Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

Alignment behaviour of symmetrical and asymmetrical triphenylenes possessing fluoroalkylated side chains on modified substrates

Naohiro Terasawa[a]; Hirosato Monobe[b]
[a] Research Institute for Cell Engineering, National Institute of Advanced Industrial Science and Technology (AIST), Osaka, 563-8577 Japan [b] Nanotechnology Research Institute, National Institute of Advanced Industrial Science and Technology (AIST), Osaka, 563-8577 Japan

To cite this Article Terasawa, Naohiro and Monobe, Hirosato(2007) 'Alignment behaviour of symmetrical and asymmetrical triphenylenes possessing fluoroalkylated side chains on modified substrates', Liquid Crystals, 34: 4, 447 — 455

To link to this Article: DOI: 10.1080/02678290701211520

URL: http://dx.doi.org/10.1080/02678290701211520

Liquid Crystals, Vol. 34, No. 4, April 2007, 447–455

Alignment behaviour of symmetrical and asymmetrical triphenylenes possessing fluoroalkylated side chains on modified substrates

NAOHIRO TERASAWA*† and HIROSATO MONOBE‡

†Research Institute for Cell Engineering, National Institute of Advanced Industrial Science and Technology (AIST), KANSAI, Midorigaoka 1-8-31, Ikeda, Osaka, 563-8577 Japan

‡Nanotechnology Research Institute, National Institute of Advanced Industrial Science and Technology (AIST), KANSAI, Midorigaoka 1-8-31, Ikeda, Osaka, 563-8577 Japan

(*Received 6 October 2006; accepted 1 December 2006*)

The alignment behaviour of triphenylene-based compounds possessing fluoroalkylated and alkyl side chains was investigated for the hexagonal columnar ($\mathrm{Col_h}$) mesophase on polyimide-, cetyltrimethylammonium bromide (CTAB)-, and indium tin oxide-coated glass substrates by polarizing optical microscopy. It was found that 2,6,10-trinonyloxy-3,7,11-tris(1*H*,1*H*,2*H*,2*H*,3*H*,3*H*-perfluorononyloxy)triphenylene and 2,6,11-trinonyloxy-3,7,10-tris(1*H*,1*H*,2*H*,2*H*,3*H*,3*H*-perfluorononyloxy)triphenylene exhibit spontaneous homeotropic alignment on these substrates. On the other hand, it was found that 2,6,10-triheptyloxy-3,7,11-tris(1*H*,1*H*,2*H*,2*H*,3*H*,3*H*-perfluoroheptyloxy)triphenylene, 2,6,11-triheptyloxy-3,7,10-tris(1*H*,1*H*,2*H*,2*H*,3*H*,3*H*-perfluoroheptyloxy)triphenylene, 2,6,10-trihexyloxy-3,7,11-tris(1*H*,1*H*,2*H*,2*H*,3*H*,3*H*-perfluorohexyloxy)triphenylene, 2,6,11-trihexyloxy-3,7,10-tris(1*H*,1*H*,2*H*,2*H*,3*H*,3*H*-perfluorohexyloxy)triphenylene, 2,6,10-tributyloxy-3,7,11-tris(1*H*,1*H*,2*H*,2*H*,3*H*,3*H*-perfluorobutyloxy)triphenylene and 2,6,11-tributyloxy-3,7,10-tris(1*H*,1*H*,2*H*,2*H*,3*H*,3*H*-perfluorobutyloxy)triphenylene do not show such spontaneous homeotropic alignment on these substrates. These results indicate that the spontaneous homeotropic alignment of the $\mathrm{Col_h}$ phase could be easily attained by the introduction of an appropriate length of the fluoromethylene chains in the peripheral parts of discogens. Therefore, it is suggested that the balance between the hydrocarbon part including the triphenylene core and the fluoroalkyl part determines the alignment control behaviour. Furthermore, it was found that alignment behaviour is independent of the rotation symmetry of the chemical structure but is dependent on the number of fluoromethylene chains in the chemical structure.

1. Introduction

Since the discovery of fast electronic carrier transport in a columnar mesophase, liquid crystals have been recognized as providing a new class of organic semiconductor [1–5]. For example, Adam *et al.* [3] found a fast mobility ($10^{-1}\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$) of holes in the helical columnar phase of 2,3,6,7,10,11-hexahexylthio-triphenylene for discotic liquid crystals, and Funahashi and Hanna found a fast mobility ($10^{-2}\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$) of holes and electrons in the smectic E phase of 2-phenylbenzothiazole derivatives for rod-like liquid crystals. In deed, recent studies of the electronic properties of columnar mesophases have revealed fast one-dimensional transport of charged carriers that exceeds the values of for amorphous polymers such as poly(*N*-vinylcarbazole) by two to three orders of magnitude [1, 6, 7]; this has led to applications in to xerography and laser printing as photoimaging materials. Thus, liquid crystals are recognized as providing a new class of organic semiconductor exhibiting self-organization and fluidity [8], with expectations for use in electrionic devices. These characteristic properties of mesophases are potentially applicable in areas such as EL devices, information storage, sensors and high resolution xerography. However, liquid crystals which exhibit high conductivities usually show higher orientational order and thus, tend to have higher viscosities than lower ordered liquid crystal phases such as nematic and smectic A phases. In the applications of these materials to electronic devices, liquid crystal alignment control is essential. Therefore, we need to find a method for the control of molecular alignment of such highly ordered liquid crystals.

---

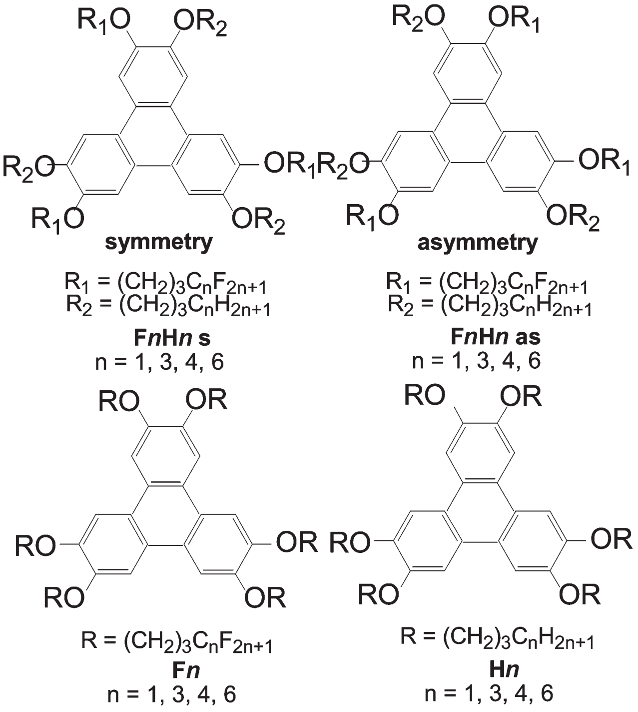
*Corresponding author. Email: terasawa-naohiro@aist.go.jp

Liquid Crystals
ISSN 0267-8292 print/ISSN 1366-5855 online © 2007 Taylor & Francis
http://www.tandf.co.uk/journals
DOI: 10.1080/02678290701211520

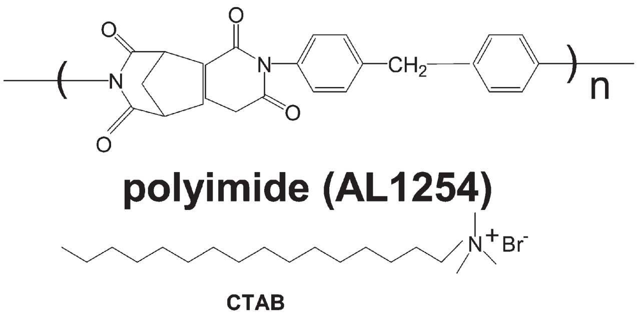
For discotic liquid crystals, there have been just a few publications on alignment behaviour [9–12]. These are reports of alignment control of discotic nematic (N_D) and rectangular columnar (Col_r) mesophases, promoting the desired alignment of liquid crystals from the substrate side. Recently, it was also reported that the columnar aggregates formed by hexa-*peri*-hexabezocoronene (HBC) mesogens lie parallel to a poly(tetrafluoroethylene) surface (planar alignment), when HBC macrocycles orient orthogonal to the polymer backbone [13]; and Hatsusaka *et al.* found that phthalocyanine derivatives exhibit spontaneous uniform homeotropic alignment for the tetragonal columnar (Col_{tet}) mesophase between two soda-lime or quartz glass plates [5].

As another method for aligning liquid crystal molecules, the alignment control of a columnar mesophase of 2,3,6,7,10,11-hexyloxytriphenylene by vibrational excitation has been reported [14, 15]. However, it was not previously known as a general molecular design principle that chemical modification of a mesogen could provide a certain controllability of the molecular alignment for a columnar mesophase without changing its mesomorphism. It has recently, been found that the introduction of a fluoroalkyl group into the peripheral chains of triphenylene mesogens could encourage homeotropic alignment of the hexagonal columnar (Col_h) mesophase on a variety of substrates, indicating a new concept of molecular approach for the alignment control of a columnar mesophase [16, 17].

In this work, the alignment behaviour of the Col_h phase for several homologues of a novel triphenylene derivative possessing three fluoroalkyl chains (**F1H1s–F6H6s** and **F1H1as–F6H6as**) was investigated for polyimide-, cetyltrimethylammonium bromide (CTAB)- and indium tin oxide (ITO)-coated substrates by polarizing optical microscopy (POM) and the results compared with those for the corresponding triphenylene derivatives possessing six fluoroalkylated side chains (**F1–F6**) and the hydrocarbon homologues (**H1–H6**). For structures, see schemes 1 and 2. Two types of the homologues (**F1H1s–F6H6s** and **F1H1as–F6H6as**) (symmetrical and asymmetrical in the rotational symmetry) have been synthesized as novel triphenylene compounds possessing fluoroalkyl and alkyl side chains by an alternative method. X-ray diffraction and DSC measurements showed that these homologues exhibit the Col_h mesophase. The phase transition temperatures (Col_h–I) for all the symmetrical and asymmetrical fluoroalkyloxytriphenylenes increase to *c.* 180°C, in comparison with fluoroalkyloxytriphenylenes possessing six fluoroalkyl side chains, and alkyloxytriphenylenes; these transition temperatures are independent of fluoromethylene chain length and the rotation symmetry of the chemical structure. All the symmetrical and asymmetrical fluoroalkyloxytriphenylenes possessing three fluoroalkyl side chains are thermally stabilized, compared with fluoroalkyloxytriphenylenes possessing six fluoroalkyl side chains (**F1–F6**) and alkyloxytriphenylenes (**H1–H6**) [18].



Scheme 1. Structures of symmetrical and asymmetrical fluoroalkyloxytriphenylenes (***Fn*Hn* s** and **F*n*H*n* as**), fluoroalkyloxytriphenylenes (**F*n***) and alkyloxytriphenylenes (**H*n***).



Scheme 2. Structures of polyimide (AL1254) and CTAB.

2. Experimental

2.1. *Compounds*

Compounds **F1H–F6H6** were synthesized according to methods described in the literature [19–22]. The phase transition parameters of **F1H1s–F6H6s**, **F1H1as–F6H6as**, **F1–F6** and **H1–H6** are shown in table 1. Commercially available CTAB and polyimide JSR Co. Ltd (AL1254) were purchased.

2.2. *Sample preparations and texture observations*

Glass substrates were cleaned in an ozone cleaner, and coated with polyimide by spin-coating (1000 rpm for 1 min), followed by drying at 180°C in air for 2 h. CTAB coating of a substrate was carried out by dipping the substrate into a saturated aqueous solution of CTAB; it was then dried under N_2. The mesogens were sandwiched between substrates using silica beads (diameter: 2 μm) as spacer. Textures were observed under crossed polarizers using a polarizing microscope (Olympus BH-2) in conjunction with a Mettler FP80HT hot stage.

3. Results and discussion

The alignment behaviour of the Col_h phase for several homologues of the novel triphenylene derivatives **F1H1s–F6H6s** and **F1H1as–F6H6as** was investigated by POM and the results were compared with those for compounds **F1–F6** and **H1–H6**.

The optical textures using polyimide-coated substrates for **F1H1s–F6H6s** and **F1H1as–F6H6as** are shown in figures 1 and 2, respectively. It was found that **F6H6s** and **F6H6as** spontaneously form a homeotropic alignment on repeatedly raising and lowering the temperature at 1°C min^{-1} around the clearing point, while **F1H1s–F4H4s** and **F1H1as–F4H4as** exhibit non-uniformity for the alignment. Polyimide is widely used to obtain a homogeneous alignment for rod-like liquid crystals [23, 24]. For discotic liquid crystals, it was reported that the N_D phase of 2,3,6,7,10,11-hexakis(4-*n*-

Table 1. Phase transition parameters of symmetrical and asymmetrical fluoroalkyloxytriphenylenes(**F*n*H*n* s** and **F*n*H*n* as**), fluoroalkyloxytriphenylenes (**F*n***) and alkyloxytriphenylenes (**H*n***). Cr=crystal, Col_h=hexagonal columnar, Col_{hp}=plastic hexagonal columnar, I=isotropic phase.

Compound	Transition	Temperature/°C	ΔH/kJ mol^{-1}	ΔS/J mol^{-1} K^{-1}
F1H1s	$Cr_1 \rightarrow Cr_2$	104	20.4	54.2
	$Cr_2 \rightarrow Col_h$	118	9.5	24.3
	$Col_h \rightarrow I$	181	7.1	15.7
F1H1as	$Cr \rightarrow Col_h$	139	43.3	105.0
	$Col_h \rightarrow I$	180	7.5	16.5
F1	$Cr \rightarrow Col_h$	132	22.1	54.5
	$Col_h \rightarrow I$	171	4.7	10.6
H1[a]	$Cr \rightarrow Col_{hp}$	87	24.7	68.6
	$Col_{hp} \rightarrow I$	144	20.5	49.1
F3H3s	$Cr_1 \rightarrow Cr_2$	70	21.7	63.2
	$Cr_2 \rightarrow Col_h$	74	20.2	58.1
	$Col_h \rightarrow I$	180	4.9	10.9
F3H3as	$Cr \rightarrow Col_h$	88	44.8	123.8
	$Col_h \rightarrow I$	178	4.9	11.0
F3	$Cr \rightarrow Col_h$	130	48.0	119.2
	$Col_h \rightarrow I$	149	3.7	8.8
H3	$Cr \rightarrow Col_h$	67	39.2	115.3
	$Col_h \rightarrow I$	99	5.5	14.8
F4H4s	$Cr \rightarrow Col_h$	57	50.6	153.1
	$Col_h \rightarrow I$	184	4.5	9.8
F4H4as	$Cr \rightarrow Col_h$	67	45.3	133.0
	$Col_h \rightarrow I$	181	5.0	11.0
F4	$Cr \rightarrow Col_h$	116	55.1	141.5
	$Col_h \rightarrow I$	157	4.0	9.4
H4	$Cr \rightarrow Col_h$	64	56.5	167.6
	$Col_h \rightarrow I$	89	4.4	12.1
F6H6s	$Cr \rightarrow Col_h$	51	46.0	142.2
	$Col_h \rightarrow I$	184	6.4	14.0
F6H6as	$Cr_1 \rightarrow Cr_2$	45	12.1	38.1
	$Cr_2 \rightarrow Col_h$	51	46.9	144.6
	$Col_h \rightarrow I$	182	7.2	15.7
F6	$Cr \rightarrow Col_h$	89	55.2	152.6
	$Col_h \rightarrow I$	183	5.2	11.4
H6	$Cr \rightarrow Col_h$	56	72.9	221.5
	$Col_h \rightarrow I$	77	2.7	7.7

[a] Col_{hp}: plastic hexagonal columnat phase.

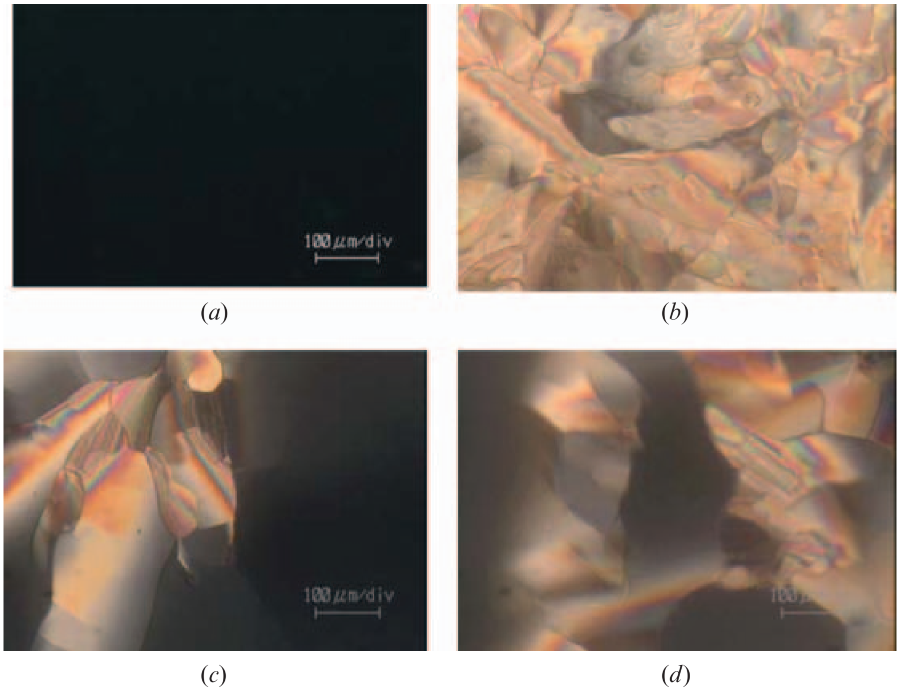
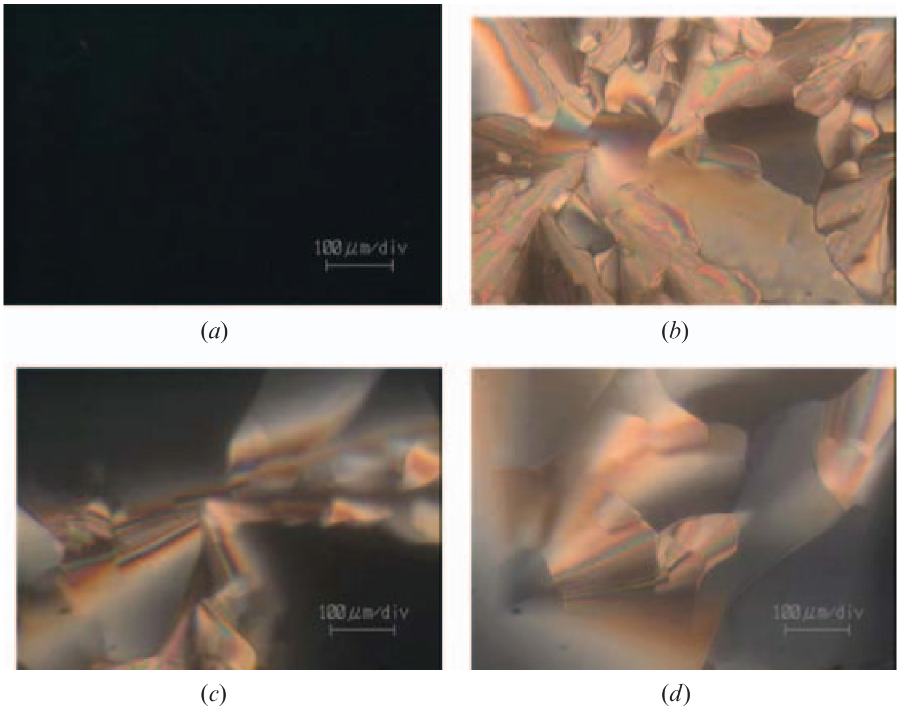


Figure 1. Polarized optical textures of the columnar mesophase on polyimide-coated substrates for (*a*) **F6H6s** (175°C), (*b*) **F4H4s** (180°C), (*c*) **F3H3s** (170°C) and (*d*) **F1H1s** (175°C).



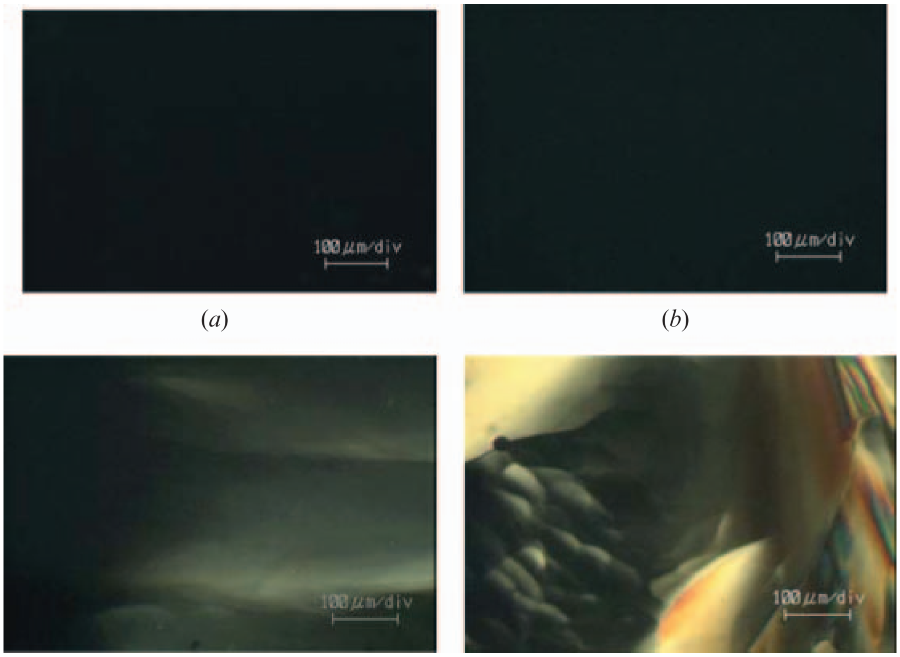
(*a*) (*b*) (*c*) (*d*)

Figure 2. Polarized optical textures of the columnar mesophase on polyimide-coated substrates for (*a*) **F6H6as** (175°C), (*b*) **F4H4as** (175°C), (*c*) **F3H3as** (170°C) and (*d*) **F1H1as** (175°C).

octyloxybezoyloxy)triphenylene exhibits a homeotropic alignment between polyimide-coated substrates [9]. Another report states that no clear tendency towards spontaneous alignment behaviour on polyimide film could be seen with the N_D phase of the same compound [12]. Furthermore, it was reported that triphenylene derivatives possessing six fluoroalkylated side chains (**F4** and **F6**) spontaneously form a homeotropic alignment between polyimide-coated substrates, on repeatedly raising and lowering the temperature at 1°C min^{-1} around the clearing point, while **F3**–**F1** and **H6**–**H1** show non-uniform alignment; (see figures 3 and 4, respectively) [16, 17]. Thus, the results for a triphenylene derivative possessing three fluoroalkyl chains were different from the results for one possessing six fluoroalkyl chains. In this work, we found that spontaneous homeotropic alignment of the Col_h phase could easily be attained by the introduction of a different appropriate length of fluoromethylene chain into the peripheral parts of the discogens, in contrast to the case for compounds possessing six fluoroalkylated side chains between the polyimide-coated substrates. It is suggested that the interaction between fluoroalkyl chain and substrate surface is significant for alignment behaviour.

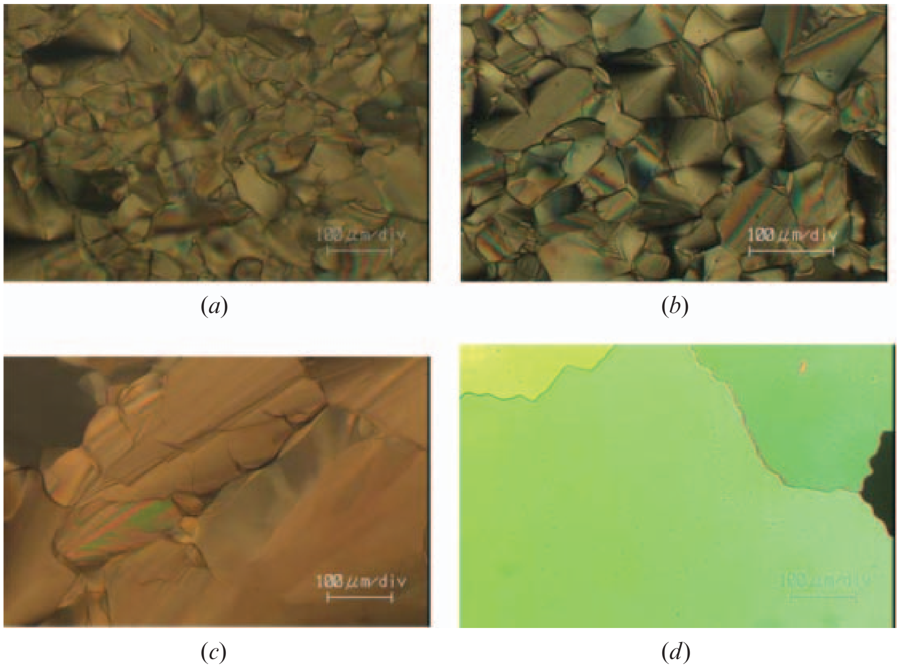
CTAB is a typical material with which to obtain homeotropic alignment for rod-like nematic liquid crystals. Therefore, it could be expected that a planar alignment would also be obtained for CTAB-coated substrates in the Col_h mesophase of alkyloxytriphenylenes, considering the interaction between the alkyl tails of the mesogens and the surface molecules. The textures formed in samples between CTAB-coated substrates were similar to those for polyimide-coated substrates, when the temperature was repeatedly raised and lowered at 1°C min^{-1} around the clearing point (Figures 5 and 6). A homeotropic texture formed spontaneously in the Col_h phase of **F6H6s** and **F6H6as**, while **F1H1s**–**F4H4s** and **F1H1as**–**F4H4as** exhibit non-uniformity of alignment. Furthermore, similarly for polyimide-coated substrates, it was reported that **F4** and **F6** spontaneously form a homeotropic alignment, while **F1**–**F3** and **H1**–**H6** show non-uniform alignment between CTAB-coated substrates [16, 17]. It is suggested that alignment behaviour for **F6H6s** and **F6H6as** is independent of the substrate surface type.

Textures for triphenylene derivatives possessing three fluoroalkyl chains between ITO-coated substrates show a similar behaviour to those between polyimide- and CTAB-coated substrates (figures 7 and 8). This similarity is also seen for derivatives possessing six fluoroalkyl chains. It can be seen that the alignment behaviour of fluoroalkyloxytriphenylenes depends on the length of the fluoromethylene part of the chain, independently of the substrate surface.



(*a*) (*b*)
(*c*) (*d*)

Figure 3. Polarized optical textures of the columnar mesophase on polyimide-coated substrates for (*a*) **F6** (175°C), (*b*) **F4** (100°C), (*c*) **F3** (147°C) and (*d*) **F1** (165°C).

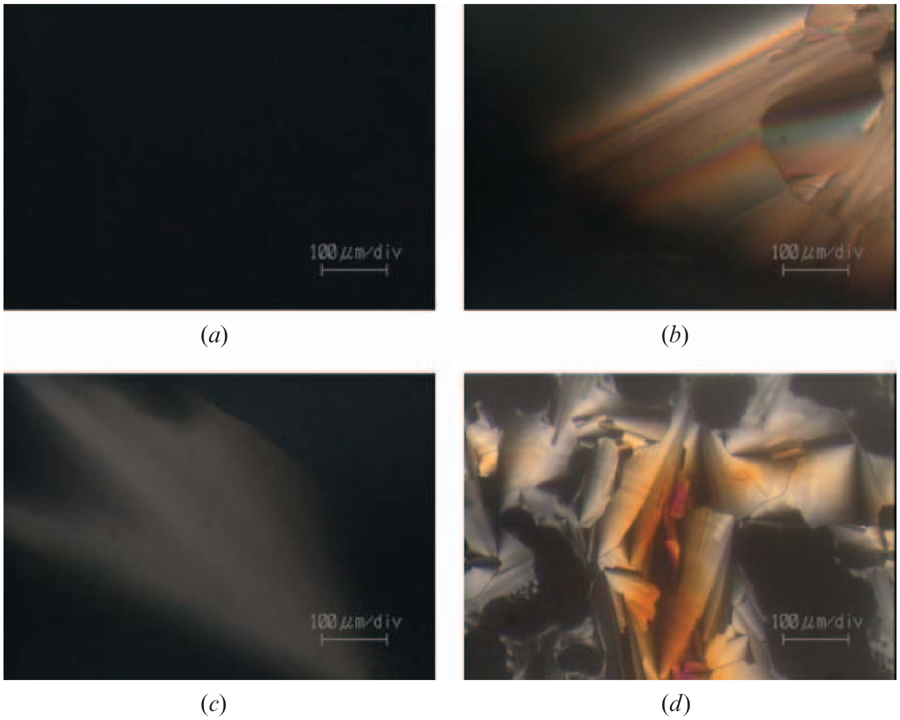


(*a*) (*b*)

(*c*) (*d*)

Figure 4. Polarized optical textures of the columnar mesophase on polyimide-coated substrates for (*a*) **H6** (75°C), (*b*) **H4** (80°C), (*c*) **H3** (97°C) and (*d*) **H1** (110°C).

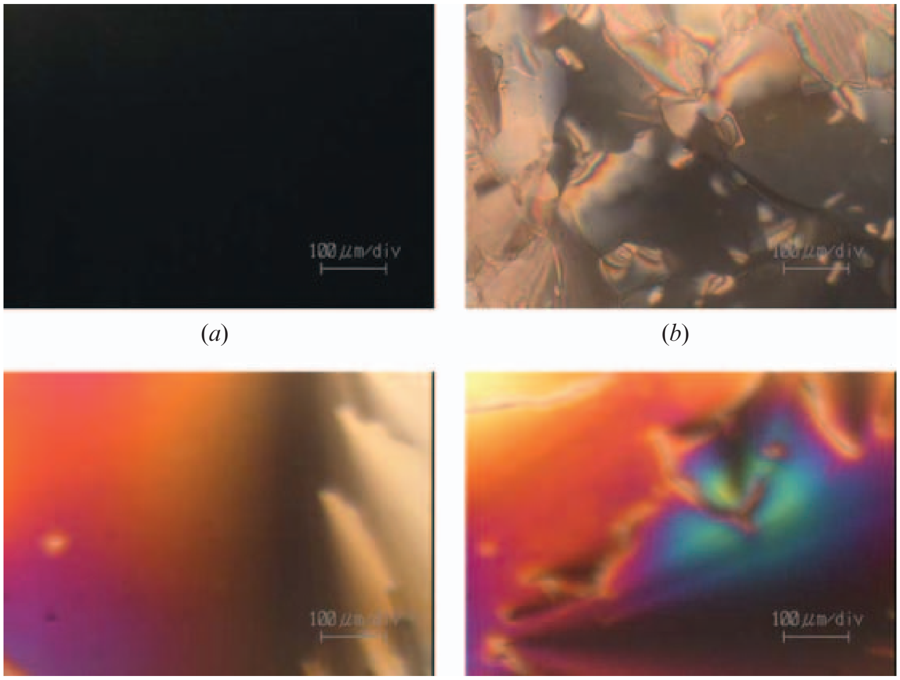
The alignment behaviour observed in this work is summarized in table 2. It is interesting that **F6H6s**, **F6H6as**, **F6** and **F4** tend to show a spontaneous homeotropic alignment on polyimide-, CTAB- and ITO-coated glass substrates, while **F1H1s–F4H4s**, **F1H1as–F4H4as**, **F1–F3** and **H1–H6** tend to show only



(*a*) (*b*)

(*c*) (*d*)

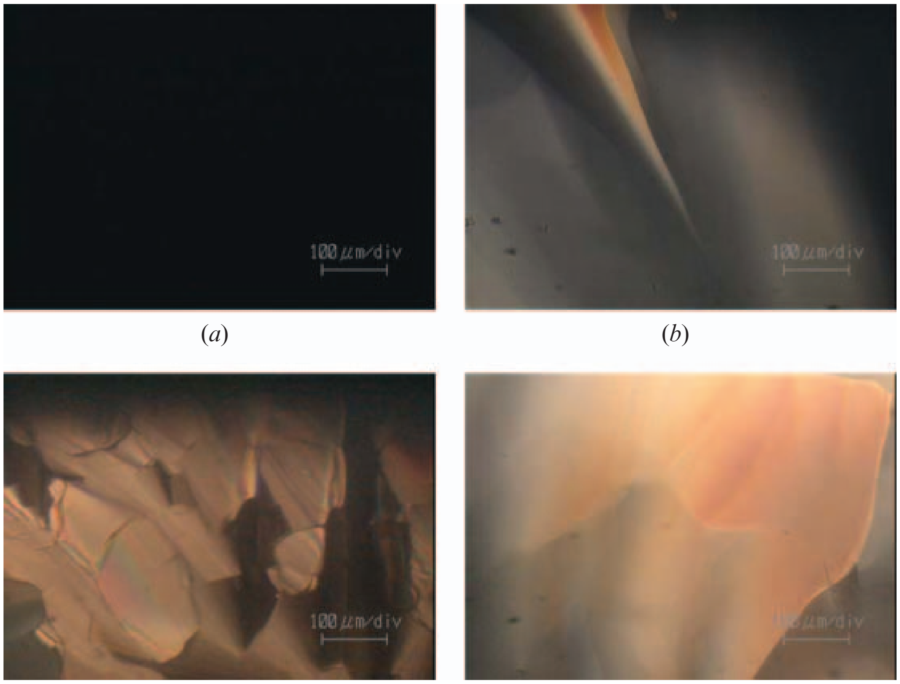
Figure 5. Polarized optical textures of the columnar mesophase on CTAB-coated substrates for (*a*) **F6H6s** (180°C), (*b*) **F4H4s** (175°C), (*c*) **F3H3s** (175°C) and (*d*) **F1H1s** (175°C).



(*a*) (*b*)

(*c*) (*d*)

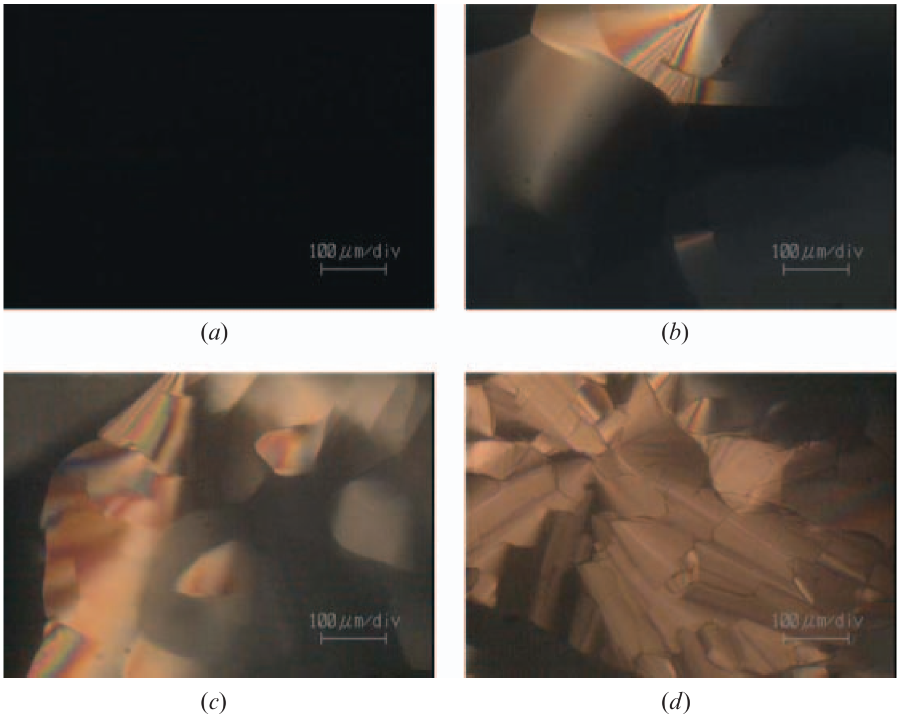
Figure 6. Polarized optical textures of the columnar mesophase on CTAB-coated substrates for (*a*) **F6H6as** (175°C), (*b*) **F4H4as** (175°C), (*c*) **F3H3as** (175°C) and (*d*) **F1H1as** (175°C).



(*a*) (*b*)

(*c*) (*d*)

Figure 7. Polarized optical textures of the columnar mesophase on ITO-coated substrates for (*a*) **F6H6s** (180°C), (*b*) **F4H4s** (175°C), (*c*) **F3H3s** (175°C) and (*d*) **F1H1s** (175°C).



(*a*) (*b*)

(*c*) (*d*)

Figure 8. Polarized optical textures of the columnar mesophase on ITO-coated substrates for (*a*) **F6H6as** (180°C), (*b*) **F4H4as** (175°C), (*c*) **F3H3as** (170°C) and (*d*) **F1H1as** (170°C).

non-uniform alignment. This indicates that homeotropic alignment in the $\mathrm{Col_h}$ phase could easily be attained by the introduction of appropriate lengths of fluoromethylene chain in the peripheral parts of the discogens without the disappearance of the $\mathrm{Col_h}$ mesophase. In the case of **F6H6s** and **F6H6as**, compounds possessing three fluoroalkylated side chains, spontaneous homeotropic alignment is shown on polyimide-, CTAB- and ITO-coated glass substrates. This indicates that alignment behaviour is independent of the rotation symmetry of the chemical structure. The fact that, **F6H6s**, **F6H6as**, **F4** and **F6** tend to show spontaneous homeotropic alignment on polyimide-, CTAB- and ITO-coated glass substrates, indicates that alignment behaviour is dependent on the length of the fluoromethylene chain of the chemical structure. As the introduction of three fluoromethylene chains of an appropriate length could easily induce homeotropic alignment in the $\mathrm{Col_h}$ phase, it is suggested that the balance between the hydrocarbon part, including the triphenylene core, and the fluoroalkyl part determines the alignment control behaviour.

4. Conclusion

It is indicated that spontaneous homeotropic alignment of the columnar phase can be easily attained by the introduction of fluoromethylene groups in the peripheral chains of a triphenylene mesogen. Furthermore, it is indicated that alignment behaviour is independent of the rotation symmetry of the chemical structure, and is dependent on the length of the fluoromethylene chains in the chemical structure. The introduction of fluoromethylene chains of appropriate length into the

Table 2. Alignment behaviour of the columnar phase for **F1H1s–F6H6s**, **F1H1as–F6H6as**, **F1–F6** and **H1–H6**

	Substrate		
Compound	Polyimide	CTAB	ITO
F6H6s and **F6H6as**	homeotropic	homeotropic	homeotropic
F1H1s–F4H4s and **F1H1as–F4H4as**	non-uniform	non-uniform	non-uniform
F4 and **F6**	homeotropic	homeotropic	homeotropic
F1 and **F3**	non-uniform	non-uniform	non-uniform
H1, **H3**, **H4** and **H6**	non-uniform	non-uniform	non-uniform

peripheral tails of discotic liquid crystals may provide a new molecular design technique for realizing spontaneous homeotropic alignment of the $\mathrm{Col_h}$ phase. This alignment behaviour implies that molecular alignment for the columnar mesophase may be controlled by chemical modification of the molecular structure. This is interesting and important in terms of device fabrication as well as of charge carrier mobility measurements by the TOF method for columnar mesophases. This technique may also provide a new alignment control for a broad range of highly ordered liquid crystals.

References

[1] D. Adam, P. Schuhmacher, J. Simmerer, L. Häussling, K. Siemensmeyer, K.H. Etzbach, H. Ringsdorf, D. Haarer. *Nature*, **371**, 141 (1994).

[2] M. Funahashi, J. Hanna. *Appl. Phys. Lett.*, **73**, 3733 (1998).

[3] D. Adam, F. Closs, T. Frey, D. Funhoff, D. Haarer, H. Ringsdorf, P. Schuhmacher, K. Siemensmeyer. *Phys. Rev. Lett.*, **70**, 457 (1993).

[4] A.M. van de Craats, J.M. Warman, A. Fechtenkötter, J.D. Brand, M.A. Harbison, K. Müllen. *Adv. Mater.*, **11**, 1469 (1999).

[5] K. Hatsusaka, K. Ohta, I. Yamamoto, H. Shirai. *J. mater. Chem.*, **11**, 423 (2001).

[6] T. Christ, B. Glusen, A. Geriner, A. Kettner, R. Sander, V. Stumpflen, V. Tsukruk, J.H. Wendorff. *Adv. Mater.*, **9**, 48 (1997).

[7] I.H. Stapff, V. Stumpflen, J.H. Wendorff, D.B. Spoohn, D. Mobius. *Liq. Cryst.*, **23**, 613 (1997).

[8] K. Kogo, T. Goda, M. Funahashi, J. Hanna. *Appl. Phys. Lett.*, **73**, 1595 (1998).

[9] H. Monobe, S. Mima, T. Sugino, Y. Shimizu. *Liq. Cryst.*, **28**, 1253 (2001).

[10] H. Monobe, H. Azehara, Y. Shimizu, M. Fujihira. *Chem. Lett.*, 1268 (2001).

[11] K. Kawata. *Chem. Record*, **2**, 59 (2002).

[12] S. Ikeda, Y. Takanishi, K. Ishikawa, H. Takezoe. *Mol. Cryst. Liq. Cryst.*, **329**, 589 (1999).

[13] A.M. van de Craats, N. Stutzman, O. Bunk, M.M. Nielsen, M. Watson, K. Müllen, H.D. Chanzy, H. Sirringhaus, R.H. Friend. *Adv. Mater.*, **15**, 495 (2003).

[14] H. Monobe, K. Awazu, Y. Shimizu. *Adv. Mater.*, **12**, 1495 (2000).

[15] H. Monobe, K. Kiyohara, N. Terasawa, M. Heya, K. Awazu, Y. Shimizu. *Chem. Lett.*, **32**, 870 (2003).

[16] N. Terasawa, H. Monobe, K. Kiyohara, Y. Shimizu. *Chem. Commun.*, 1678 (2003).

[17] N. Terasawa, N. Tanigaki, H. Monobe, K. Kiyohara. *J. fluorine Chem.*, **127**, 1096 (2006).

[18] N. Terasawa, H. Monobe, K. Kiyohara. *Liq. Cryst.* (to be published).

[19] M.T. Allen, K.D.M. Harris, B.M. Kariyuki, N. Kumari, J.A. Preece, S. Diele, D. Lose, T. Hegmann, C. Tschierske. *Liq. Cryst.*, **27**, 689 (2000).

[20] N. Boden, R.J. Bushby, Z.B. Lu. *Liq. Cryst.*, **25**, 47 (1998).

[21] H. Liu, H. Nohira. *Liq. Cryst.*, **20**, 581 (1996).

[22] R. Asep, Y. Aoki, T. Hirose, H. Nohira. *Mol. Cryst. liq. Cryst.*, **346**, 51 (2000).

[23] J. Cognard. *Mol. Cryst. liq. Cryst.*, **1**, 1 (1982).

[24] S. Kobayashi, Y. Iimura, M. Nishikawa. *SID '94 Dig.*, 78 (1994).