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Liquid Crystals

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To cite this Article Okamoto, Kazuo , Kawamura, Takumi , Sone, Masato and Ogino, Kenji(2007) 'Study on liquid crystallinity in 2,9-dialkylpentacenes', Liquid Crystals, 34: 9, 1001 — 1007
To link to this Article: DOI: 10.1080/02678290701478970
URL: http://dx.doi.org/10.1080/02678290701478970

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Liquid Crystals, Vol. 34, No. 9, September 2007, 1001–1007

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Study on liquid crystallinity in 2,9-dialkylpentacenes

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(*Received 30 October 2006; accepted in revised form 26 April 2007*)

A series of semiconducting and symmetrical 2,9-dialkylpentacenes was successfully synthesized via a five-step process and their structures confirmed by ^{1}H NMR, IR and elemental analyses. Their liquid crystallinity was investigated by differential scanning calorimetry and polarizing optical microscopy. The introduction of alkyl chains also improved their solubility. For alkyl chains longer than butyl, focal conic or baton texture was observed, indicating the existence of an ordered smectic phase. Thermal analyses revealed that the both melting and smectic–isotropic transition temperatures show an odd–even effect when the alkyl chain is larger than heptyl or octyl. The synthesized compounds are promising candidates for semiconductors in organic field-effect transistors because their liquid crystallinity allows easy molecular alignment in the device fabrication process.

1. Introduction

Organic electronics have attracted much attention because of their easier fabrication processes compared with silicon technologies, which require high-temperature and high-vacuum deposition processes. The organic thin field-effect transistor (OTFT) is one of the most attractive applications in organic electronics [1–2]. Although many kinds of linear acenes have been used as organic semiconductors in OTFTs, pentacene is the most popular and promising material among them since it offers high performance, e.g. higher mobility and better on–off ratio (similar to that of amorphous silicon TFTs), superior environmental stability and improved reliability [3]. However, non-substituted pentacene has a drawback for the application of solution processes, since it is essentially insoluble in organic solvents at room temperature. It is expected that the introduction of alkyl chains to a pentacene ring will lead to increased solubility in organic solvents, and that they are applicable to solution processes, including spin coating, spray coating, screen printing or ink-jet printing [4–5].

It is well known that molecular packing in a thin film of pentacene also plays an important role for high performance. Generally, molecular ordering is disturbed by the introduction of substituents, leading to poor performance. Precise molecular design, however, enables the appropriately ordered molecular packing for higher mobility and performance in OTFTs [6, 7]. Introduction of an alkyl chain also makes it possible to afford liquid crystallinity resulting in regular molecular packing, since many compounds showing liquid crystallinity contain a rigid core substituted with flexible alkyl chains. The self-assembly properties of liquid crystalline compounds provide a potential for high-performance OTFTs in solution processes. Indeed, substituted hexabenzocoronenes (HBCs), which can be processed from solution to form films with supermolecularly ordered columnar stacks lying parallel to the substrate, have been applied to OTFT devices [8]. Apart from OTFT applications, calamitic [9, 10] or discotic [11–13] liquid crystals exhibit higher hole and electron mobilities compared with the amorphous state. Their excellent carrier transport ability, which depends on neither temperature nor electric field, is attractive for device applications.

In this paper we report the synthesis of a series of dialkyl-substituted pentacenes and an investigation of their liquid crystallinity. The chemical structure of the synthesized pentacenes is shown in figure 1. Alkyl substituents at the 2 and 9 positions cause less disturbance to the packing of the pentacene cores, compared with those at other positions. As far as we know, this is the first report concerning the liquid crystallinity of pentacene derivatives. Since the regular packing or orientation of liquid crystalline materials has been controlled by easy processes, e.g. rubbing treatments, oblique evaporation of silicone oxide and polarized radiation [14–17], processability for the fabrication of OTFTs is expected to be much improved.

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Liquid Crystals
ISSN 0267-8292 print/ISSN 1366-5855 online © 2007 Taylor & Francis
http://www.tandf.co.uk/journals
DOI: 10.1080/02678290701478970

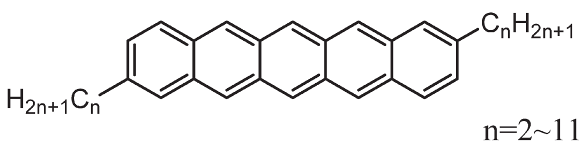

Figure 1. Chemical structure of 2,9-dialkylpentacenes.

2. Experimental

2,9-Dialkylpentacenes were synthesised using the method described by Vogel *et al.* [18]. The synthetic route is shown in figure 2.

Commercially available reagents were used without further purification, unless otherwise noted. All intermediates and products were characterized using FT-IR spectroscopy (JASCO, FT/IR-460 Plus with samples in KBr pellet form), ^{1}H NMR spectroscopy (Varian, Marcury Plus 400MHz) and/or elemental analysis (J-SCIENCE LAB, JM10). The purities of intermediates were checked using reversed-phase HPLC with a UV detector operated at 254 nm [column, Inertsil ODS-3V (40°C); eluent, acetonitrile/THF/acetic acid = 85/15/1].

The synthesis of 2,9-dinonylpentacene is described in detail below. The other 2,9-disubstituted pentacenes were synthesised by utilizing the corresponding alkylbenzenes as starting materials.

2.1. *Synthesis of 2,5-bis(4-nonylbenzoyl)terephthalic acid*

A solution of nonylbenzene (50.0 g, 0.25 mol) (bought from Acros Organics) and pyridine (19.4 g, 0.25 mol) in 84 ml of dry 1,2-dichloroethane was added to a mixture of aluminium chloride (34.3 g, 0.26 mol) and pyromellitic dianhydride (26.7 g, 0.12 mol) in 133 ml of 1,2-dichloroethane under a nitrogen atmosphere, keeping the temperature between −15 and 0°C during the addition. The reaction mixture was stirred overnight at room temperature. Then another 34.3 g (0.26 mol) of aluminium chloride was added to the mixture. After stirring for 6 h at 40°C, the mixture was poured into a mixture of ice (534 g) and concentrated hydrochloric acid (200 ml) and stirred for 1 h at room temperature. After the addition of ethyl acetate (534 ml) and THF (534 ml), the organic layer was separated and was washed twice using 1300 ml of water. The organic layer was dried over $MgSO_4$, and filtered. After the evaporation of the solvents, the crude yellow product was purified by washing twice with 147 ml of ethyl acetate, and dried to give a of white powder. Yield 25.7 g (34%) (purity, 99% with HPLC). FT-IR (KBr, cm^{-1}): 3423, 2955, 2924, 2853, 2675, 2559, 1693, 1670, 1607, 1493, 1416, 1313, 1281, 1254, 955, 916, 800. ^{1}H NMR (400 MHz, DMSO, δ ppm): 0.84 (t, 6H), 1.20–1.30 (m, 24H), 1.58 (m, 4H), 2.64 (t, 4H), 7.34 (d, 4H), 7.64 (d, 4H), 7.87 (s, 2H).

2.2. *Synthesis of 2,5-bis(4-nonylbenzyl)terephthalic acid*

A mixture of 2,5-bis(4-nonylbenzoyl)terephthalic acid (25.0 g, 0.040 mol) and 2.2 g of 5% palladium carbon (NX type) (bought from N.E. Chemcat Corporation) in 500 ml of THF was heated at 60°C for 24 h under an atmosphere of hydrogen at 0.3 MPa. After the reaction, the mixture was filtered through a Celite® filter to remove the catalyst. The filtrate was concentrated in vacuo, and the crude product was purified by washing with 500 ml of hexane, and dried to give a white powder. Yield 13.4 g (56%) (purity, 95% with HPLC). FT-IR (KBr, cm^{-1}): 3431, 2957, 2922, 2851, 2646, 2534, 1697, 1680, 1609, 1512, 1499, 1456, 1437, 1410, 1281, 935, 770. ^{1}H NMR (400 MHz, DMSO-d6, δ ppm): 0.82 (t, 6H), 1.20–1.23 (m, 24H), 1.49 (m, 4H), 2.49 (t, 4H), 4.25 (s, 4H), 7.03 (m, 8H), 7.62 (s, 2H).

2.3. *Synthesis of 3,10-dinonyl-7,14-dihydropentacene-5,12-dione*

A mixture of 2,5-bis(4-nonylbenzyl)terephthalic acid (10.0 g, 0.017 mol) and trifluoromethanesulfonic acid (50 ml) was stirred under a nitrogen atmosphere overnight at room temperature. The mixture was poured into the mixture of 400 g of ice and 400 g of water. The precipitate was collected by filtration and washed with 400 ml of 5% aqueous sodium carbonate and then twice

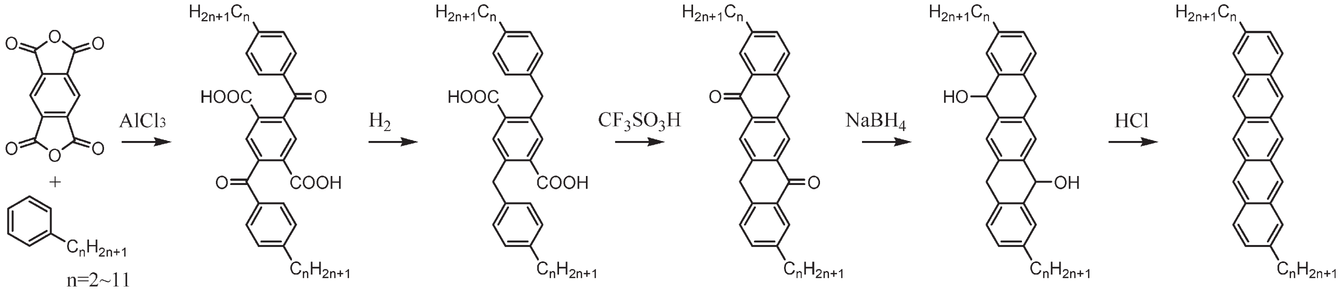

Figure 2. Synthetic scheme for 2,9-dialkylpentacenes.

with 800 ml of water. The precipitate was dried to give a dark brown powder. Yield: 7.3 g (78%). FT-IR (KBr, cm^{-1}): 3045, 2957, 2926, 2851, 1649, 1612, 1501, 1466, 1393, 1344, 1302, 1271, 1168, 941, 752. Due to insolubility in appropriate organic solvents, no NMR and HPLC purity data were obtained.

2.4. *Synthesis of 2,9-dinonylpentacene*

A mixture of 3,10-dinonyl-7,14-dihydropentacene-5,12-dione (7.00 g, 0.012 mol) and sodium borohydride (3.76 g, 0.099 mol) in 60 ml of bis(2-methoxyethyl) ether was heated at 40°C for 12 h under a nitrogen atmosphere. After the addition of isopropanol (42 ml), the mixture was heated at 40°C for 6 h. The mixture was then cooled to room temperature and 105 ml of acetic acid was added dropwise. The mixture was kept at 60°C for 2 h. After the addition of 35 ml of concentrated hydrochloric acid, the mixture was heated at 60°C for 2 h, then cooled to room temperature and filtered. The precipitate was washed successively with 175 ml of hot water, 175 ml of acetone, 21 ml of tetrahydrofuran and 175 ml of acetone. The precipitate was dried to give a dark blue powder. Yield: 3.45 g (52%). FT-IR (KBr, cm^{-1}): 2956, 2921, 2851, 1672, 1619, 1463, 1299, 910. ^1H NMR (400 MHz, 100°C, 1,1,2,2-tetrachloroethane-d2, δ ppm): 0.93 (t, 6H), 1.2–1.5 (m, 24H), 1.82 (quint, 4H), 2.83 (t, 4H), 7.23 (d, 2H), 7.69 (s, 2H), 7.88 (d, 2H), 8.56 (s, 2H), 8.61 (s, 2H), 8.91 (s, 2H). Elemental analysis: calcd. for $C_{40}H_{50}$, C 90.51, H 9.49; found, C 90.01, H 9.39%.

2.5. *Synthesis of other 2,9-dialkylpentacenes*

2.5.1. 2,9-diethylpentacene. FT-IR (KBr, cm^{-1}): 2964, 2929, 2871, 1673, 1619, 1456, 1296, 1277, 909. Elemental analysis: calcd. for $C_{26}H_{22}$, C 93.37, H 6.63; found, C 92.28, H 6.43%. Due to its low solubility in 1,1,2,2-tetrachloroethane, no NMR data were obtained.

2.5.2. 2,9-dipropylpentacene. FT-IR (KBr, cm^{-1}): 2955, 2928, 2868, 1670, 1621, 1456, 1297, 1273, 910. ^1H NMR (400 MHz, 100°C, 1,1,2,2-tetrachloroethane-d2, δ ppm): 1.07 (t, 6H), 1.84 (sext, 4H), 2.80 (t, 4H), 7.23 (d, 2H), 7.69 (s, 2H), 7.88 (d, 2H), 8.56 (s, 2H), 8.61 (s, 2H), 8.91 (s, 2H). Elemental analysis: calcd. for $C_{28}H_{26}$, C 92.77, H 7.23; found, C 91.72, H 6.99%.

2.5.3. 2,9-dibutylpentacene. FT-IR (KBr, cm^{-1}): 2956, 2927, 2858, 1632, 1463, 1298, 910. ^1H NMR (400 MHz, 100°C, 1,1,2,2-tetrachloroethane-d2, δ ppm): 1.03 (t, 6H), 1.51 (sext, 4H), 1.81 (quint, 4H), 2.82 (t, 4H), 7.23(d, 2H), 7.69 (s, 2H), 7.88 (d, 2H), 8.56 (s, 2H), 8.61 (s, 2H), 8.91 (s, 2H). Elemental analysis: calcd. for $C_{30}H_{30}$, C 92.26, H 7.74; found, C 91.69, H 7.76%.

2.5.4. 2,9-dipentylpentacene. FT-IR (KBr, cm^{-1}): 2956, 2927, 2855, 1633, 1458, 1296, 910. ^1H NMR (400 MHz, 100°C, 1,1,2,2-tetrachloroethane-d2, δ ppm): 0.99 (t, 6H), 1.3–1.5 (m, 8H), 1.83 (quint, 4H), 2.83 (t, 4H), 7.23 (d, 2H), 7.69 (s, 2H), 7.88 (d, 2H), 8.56 (s, 2H), 8.61 (s, 2H), 8.91 (s, 2H). Elemental analysis: calcd. for $C_{32}H_{34}$, C 91.81, H 8.19; found, C 91.33, H 7.88%.

2.5.5. 2,9-dihexylpentacene. FT-IR (KBr, cm^{-1}): 2955, 2925, 2853, 1630, 1459, 1296, 910. ^1H NMR (400 MHz, 100°C, 1,1,2,2-tetrachloroethane-d2, δ ppm): 0.95 (t, 6H), 1.3–1.5 (m, 12H), 1.83 (quint, 4H), 2.83 (t, 4H), 7.23 (d, 2H), 7.69 (s, 2H), 7.88 (d, 2H), 8.56 (s, 2H), 8.61 (s, 2H), 8.91 (s, 2H). Elemental analysis: calcd. for $C_{34}H_{38}$, C 91.42, H 8.58; found, C 91.20, H 8.47%.

2.5.6. 2,9-diheptylpentacene. FT-IR (KBr, cm^{-1}): 2956, 2924, 2853, 1632, 1465, 1296, 910. ^1H NMR (400 MHz, 100°C, 1,1,2,2-tetrachloroethane-d2, δ ppm): 0.95 (t, 6H), 1.3–1.5 (m, 16H), 1.82 (quint, 4H), 2.83 (t, 4H), 7.23 (d, 2H), 7.69 (s, 2H), 7.88 (d, 2H), 8.56 (s, 2H), 8.61 (s, 2H), 8.91 (s, 2H). Elemental analysis: calcd. for $C_{36}H_{42}$, C 91.08, H 8.92; found, C 90.81, H, 8.68%.

2.5.7. 2,9-dioctylpentacene. FT-IR (KBr, cm^{-1}): 2923, 2852, 1672, 1619, 1462, 1299, 910. ^1H NMR (400 MHz, 100°C, 1,1,2,2-tetrachloroethane-d2, δ ppm): 0.94 (t, 6H), 1.2–1.5 (m, 20H), 1.82 (quint, 4H), 2.83 (t, 4H), 7.23 (d, 2H), 7.69 (s, 2H), 7.88 (d, 2H), 8.56 (s, 2H), 8.61 (s, 2H), 8.91 (s, 2H). Elemental analysis: calcd. for $C_{38}H_{46}$, C 90.78, H 9.22; found, C 90.43, H 9.02%.

2.5.8. 2,9-didecylpentacene. FT-IR (KBr, cm^{-1}): 2955, 2923, 2852, 1672, 1619, 1467, 1300, 910. ^1H NMR (400 MHz, 100°C, 1,1,2,2-tetrachloroethane-d2, δ ppm): 0.93 (t, 6H), 1.2–1.5 (m, 28H), 1.82 (quint, 4H), 2.83 (t, 4H), 7.23 (d, 2H), 7.69 (s, 2H), 7.88 (d, 2H), 8.56 (s, 2H), 8.61 (s, 2H), 8.91 (s, 2H). Elemental analysis: calcd. for $C_{42}H_{54}$, C 90.26, H 9.74; found, C 90.11, H 9.93%.

2.5.9. 2,9-diundecylpentacene. FT-IR (KBr, cm^{-1}): 2955, 2923, 2851, 1673, 1632, 1467, 1300, 910. ^1H NMR (400 MHz, 100°C, 1,1,2,2-tetrachloroethane-d2, δ ppm): 0.93 (t, 6H), 1.2–1.5 (m, 32H), 1.82 (quint, 4H), 2.83 (t, 4H), 7.23 (d, 2H), 7.69 (s, 2H), 7.88 (d, 2H), 8.56 (s, 2H), 8.61 (s, 2H), 8.91 (s, 2H). Elemental analysis: calcd. for $C_{44}H_{58}$, C 90.04, H 9.96; found, C 89.75, H 9.87%.

2.6. *Thermal analysis and polarizing optical microscope observation*

The phase transition behaviour and aggregation state were investigated by differential scanning calorimetry

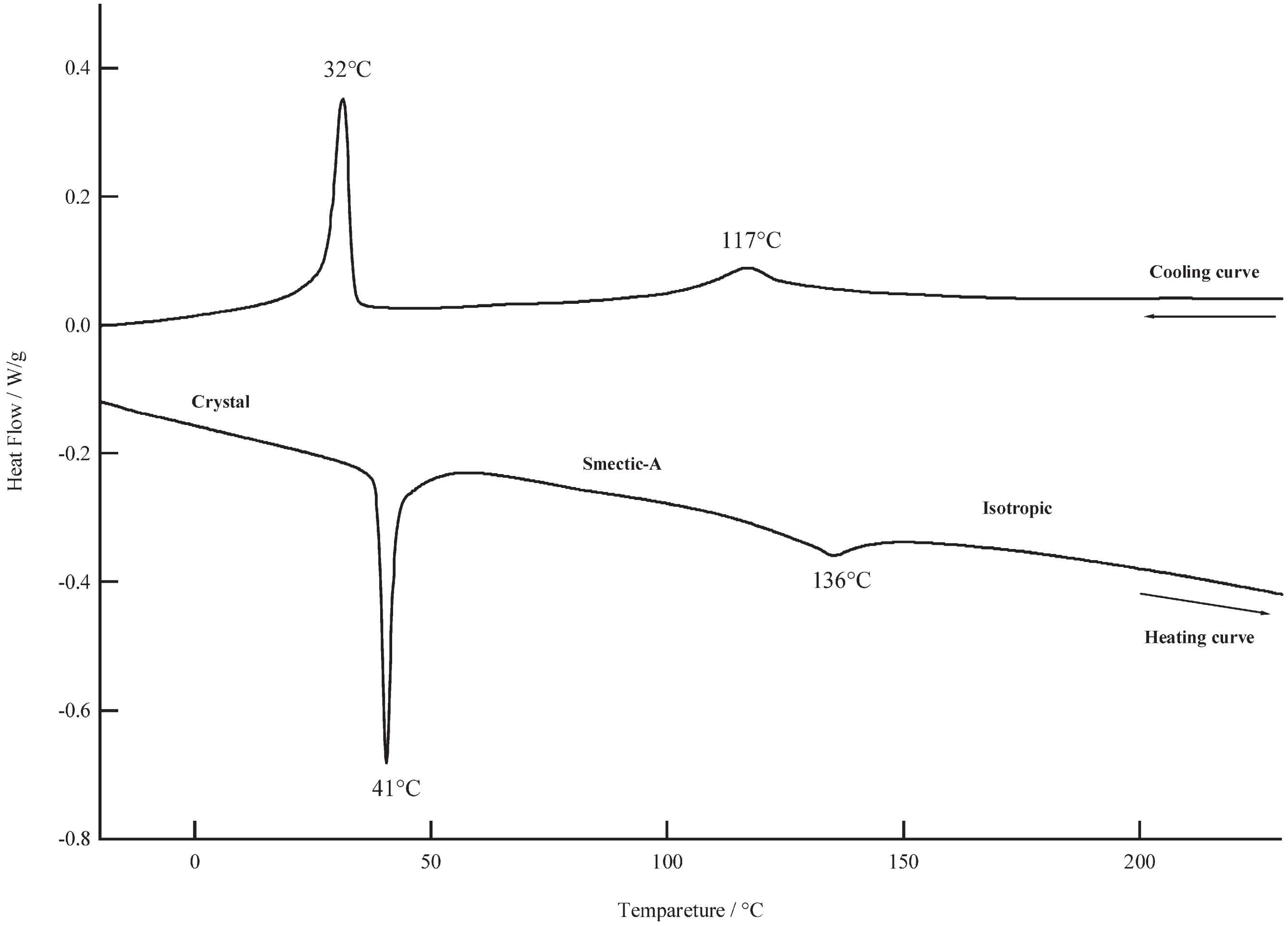

Figure 3. DSC heating and cooling curves for 2,9-dinonylpentacene.

(DSC, TA Instruments Q10) under nitrogen flow and polarizing optical microscopy (POM, Nikon E600 POL equipped with a hot stage, Mettler FP82HT and FP90). The heating profile in all cases was heat, cool and reheat at 10°C min^{-1}. Thermal data were normally extracted from the second heating trace. POM observations were conducted in during the cooling process at 10°C min^{-1} for phase characterization. Soxhlet extraction with acetone was conducted before all analyses and thermal characterization.

3. Results and discussion

3.1. *Molecular characterizations*

A series of dialkylpentacenes were successfully synthesized via multistep reactions (see figure 2). IR spectra showed characteristic absorptions at 2900, 1300 and 900 cm^{-1} assigned to C–H stretching, ring stretching and CH out-of-plain vibrations, respectively [14]. Improved solubility made it possible to measure ^{1}H NMR spectra (in deuterated 1, 1, 2, 2-tetrachloroethane at 100°C). Elemental analyses and normal phase HPLC (silica/toluene) revealed the sufficient purity (>98%) after washing with Soxhlet extraction. Although it was possible to further purify the products by sublimation, the following experiments were conducted on products just after extraction. All the dialkylpentacenes are dark blue solids that are slightly soluble in organic solvents such as toluene, tetrahydrofuran and chloroform. For example, the solubility of 2,9-dinonylpentacene in toluene is more than 0.5 mg ml^{-1} at room temperature. UV–visible spectra of 1,1,2,2-tetrachloroethane solutions showed five characteristic absorptions around 430, 466, 500, 537 and 582 nm. Unfortunately, the solutions were rather unstable and were bleached within 30 min when exposed to air and/or light. Thermal gravimetric analyses revealed that the products are stable until 300°C, whereas the weight loss of unsubstituted pentacene started at 260°C (due to sublimation).

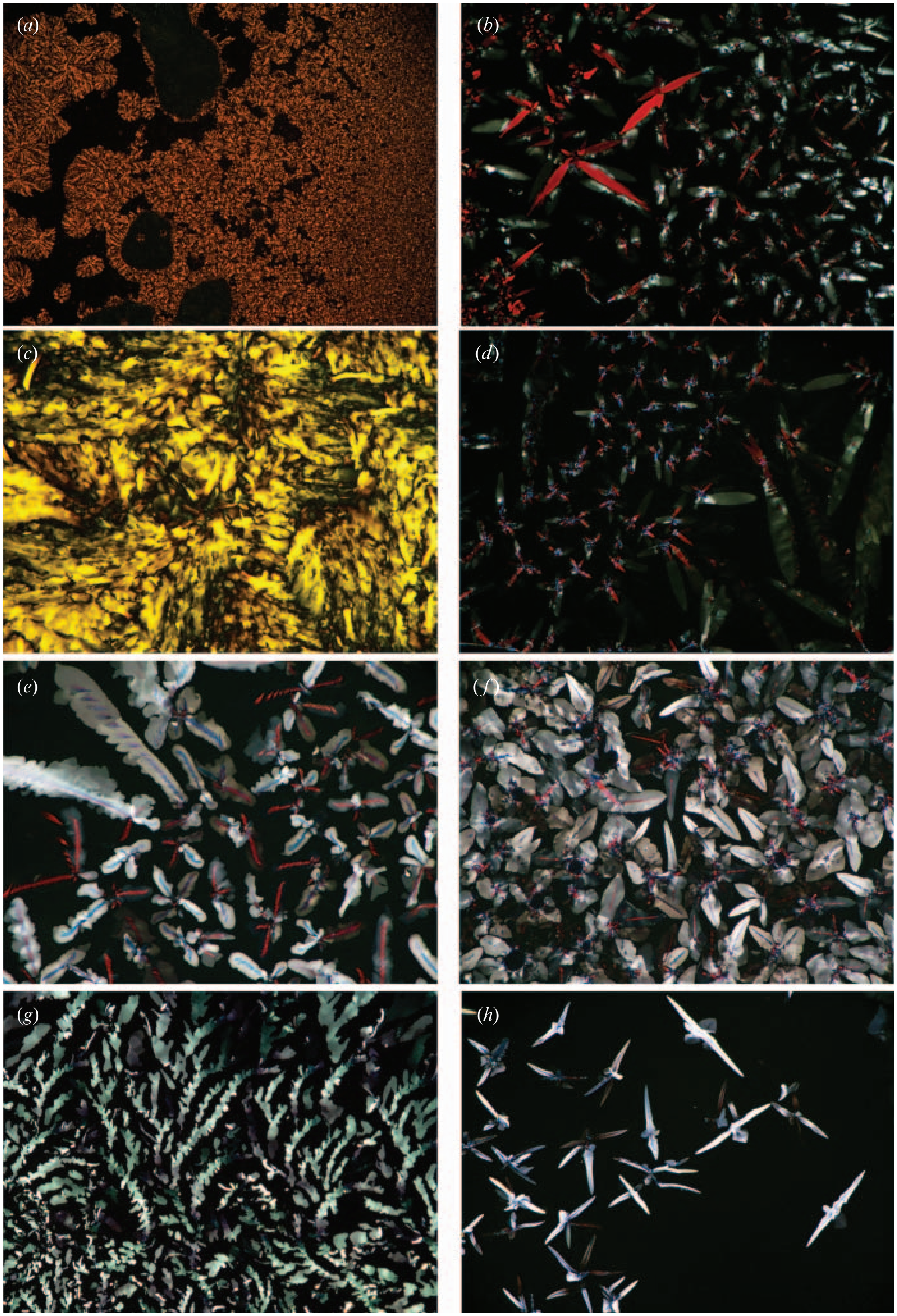

Figure 4. Polarizing optical photomicrographs of 2,9-dialkylpentacenes in the smectic A phase: (a) 2,9-dibutylpentacene, T=175°C; (b) 2,9-dipentylpentacene, T=163°C; (c) 2,9-dihexylpentacene, T=169°C; (d) 2,9-diheptylpentacene, T=167°C; (e) 2,9-dioctylpentacene, T=160°C; (f) 2,9-dinonylpentacene, T=134°C; (g) 2,9-didecylpentacene, T=167°C; (h) 2,9-diundecylpentacene, T=159°C.

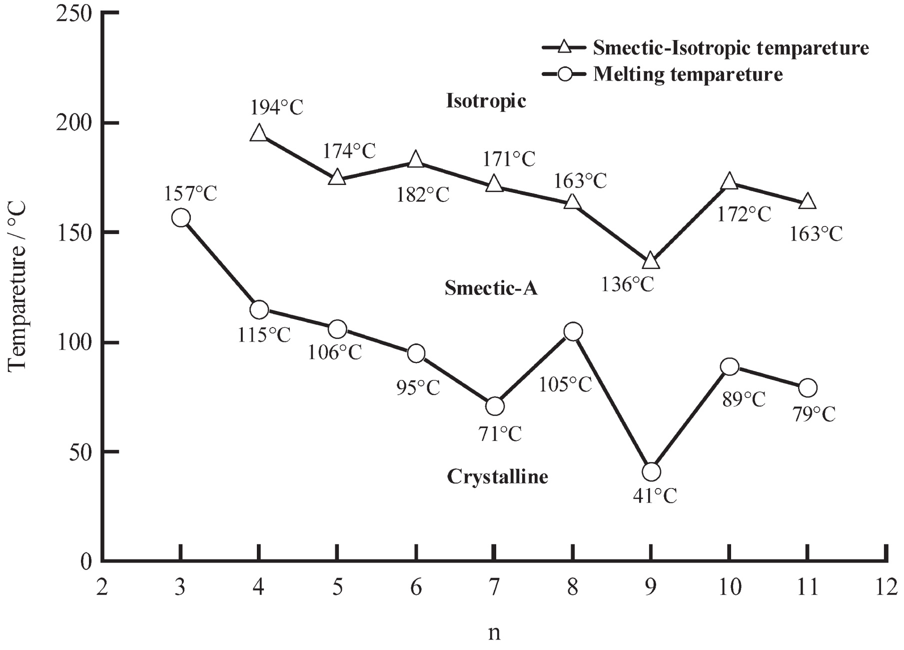

Figure 5. Dependence of transition temperatures on alkyl chain length (*n*): (○) melting temperature; (Δ) smectic–isotropic transition temperature.

3.2. *Phase behaviour and aggregation state of 2,9-dialkylpentacenes*

All the pentacene derivatives synthesized in this study were characterized using POM and DSC. Figure 3 shows the DSC heating and cooling curves for 2,9-dinonylpentacene. The upper line in figure 3 corresponds to the cooling curve and the lower line to the heating curve of 2,9-dinonylpentacene. The curves indicate that an intermediate phase exists between the crystalline and isotropic phases.

Figure 4 shows polarizing optical photomicrographs of the 2,9-dialkylpentacenes. As shown in figure 4 a, a weak focal conic texture was observed in 2,9-dibutylpentacene at 175°C. Focal conic texture is one of the optical textures observed in an ordered smectic phase. This type of texture was more clearly observed in 2,9-dihexylpentacene at 169°C compared with its dibutyl homologue, as shown in figure 4 c. Figure 4 b shows baton texture observed in 2,9-dipentylpentacene at 163°C. The baton texture is also one of the optical textures seen in an ordered smectic phase. As shown in figures 4 d–4 h, baton textures were observed in 2,9-diheptylpentacene at 167°C, 2,9-dioctylpentacene at 160°C, 2,9-dinonylpentacene at 134°C and 2,9-diundecylpentacene at 159°C. It was found that an ordered smectic phase was observed when the alkyl chains were in the range from C4 to C11. In the case of diethyl- and dipropylpentacenes, no intermediate phase was observed.

A smectic phase is generally observed when the interaction along a long molecular axis is smaller than that along the short axis. It seems that this situation is true of the dialkylpentacenes presented here, since the non-polar nature of the molecules weakens the interaction along molecular long axis and the strong π–π interaction between pentacene rigid cores is suggested from insoluble nature of pentacene itself. The longer alkyl chains decrease the interaction along the long molecular axis and the contribution of the interaction along the short axis is relatively increased. It is possible that the pentacene rigid core segment has face-to-face configuration due to the π–π interaction [19].

The dependence of the melting temperatures and smectic–isotropic transition temperatures on the length of substituted alkyl chain is shown in figure 5. It can be seen that both the melting and clearing temperatures depend strongly on the length and parity of the flexible alkyl chains. The melting temperatures monotonously decreased up to n=7 and exhibited a clear odd–even effect when n is larger than 7, in which even members show the higher values. The smectic–isotropic transition temperatures also decrease up to n=8 and exhibit a slight odd–even effect in the large n region. In both transitions, the even members show higher values.

The minimum transition temperatures were observed in the 2,9-nonylpentacene (n=9). The space-filling model of 2,9-nonylpentacene (n=9), shown in figure 6, indicates that the lengths of the alkyl chain and pentacene unit in this molecule are almost the same. It can be assumed that

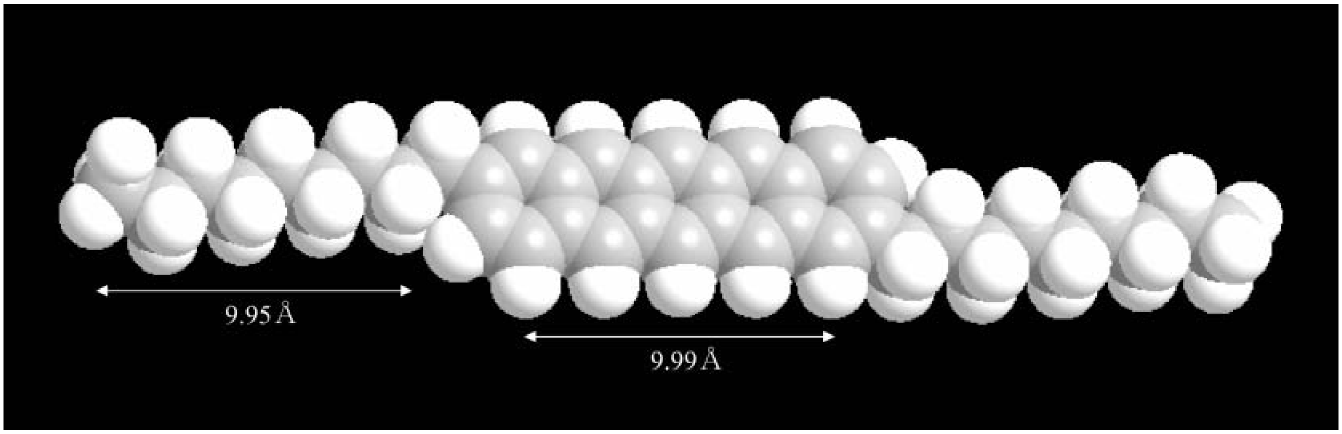

Figure 6. Space-filling model of 2,9-dinonylpentacene.

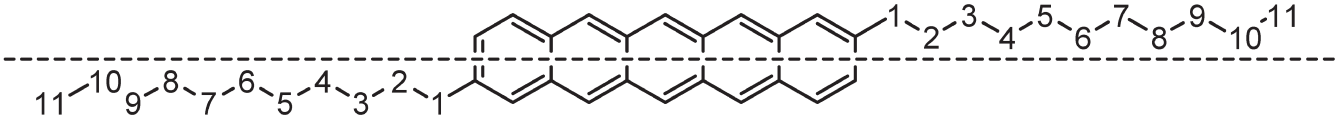

Figure 7. Structure of dialkylpentacenes and their long molecular axis.

this structure makes the molecular packing unstable, leading to the lowest transition temperatures.

As shown in figure 7, homologues with the odd alkyl chains exhibit non-colinearity to the rigid pentacene core segments, assuming an all-trans conformation geometry, resulting in low transition temperatures. On the other hand, the even members show colinearity resulting in high transition temperatures. This consideration is consistent with a previous report concerned with cyano-terminated twin liquid crystals [20].

4. Conclusion

We have reported the synthesis and liquid crystallinity of 2,9-dialkylpentacenes, for which the solubility is also improved. DSC thermograms and POM observations revealed that a stable smectic phase is observed over a relatively wide temperature range when the length of the terminal alkyl chain (*n*) is in the range 4–11. As a consequence, the series of 2,9-dialkylpentacenes are promising candidates for key materials in organic electronics. By utilizing their liquid crystallinity and processability, it could be possible to develop novel wet techniques for fabrication of high-performance OTFTs. Molecular orientation and OTFT device evaluation are currently under investigation.

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