecafluoro-1-decanol dissolved in 1, 4-dioxane (3 ml) were added and the resulting mixture was stirred at 80°C for 5 h. The reaction mixture was filtered and the solvent removed by evaporation under reduced pressure. The residue was purified using column chromatography on silica gel using a dichloromethane-hexane (2:3) mixture as the eluent and recrystallized from ethanol, giving the desired product: yield: 0.2 g (60%). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.27$ (s, 2H, Ar-H), 4.58 (t, $J = 6.4$ Hz, 2H, CH_2OCO), 4.03–3.93 (m, 6H, OCH_2), 2.65–2.51 (m, 2H, CF_2CH_2), 1.87–1.30 (m, 60H, CH_2), 0.96 (t, 9H, CH_3); IR (KBr): 2942, 2862, 1721, 1604, 1248, 1211, 822 cm^{-1}.

2.2. Liquid-Crystalline and Physical Properties

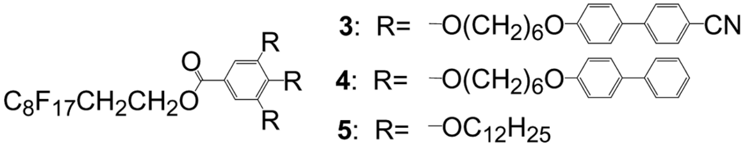
The initial phase assignments and corresponding transition temperatures for the final products were determined by optical polarized light microscopy using a polarizing microscope (Optiphot-pol; Nikon Corp.) equipped with a hot stage and FP80 control processor (FP82; Mettler Inst. Corp.). Temperatures and enthalpies of transition were investigated using differential scanning calorimetry (DSC) with a calorimeter (DSC6200; Seiko Instruments Inc.). The materials were studied at a scanning rate of 5°C min^{-1} after being encapsulated in aluminum pans.

3. RESULTS AND DISCUSSION

Transition temperatures and transition enthalpies of novel compounds **4** and **5** determined by optical microscopy and differential scanning calorimetry (DSC) are listed in Table 1. Those of compound **3** are also shown in Table 1 [21].

Compound **3** possessing three cyanobiphenyl mesogenic moieties showed the phase sequence of Iso-SmA-Cub_V-Cr [21]. However, compound **4** possessing biphenyl groups instead of three cyanobiphenyl groups of compound **3** showed the phase sequence of Iso-Col-X, but not the SmA and Cub_V phases. Figure 2 shows the optical textures of the Col and X phases. In the Col phase, a spherulitic texture typical for a hexagonal columnar phase was observed (Fig. 2a). In the X phase, a mosaic texture was observed (Fig. 2b). A large enthalpy change (23.8 $kJmol^{-1}$) of the Col to X transition suggests that the X phase has a highly ordered three dimensional structure. X-ray measurements are necessary to clear phase structures of Col and X phases.

TABLE 1 Transition Temperatures (°C) and Transition Enthalpies (kJ mol^{-1}) (in Square Brackets) of Compounds **3–5**



Compound	Transition temperatures (°C) [ΔH/kJmol^{-1}]	
3	Iso 155.0 [5.4] SmA 135.9 [3.5] Cub$_V$ 9.3 G	mp 83.2
4[a]	Iso 87.9 [2.7] Col 73.3 [23.8] X[b]	mp 104.7
5	Iso 20.1 [50.4] Cr	mp 39.0

[a] Recrystallization was not observed on cooling to −30°C by differential scanning calorimetry at a scanning rate of 5°C min^{-1}. [b] X: an unidentified higher ordered phase.

Appearance of the columnar phase of compound **4** can be explained in terms of the interface curvature between the mesogenic groups and the semiperfluorinated alkyl chain. Furthermore, compound **5** possessing only the alkyl chains without rigid biphenyl cores showed no mesogenic properties.

Let us discuss structural effects of the amphiphilic oligomers on appearance of the Cub$_V$ phase. Replacing the cyanobiphenyl groups of compound **3** by the biphenyl groups or the alkyl chains was found to vanish the SmA and Cub$_V$ phases, suggesting the cyanobiphenyl groups of compound **3** play an important role in the appearance of the SmA and Cub$_V$ phases. In our previous study, results of the XRD study suggested that the SmA phase of compound **3** has a fluctuated layer structure [21]. The competition of the steric effect attributable

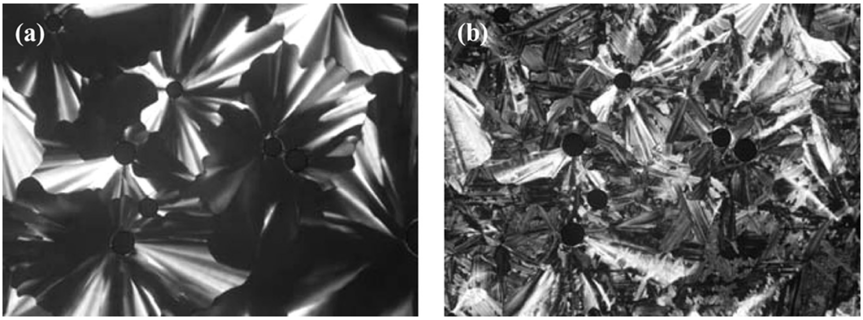


FIGURE 2 Optical textures of a) the Col phase at 86.2°C and b) the X phase at 72.2°C for compound **4**.

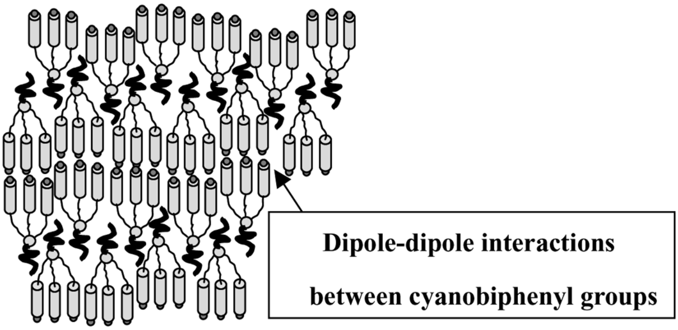


FIGURE 3 Molecular arrangements suggested for compound **3** in the SmA phase.

to the pronounced taper shape and the segregation effect attributable to the incompatibility between the fluorinated alkyl chains and the cyanobiphenyl groups of compound **3** might give rise to that fluctuation. Figure 3 shows possible molecular arrangements for the SmA phase of compound **3**. A typical nematogen, 4′-hexyloxybiphenyl-4-carbonitrile (**6OCB**) is known to dimerize by antiparallel cyano-cyano dipole interactions in the nematic phase. Furthermore, numerous examples of the same phenomena are observed in cyanobiphenyl SmA materials [22,23]. In the fluctuated layer structure, partial intercalation and strong antiparallel dipole-dipole interactions between the cyanobiphenyl groups of adjacent layers are considered to exist and stabilize the fluctuated layer structure. Furthermore, the fluctuations in the SmA phase might engender the formation of the $\mathrm{Cub_V}$ phase. Therefore, compound **4** without strong dipole moments of the cyano groups could show no SmA and $\mathrm{Cub_V}$ phases.

On the other hand, an undulatory deformation mode for a nonequilibrium lamellar structure is known to exist as the unstable transient state between the lamellar and the Cub (Gyroid with a space group *Ia3d*) phases in some diblock copolymers [24]. Recently, fluctuations of lamellar structure prior to a lamellar to gyroid transition in a nonionic surfactant system were observed [25]. In compound **3**, however, the fluctuated lamellar structure in the SmA phase is thought to be stabilized by competition and cooperation of the steric effect attributable to the pronounced taper shape, the segregation effect attributable to the incompatibility between the fluorinated alkyl chains and the cyanobiphenyl groups, and the dimerization effect attributable to strong dipole-dipole interactions between the cyanobiphenyl groups, which can produce the $\mathrm{Cub_V}$ phase.

4. CONCLUSION

In summary, the structural modifications of amphiphilic liquid-crystalline oligomer **3** were performed, and the structure-property relationships indicate that: 1) formation of the columnar phases is dominated by the interface curvature between the mesogenic groups and the semiperfluorinated alkyl chain, and 2) strong dipole-dipole interactions between the cyanobiphenyl groups stabilize the fluctuation of the layer structure in the SmA, which can produce the $\mathrm{Cub_V}$ phase.

REFERENCES

[1] Seddon, J. M. & Templer, R. H. (1995). Structure and dynamics of membrane. In: *Handbook of Biological Physics*, Lipowsky, R. & Sackmann, E. (Eds.), Elsevier: Amsterdam, Vol. 1, 97–160.

[2] a) Goodby, J. W., Mehl, G. H., Saez, I. M., Tuffin, R. P., Machenzie, G., Auzely-Velty, R., Benvegnu, T., & Plusquellec, D. (1995). *Chem. Commun.*, 2057; b) Saez, I. & Goodby, J. W. (2005). *J. Mater. Chem.*, *15*, 26; c) Tschierske, C. (2001). *J. Mater. Chem.*, *11*, 2647; d) Tschierske, C. (1998). *J. Mater. Chem.*, *8*, 1485; e) Kato, T. (2002). *Science*, *295*, 2414; f) Kato, T., Mizoshita, N., & Kishimoto, K. (2006). *Angew. Chem. Int. Ed.*, *45*, 38.

[3] Diele, S. & Göring, P. (1998). Low molecular weight liquid crystals II. In: *Handbook of liquid Crystals*, Demus, D., Goodby, J. W., Gray, G. W., Spiess, H.-W., & Vill, V. (Eds.), Wiley-VCH: Weinheim, Vol. 2B, 887–900.

[4] Mariani, P., Vuzzati, V., & Delacroix, H. (1998). *J. Mol. Biol.*, *204*, 165.

[5] Gulic, A., Delacroix, H., Kirschner, G., & Juzzati, V. (1995). *J. Phys. II Fr.*, *5*, 445.

[6] a) Gray, G. W., Jones, B., & Marson, F. (1957). *J. Chem. Soc.*, 393; b) Demus, D., Kunicke, G., Neelsen, J., & Sackmann, H. (1968). *Z. Naturforsch., Teil A.*, *23*, 84; c) Diele, S., Brandt, P., & Sackmann, H. (1992). *Mol. Cryst. Liq. Cryst.*, *17*, 163; d) Kutsumizu, S., Yamada, M., & Yano, S. (1994). *Liq. Cryst.*, *16*, 1109.

[7] a) Etherington, G., Leadbetter, A. J., Wang, X. J., Gray, G. W., & Tajbakhsh, T. (1986). *Liq. Cryst.*, *1*, 209; b) Yano, S., Mori, Y., & Kutsumizu, S. (1991). *Liq. Cryst.*, *9*, 907.

[8] a) Schubert, H., Hausschild, J., Demus, D., & Hoffmann, S. (1978). *Z. Chem.*, *18*, 256; b) Demus, D., Gloza, A., Hartun, H., Rapthel, I., & Wiegeleben, A. (1981). *Cryst. Res. Technol.*, *16*, 1445.

[9] Nguyen, H.-T., Destrade, C., & Malthete, J. (1997). *Adv. Mater.*, *9*, 375.

[10] a) Fang, Y., Levelut, A. M., & Destrade, C. (1990). *Liq. Cryst.*, *7*, 265; b) Levelut, A. M. & Fang, Y. (1990). *Colloq. Phys.*, *C7*, 299; c) Malthete, J., Nguyen, H. T., & Destrade, C. (1993). *Liq. Cryst.*, *13*, 17; d) Nguyen, H. T., Destrade, C., & Malthete, J. (1990). *Liq. Cryst.*, *8*, 797; e) Rowe, K. E. & Bruce, D. W. (1998). *J. Mater. Chem.*, *8*, 331.

[11] a) Bruce, D. W., Dunmur, D. A., Hudson, S. A., Lalinde, E., Maitlis, P. M., McDonald, M. P., Orr, R., Styring, P., Cherodian, A. S., Richardson, R. M., Feijoo, J. L., & Ungar, G. (1991). *Mol. Cryst. Liq. Cryst.*, *206*, 79; b) Bruce, D. W., Davis, S. C., Dunmur, D. A., Hudson, S. A., Maitlis, P. M., & Styring, P. (1992). *Mol. Cryst. Liq. Cryst.*, *215*, 1; c) Bruce, D. W. & Hudson, S. A. (1994). *J. Mater. Chem.*, *4*, 479; d) Bruce, D. W., Donnino, B., Guillon, D., Heinrich, B., & Ibn-Elhj, M. (1995). *Liq. Cryst.*, *19*, 537; e) Bruce, D. W., Donnino, B., Hudson, S. A., Levelut, A. M., Megtert, S., Petermann, D., & Veber, M. (1995). *J. Phys. ii (Fr.)*, *5*, 289; f) Fazio, D.,

Mongin, C., Donnino, B., Galerne, Y., Guillon, D., & Bruce, D. W. (2001). *J. Mater. Chem.*, *11*, 2852.

[12] Tschierske, C. (1991). *Prog. Polym. Sci.*, *21*, 775.

[13] a) Borisch, K., Diele, S., Göring, P., & Tschierske, C. (1996). *Chem. Commun.*, 237; b) Borisch, K., Diele, S., Göring, P., Müller, H., & Tschierske, C. (1997). *Liq. Cryst.*, *22*, 427; c) Borisch, K., Diele, S., Göring, P., Kresse, H., & Tschierske, C. (1998). *J. Mater. Chem.*, *8*, 529.

[14] a) Borisch, K., Tschierske, C., Göring, P., & Diele, S. (1998). *Chem. Commun.*, 2711; b) Borisch, K., Tschierske, C., Göring, P., & Diele, S. (2000). *Langmuir.*, *16*, 6701.

[15] Lehn, J. M. (1995). *In Supramolecular Chemistry: Concepts and Perspectives*, VCH: Weinheim.

[16] Nishiyama, I., Yamamoto, J., Goodby, J. W., & Yokoyama, H. (2005). *Mol. Cryst. Liq. Cryst.*, *439*, 22.

[17] Yoshizawa, A., Segawa, S., & Ogasawara, F. (2005). *Chem. Mater.*, *17*, 6442.

[18] Yoshizawa, A. & Yamaguchi, A. (2002). *Chem. Commun.*, 2060.

[19] a) Rokunohe, J. & Yoshizawa, A. (2005). *J. Mater. Chem.*, *15*, 280; b) Rokunohe, J., Yamaguchi, A., & Yoshizawa, A. (2005). *Liq. Cryst.*, *32*, 207.

[20] Yamaguchi, A., Nishiyama, I., Yamamoto, J., Yokoyama, H., & Yoshizawa, A. (2005). *J. Mater. Chem.*, *15*, 280.

[21] Yamaguchi, A., Maeda, Y., Yokoyama, H., & Yoshizawa, A. (2006). *Chem. Mater.*, *18*, 5704.

[22] Gray, G. W. & Goodby, J. W. (1984). *in Smectic Liquid Crystals: Textures and Structures*, Leonard Hill: Glasgow and London.

[23] a) Leadbetter, A. J., Temme, F. P., Heidemann, A., & Howells, W. S. (1975). *Chem. Phys. Lett.*, *34*, 363; b) Leadbetter, A. J., Durrant, J. L. A., & Rugman, M. (1977). *Mol. Cryst. Liq. Cryst. Lett.*, *34*, 231; c) Leadbetter, A. J., Frost, J. C., Gaughan, J. P., Gray, G. W., & Moslely, A. (1979). *J. Phys.*, (Paris) *40*, 375; d) Bonsor, D. H., Leadbetter, A. J., & Temme, F. P. (1978). *Mol. Phys.*, *36*, 1805.

[24] a) Hjduk, D. A., Takenouchi, H., Hillmyer, M. A., & Bates, F. S. (1997). *Macromolecules*, *30*, 3788; b) Hajduk, D. A., Ho, R.-M., Hillmyer, M. A., & Bates, F. S. (1998). *J. Phys. Chem. B.*, *102*, 1356; c) Qi, S. & Wang, Z.-G. (1997). *Phys. Rev. E.*, *55*, 1682; d) Laradji, M., Shi, A.-C., Desai, R. C., & Noolandi, J. (1997). *Phys. Rev. Lett.*, *78*, 2577; e) Laradji, M., Shi, A.-C., Noolandi, J., & Desai, R. C. (1997). *Macromolecules*, *130*, 3242.

[25] Imai, M., kawaguchi, A., Saeki, A., Nakaya, K., Kato, T., Ito, K., & Amemiya, Y. (2000). *Phys. Rev. E*, *62*, 6865.