This article was downloaded by:
On: *25 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK

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

Alignment behaviour of the discotic nematic phase of 2,3,6,7,10,11-hexa(4-*n*-octyloxybenzoyloxy)triphenylene on polyimide and cetyltrimethylammonium bromide coated substrates

Hirosato Monobe; Shoji Mima; Takushi Sugino; Yo Shimizu; Masakatsu Ukon

Online publication date: 06 August 2010

To cite this Article Monobe, Hirosato , Mima, Shoji , Sugino, Takushi , Shimizu, Yo and Ukon, Masakatsu(2001) 'Alignment behaviour of the discotic nematic phase of 2,3,6,7,10,11-hexa(4-*n*-octyloxybenzoyloxy)triphenylene on polyimide and cetyltrimethylammonium bromide coated substrates', Liquid Crystals, 28: 8, 1253 — 1258

To link to this Article: DOI: 10.1080/02678290110051620

URL: http://dx.doi.org/10.1080/02678290110051620

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

LIQUID CRYSTALS, 2001, VOL. 28, NO. 8, 1253–1258

Alignment behaviour of the discotic nematic phase of 2,3,6,7,10,11-hexa(4-*n*-octyloxybenzoyloxy)triphenylene on polyimide and cetyltrimethylammonium bromide coated substrates

HIROSATO MONOBE, SHOJI MIMA, TAKUSHI SUGINO, YO SHIMIZU*
Department of Organic Materials, Osaka National Research Institute, AIST,
METI, 1-8-31 Midorigaoka, Ikeda, Osaka 563-8577, Japan

and MASAKATSU UKON
Mesophase Materials Laboratory, Japan Chemical Innovation Institute,
1-8-31 Midorigaoka, Ikeda, Osaka 563-8577, Japan

(*Received 29 December 2000; in final form 5 March 2001; accepted 8 March 2001*)

Downloaded At: 18:02 25 January 2011

The orientational behaviour of the nematic discotic phase of 2,3,6,7,10,11-hexa(4-*n*-octyloxybenzoyloxy)triphenylene (C8OBT) on substrates coated with a polyimide or cetyltrimethylammonium bromide (CTAB) was investigated by polarizing optical microscopy. The averaged order parameters and directions of the triphenylene core and the carbonyl groups of C8OBT were evaluated by an infrared dichroic method. The discotic nematic (N_D) phase of C8OBT exhibits a homeotropic alignment on a polyimide film, a typical nematic schlieren texture on a glass substrate, and a tilted or planar homogeneous alignment on a CTAB-coated substrate. The order parameter of the triphenylene core is higher on a polyimide film ($S = 0.6$) than on a CTAB-coated substrate ($S = 0.2$), whereas that of the carbonyl groups remains roughly constant at 0.2 to 0.3 independent of the substrate for the N_D phase.

1. Introduction

One of the characteristic features of liquid crystals, especially nematic liquid crystals, is the controllability of the molecular alignment exerted by the surface. At present, a rubbed polyimide-coated substrate is widely used to obtain a homogeneous alignment of rod-like mesogens [1]. Indeed, surface effects and shear flow have often been used too, in order to obtain uniformly aligned phases of discotic mesogens for studies of their potential as novel optoelectronic functional materials [2–5]. Recently, UV-vis photoalignment of discotic liquid crystal materials in the N_D phase induced by *trans-cis*-photoisomerization of an azobenzene monolayer substrate has been reported, indicating that it is possible to control the optical properties of liquid crystals and devices by photons [6, 7]. Furthermore these methodologies using organic thin films are interesting from the viewpoint of device fabrication.

Few results on molecular alignment switching of a discotic liquid crystal have been reported so far, and those that have involved external magnetic field effects [8] or photoalignment induced by infrared laser light irradiation [9, 10]. In addition, recent studies of photopolymerization in liquid crystals indicate that the molecular order of a discotic liquid crystal can be fixed in a solid polymer film [11], and this leads to applications such as widening the viewing angle of flat-panel liquid crystal displays [12]. Molecular alignment behaviour and controllability are important features in device fabrication using organic materials, and therefore it is essential to understand the mechanism of molecular alignment at the interface between discotic liquid crystals and substrates. As an aid to understanding this mechanism, knowledge of the local alignment of each part of the liquid crystal molecule provides valuable information for analysis of the interaction between the liquid crystal and substrate. Although there are many reports concerning orientational behaviour of rod-like systems, there are very few reports for discotic liquid crystals [2–5, 13].

Several studies have reported on the use of infrared dichroism to measure the molecular orientation and the order parameters of uniformly aligned columnar phases of discotic liquid crystals. Kruk *et al.*, for example, reported the evaluation of the order parameter of the

---

*Author for correspondence; e-mail: yo-shimizu@aist.go.jp

Liquid Crystals ISSN 0267-8292 print/ISSN 1366-5855 online © 2001 Taylor & Francis Ltd
http://www.tandf.co.uk/journals
DOI: 10.1080/02678290110051620

Downloaded At: 18:02 25 January 2011

columnar discotic phase of hexapentyloxytriphenylene using unpolarized infrared radiation, by comparing the IR absorption intensity of the columnar phase with that of the isotropic phase [2]. Whilst in theory this technique can also be applied to the N_D phase, few experiments have been reported due to the high transition temperature to the isotropic phase, which makes the experiment impractical, and because of the difficult problem of obtaining a uniformly aligned sample. However, this method is useful for analysing molecular alignment mechanisms of liquid crystals because of the ability to evaluate independently the order parameters and the averaged directions of individual functional groups in the molecule. This method has been extended to evaluate the dependence of the alignment of the hexagonal columnar phase of a triphenylene derivative on various types of inorganic substrate structures such as freshly cleaved mica [3]. Recently, Perova *et al.* reported the use of this method in evaluating an anchoring transition for a discotic liquid crystal on a nylon-coated substrate [4]. Favre-Nicolin *et al.* also reported the order parameters in the N_D phase of acrylate derivatives of triphenylene calculated from the refractive index using the Vuks approximation [13]. However, this method provides the parameters for the molecule as a whole, rather than those for individual functional groups. Detailed studies of the dependence of the alignment and the order parameters for each functional group within the N_D phase on substrates coated with an organic layer have not yet been reported.

In this work, the orientational behaviour for the N_D phase of 2,3,6,7,10,11-hexa(4-*n*-octyloxybenzoyloxy)triphenylene (C8OBT) on a spin-coated polyimide (JSR Co. Ltd., AL1254) film and a cetyltrimethylammonium bromide (CTAB) coated substrate has been investigated by polarizing optical microscopy (POM) involving a hot stage, and the order parameters have been evaluated by FTIR spectroscopy.

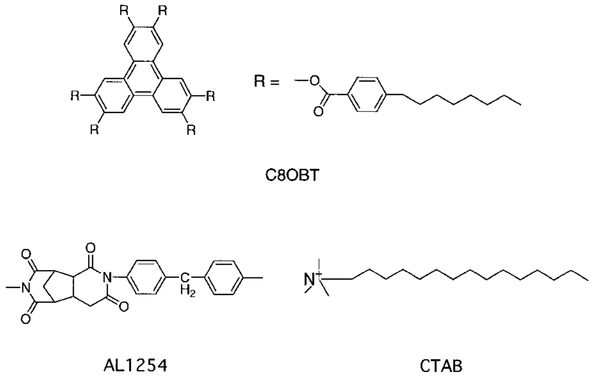
2. Experimental

2.1. *Compounds*

C8OBT was synthesized according to a literature method [14] and commercially available CTAB was used. C8OBT shows the N_D phase in a relatively low temperature region and the phase transition behaviour is shown in table 1. C8OBT shows three enantiotropic phase transitions [15] and has two mesophases; these are the rectangular columnar phase (Col_r) and the N_D phase.

2.2. *Preparations and measurements*

The polyimide film was prepared by spin-coating on a thoroughly cleaned glass substrate at 3000 rpm for 3 min; it was then heated at 90°C for 1 min, followed by drying at 180°C in air for 1 h. This film was not treated by rubbing. The thickness of the polyimide film was estimated by ellipsometry to be *c.* 45 nm. The CTAB-coated substrate was prepared by dipping glass plates into a saturated aqueous solution of CTAB. C8OBT was sandwiched between these substrates using silica bead spacers (2 µm diameter). For infrared spectra collection, BaF_2 plates were used instead of glass plates.



C8OBT

AL1254

CTAB

Scheme. Chemical structures of the compounds studied.

Table 1. Phase transition temperatures (°C) and enthalpies (kJ mol^{-1}, in italics) of C8OBT.

Crystal		Col_r		N_D		Isotropic
	150 *21*		167 *6.0*		238 *0.5*	

2.3. *Observation of alignment behaviour*

The textures of the N_D phase were observed using an Olympus BH-2 polarizing microscope in conjunction with a Mettler HT80 hot stage. The temperature dependence of the FTIR spectra was measured in order to evaluate the directions and order parameters for the triphenylene core and the carbonyl groups of C8OBT. The order parameters were evaluated by infrared dichroism following the method of Kruk *et al.* [2].

The local order parameter that describes degree of alignment of a sub-unit in the liquid crystal molecule was obtained by this method. Infrared dichroism was used and the intensity of absorption in the isotropic phase was compared with that in the mesophases. The direction angle θ of the transition moment for the infrared incident light was obtained from the absorption ratio. In other words, the manner of alignment can be identified as homogeneous-like or homeotropic-like. The estimation of the order parameter S by Kruk's method was carried out as follows:

$$S = 1 - 3/2\langle \sin^2 \theta \rangle . \qquad (1)$$

From Neff's method for unpolarized radiation [16], the integrated absorbance of the band in the mesophase I_M, and that in the isotropic phase I_{Iso} are

$$I_M = \cos^2 \psi \langle \sin^2 \theta \rangle + 1/2 \sin^2 \psi \langle 1 + \cos^2 \theta \rangle$$

$$I_{Iso} = \cos^2 \psi \langle \sin^2 \theta \rangle_{Iso} + 1/2 \sin^2 \psi \langle 1 + \cos^2 \theta \rangle_{Iso}$$

where ψ is the angle between the functional group and the normal to the substrate, and θ is the angle between the direction of the transition dipole moment and the direction of the incident IR.

In the isotropic phase:

$$\langle \sin^2 \theta \rangle_{Iso} = 2/3, \quad \langle \cos^2 \theta \rangle_{Iso} = 1/3, \quad \text{i.e. } I_{Iso} = 2/3.$$

The dichroic ratio $R_i = I_m / I_{Iso} = I_M \times 3/2$, i.e.

$$R_i = 3/2 \cos^2 \psi \langle \sin^2 \theta \rangle + 3/4 \sin^2 \psi \langle 1 + \cos^2 2\theta \rangle \qquad (2)$$

where I_M is the integrated absorbance of the band in the N_D mesophase and I_{Iso} is that in the isotropic phase. From equations (1) and (2)

$$S = 2(R_i - 1) \ (\text{for } \psi = 90°), \quad S = 1 - R_i \ (\text{for } \psi = 0°).$$

The value of θ is estimated from the dichroic ratio R_i between the isotropic phase and mesophase. A schematic diagram showing the use of the infrared dichroic method for evaluating the order parameters of individual functional groups is shown in figure 1.

The IR spectrum of C8OBT is shown in figure 2. The bands of most interest were attributed to ν_{max}/cm^{-1}: 1745 (C=O str.), 1603 (Aromatic C=C str.).

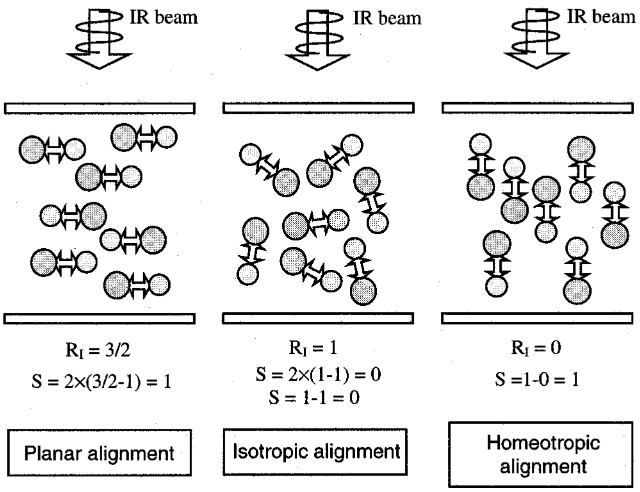


Figure 1. Diagram illustrating the infrared dichroic method used to evaluate the order parameters of chemical bonds.

Downloaded At: 18:02 25 January 2011

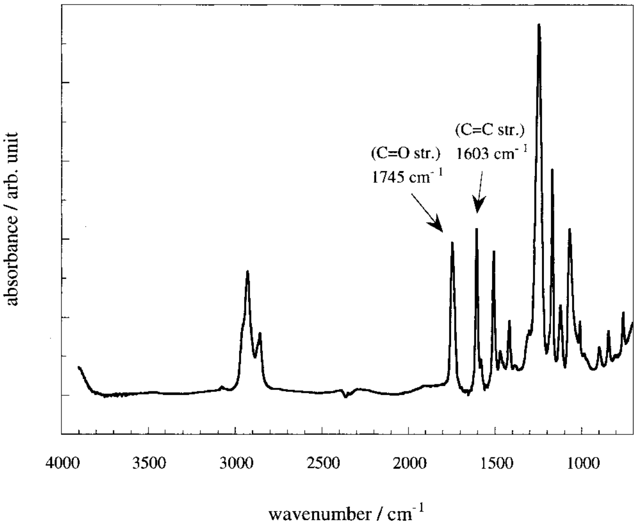


Figure 2. FTIR spectrum of a C8OBT film sandwiched by BaF_2 plates.

3. Results and discussion

3.1. *Texture observation*

As shown in figures 3 (*a*) and 3 (*b*), respectively, C8OBT shows a typical nematic schlieren texture on the glass substrate, while a homeotropic texture was observed when the substrate was polyimide film. As shown in figures 3 (*c*) and 3 (*d*), the texture on the CTAB-coated substrate shows a tilted or planar homogeneous texture in which the optical axes lie more or less parallel to the surfaces, and the molecules themselves lie on their sides on the substrate. This indicates that in the case of polyimide film, the molecular core is aligned parallel to the substrate and the polyimide film induces homeotropic alignment of the C8OBT N_D phase. In contrast, the effect of the CTAB layer is to induce alignment of the core perpendicular to the substrate. The imperfections in the texture in figure 3 (*b*) were possibly due to dust and/or blemishes in the film resulting from the preparation processes. Whilst these results show control of alignment in the N_D phase, it was found that in the Col_r phase, the C8OBT molecules do not uniformly align, but instead form fine domains directed randomly regardless of the substrates. This indicates that the intermolecular interactions in the Col_r phase are stronger than the interaction of the molecules with the substrates. These characteristics were unaffected by temperature over the full range of those mesophases.

3.2. *Order parameters and alignment behaviour*

The temperature dependence of the FTIR spectra was measured in order to evaluate the directions and the order parameters for the triphenylene core and the carbonyl groups of C8OBT in the N_D phase. An independent evaluation of the alignment behaviour of the triphenylene

Downloaded At: 18:02 25 January 2011

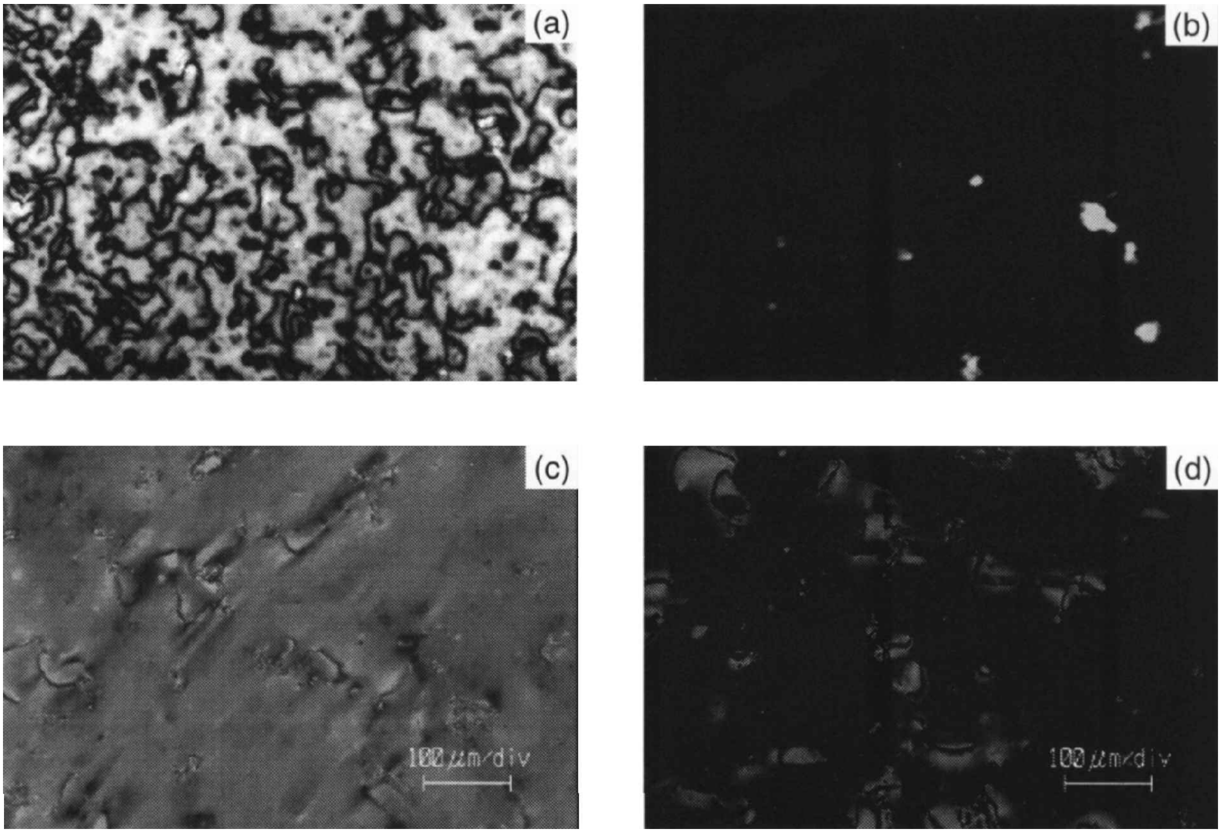


Figure 3. The textures of the N_D phase (200°C) of C8OBT when cooled from the isotropic phase and sandwiched by (*a*) glass plates, (*b*) polyimide, (*c*) CTAB, and (*d*) after the sample in (*c*) was rotated by 45° around the optical axis.

core and the carbonyl groups is important in order to analyse the interaction between the liquid crystalline molecules and the alignment layer of the substrates. Dipole–dipole interactions of the molecules with the substrate surface and the ease of movement of the carbonyl groups around chemical bonds could also be appraised.

Figure 4 shows the temperature dependence of the relative IR absorption intensity. The two characteristic absorption bands at 1603 cm^{-1} (triphenylene aromatic C=C stretch) and 1745 cm^{-1} (carbonyl C=O stretch) were used for the evaluation of the relative absorption intensity. In the case of the polyimide, the relative

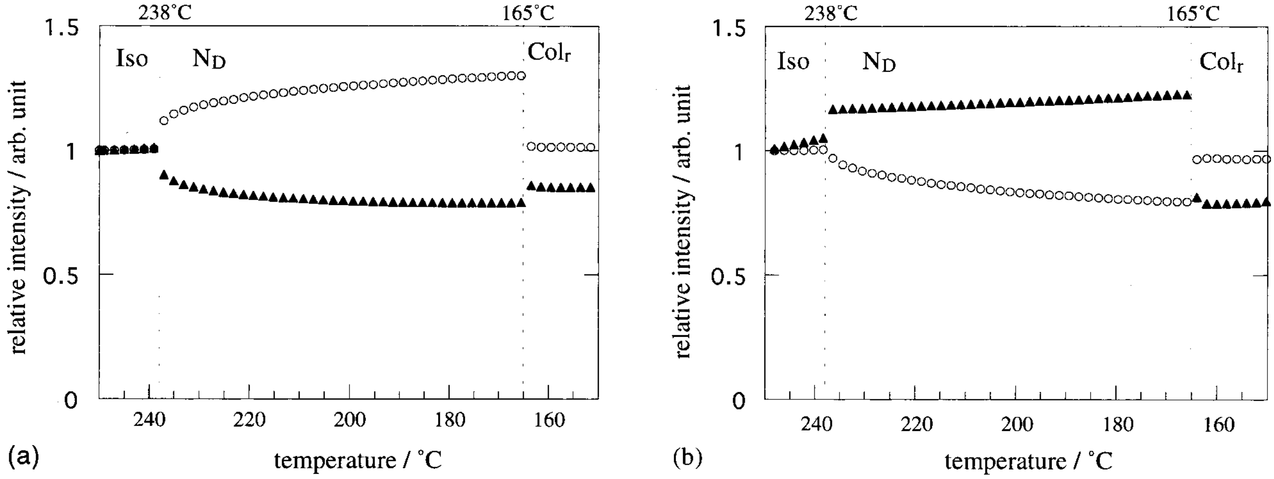


Figure 4. Temperature dependence of the IR absorption intensity relative to that of the isotropic phase for the C=O stretching vibration at 1745 cm^{-1} (▲), and the aromatic C=C stretching vibration at 1603 cm^{-1} (○): (*a*) on the polyimide film, (*b*) on CTAB.

Downloaded At: 18:02 25 January 2011

absorption intensity of the aromatic C=C bond increased in the temperature region of the N_D phase, while that for C=O decreased as shown in figure 4 (*a*). This indicates that the triphenylene core plane is parallel to the substrate, with the carbonyl groups tending to align perpendicular to the substrate coated with polyimide. On the other hand, in the case of CTAB, the relative absorption intensity of the aromatic C=C bond decreased in the temperature region of the N_D phase, while that of the C=O groups increased as shown in figure 4 (*b*). This indicates that the triphenylene core plane tends to align perpendicular to the substrate, while the carbonyl groups align parallel to the substrate, contrary to the behaviour on the polyimide substrate. The direction of these groups is determined from the change in the relative IR absorption intensity between the isotropic and the N_D phases. These results agree with the POM observations.

The temperature dependence of the order parameters of the triphenylene core and the carbonyl groups were evaluated and are shown in figure 5. When the substrate is the polyimide film, the order parameter in the N_D phase of both the triphenylene core and carbonyl groups increases with decreasing temperature. A similar behaviour is observed on the CTAB-coated substrate, although the effect of temperature is less marked for the order parameter of the carbonyl groups. This may indicate that in the N_D phase the triphenylene cores are mutually well aligned, as the molecular fluctuations get smaller with decreasing temperature for both substrates, while the carbonyl groups become gradually aligned with decreasing temperature for the CTAB-coated substrate in the N_D phase.

The directions and the order parameters at 170°C of both the triphenylene core plane and the carbonyl groups are summarized in table 2. These results agree with the results of the POM texture observations for the N_D phase. The order parameter of the triphenylene core on the polyimide ($S = 0.6$) is higher than that on CTAB ($S = 0.2$), though the values for the carbonyl groups are roughly comparable ($S = 0.2 \sim 0.3$) for each substrate in the N_D phase. We believe that the triphenylene core of C8OBT is strongly anchored parallel to the polyimide, while it loosely aligns perpendicular to the CTAB-coated substrate due to the small interactions between the substituent alkyl chains of C8OBT and the long alkyl chain of CTAB. This causes the higher value of the order parameter of the triphenylene core on the polyimide film. This order parameter of the triphenylene core is a little small compared with that evaluated from the ordinary and extraordinary refractive indices of acrylate derivatives of triphenylene ($S = 0.7$) [13]. This could be caused by the absorption by the phenyl rings of the benzoate substituents of C8OBT. According to modelling studies of triphenylene benzoates [17], the phenyl rings tend to form an angle of 80° with the triphenylene core; while the angle between the plane of the peripheral phenyl ring and the plane of the ester linkage which contains the carbonyl group is negligible.

Table 2. The directional alignment and order parameters *S* of the triphenylene core and carbonyl groups of C8OBT in the N_D phase at 170°C.

Substrate	Functional group	*S*	Director to the substrate
Polyimide	triphenylene	0.60	parallel
	carbonyl	0.21	perpendicular
CTAB	triphenylene	0.21	perpendicular
	carbonyl	0.33	parallel

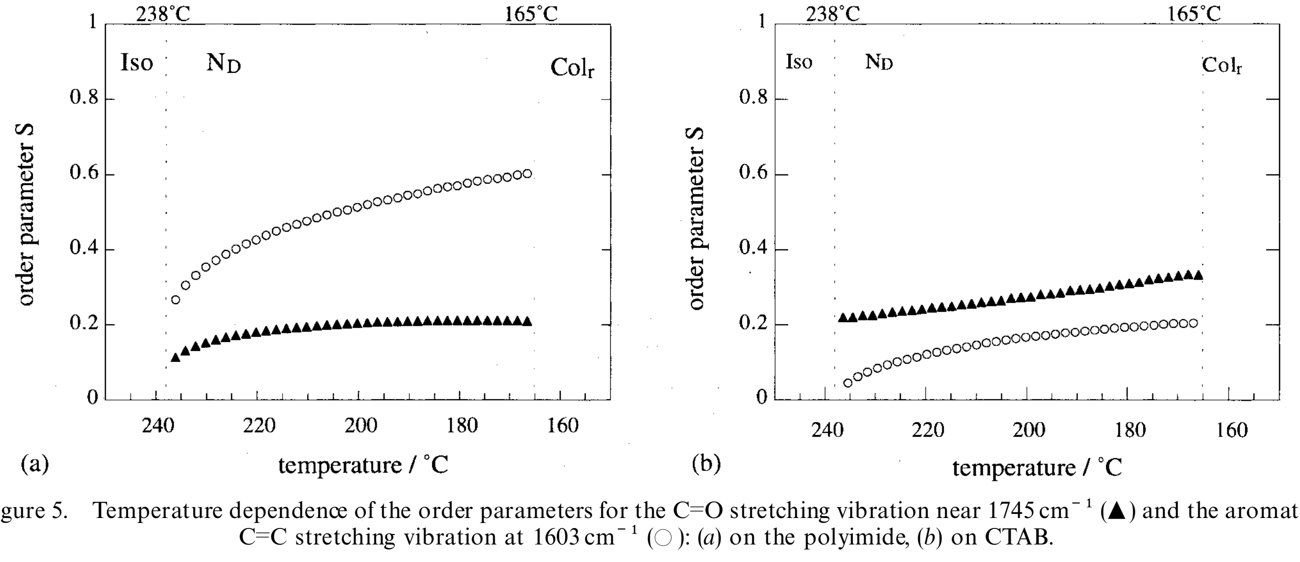


Figure 5. Temperature dependence of the order parameters for the C=O stretching vibration near 1745 cm^{-1} (▲) and the aromatic C=C stretching vibration at 1603 cm^{-1} (○): (*a*) on the polyimide, (*b*) on CTAB.

The order parameter of the carbonyl groups shows a weak dependence on the substrate and a relatively small value. It could be inferred that no special interaction exists between the carbonyl groups of the peripheral phenyl rings and the substrate, in contrast to that between the triphenylene cores themselves and between the core plane and films of substrate.

4. Conclusion

The orientational behaviour of a nematic discotic liquid crystalline triphenylene, C8OBT, was investigated on substrates coated with a polyimide or with CTAB. In the case of the polyimide film, the molecular core is uniformly parallel to the substrate, while the effect of the CTAB layer is to induce alignment of the core perpendicular to the substrate. Infrared dichroism has been used to evaluate the order parameters of the functional groups. The quantitative evaluation of the alignment of each functional group in a liquid crystalline molecule could be used widely for the interpretation of molecular alignment mechanisms at the interface between discotic mesogens and substrates.

The authors would like to acknowledge the financial support of the Agency of Industrial Science and Technology (AIST), Ministry of International Trade and Industry (MITI) under the national R&D project, 'Harmonised Molecular Materials' operated in the Industrial Science and Technology Frontier Program of AIST-MITI.

Downloaded At: 18:02 25 January 2011

References

[1] Chandrasekhar, S., 1992, *Liquid Crystals*, 2nd Edn (Cambridge: Cambridge University Press).

[2] Kruk, G., Kocot, A., Wrzalik, R., Vij, J. K., Karthaus, O., and Ringsdorf, H., 1993, *Liq. Cryst.*, **14,** 807.

[3] Perova, T. S., and Vij, J. K., 1995, *Adv. Mater.*, **7,** 919.

[4] Perova, T. S., Vij, J. K., and Kocot, A., 1998, *Europhys. Lett.*, **44,** 198.

[5] Sakamoto, K., Arafune, R., Ito, N., Ushioda, S., Suzuki, Y., and Morokawa, S., 1996, *J. appl. Phys.*, **80,** 431.

[6] Ichimura, K., 2000, *Chem. Rev.*, **100,** 1847.

[7] Ichimura, K., Furumi, S., Morino, S., Kidowaki, M., Nakagawa, M., Ogawa, M., and Nishiura, Y., 2000, *Adv. Mater.*, **12,** 950.

[8] Ikeda, S., Takanishi, Y., Ishikawa, K., and Takezoe, H., 1999, *Mol. Cryst. liq. Cryst.*, **329,** 1201.

[9] Monobe, H., Awazu, K., and Shimizu, Y., 2000, *Adv. Mater.*, **12,** 1495.

[10] Monobe, H., Awazu, K., and Shimizu, Y., *Mol. Cryst. liq. Cryst.* (in the press).

[11] Mertesdorf, C., Ringsdorf, H., and Stumpe, J., 1991, *Liq. Cryst.*, **9,** 337.

[12] Mori, H., Itoh, Y., Nishimura, Y., Nakamura, T., and Shinagawa, Y., 1996, *Jpn. J. appl. Phys. 1*, **36,** 143.

[13] Favre-Nicolin, C. D., Lub, J. L., and van der Sluis, P., 1997, *Mol. Cryst. liq. Cryst.*, **299,** 157.

[14] Nguyen, H. T., Gasparoux, H., and Destrade, C., 1981, *Mol. Cryst. liq. Cryst.*, **68,** 1049.

[15] Destrade, C., Nguyen, H. T., Gasparoux, H., Malthete, J., and Levelut, A. M., 1981, *Mol. Cryst. liq. Cryst.*, **71,** 111.

[16] Neff, V. D., Gulrich, L. W., and Brown, G. H., 1966, *Mol. Cryst.*, **1,** 225.

[17] Hindmarsh, P., Watson, M. J., Hird, M., and Goodby, J. W., 1995, *J. mater. Chem.*, **5,** 2111.