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

Liquid-crystalline behaviour of benzobisthiazole derivatives as a rigid rod polymer model

O. -K. Kim[a]; H. S. Lee[ab]; T. H. Yoon[ab]; R. Shashidhar[bc]
[a] Materials Chemistry Branch, Code 6120, Naval Research Laboratory, Washington, D.C., U.S.A. [b] Geo-Centers, Inc., Fort Washington, Maryland, U.S.A. [c] Naval Research Laboratory, Center for Bio/Molecular Science and Engineering, Code 6090, Washington, D.C., U.S.A.

To cite this Article Kim, O. -K. , Lee, H. S. , Yoon, T. H. and Shashidhar, R.(1991) 'Liquid-crystalline behaviour of benzobisthiazole derivatives as a rigid rod polymer model', Liquid Crystals, 10: 5, 725 — 731
To link to this Article: DOI: 10.1080/02678299108241740
URL: http://dx.doi.org/10.1080/02678299108241740

LIQUID CRYSTALS, 1991, VOL. 10, NO. 5, 725–731

Liquid-crystalline behaviour of benzobisthiazole derivatives as a rigid rod polymer model

by O.-K. KIM†*, H. S. LEE†§, T. H. YOON†§
and R. SHASHIDHAR‡§

† Materials Chemistry Branch, Code 6120, ‡ Center for Bio/Molecular Science and Engineering, Code 6090, Naval Research Laboratory, Washington, D.C. 20375, U.S.A.

(*Received 21 February 1991; accepted 11 June 1991*)

Novel materials with a new type of rigid core, namely benzobisthiazole, have been synthesized. The exhibition of liquid-crystallinity is found to be dependent upon the linkage between the rigid core and the alkyloxy phenyl terminal moieties. An interesting feature is the occurrence of tilted smectic phases (smectic C and smectic F) even though there is no significant central dipole moment transverse to the molecule.

1. Introduction

Benzobisthiazole (BBT) is an active component of poly(4-phenylene benzobisthiazole) [1], a highly ordered rigid rod polymer possessing a high modulus and high strength [2, 3]. However, a drawback of the polymer property is its insolubility in organic solvents. Several different approaches have been made to improve its processability by making block copolymers [3] with a coil block or complex formation with Lewis acids [4]. An alternative approach to this could be a thermotropic liquid crystal formation by introducing flexible spacers (or side-chains) between (or on to) the rigid rod units. Such a structural modification can lead to the improvement of physical properties of stiff chain macromolecules by lowering the melting point and increasing the solubility [5].

As a first step in this direction, we have undertaken a study of the liquid-crystalline behaviour of rigid rod model compounds with BBT as the mesogenic core. In the model compounds, BBT is symmetrically atttached either directly or through thiomethylene linkages to the 4-alkyloxy-benzene residue (see figure 1).

In this report we discuss the liquid-crystalline behaviour of these materials with respect to the BBT linkage and alkyloxy chain length. This is the first example of liquid-crystalline behaviour observed with BBT as the mesogenic core.

2. Experimental

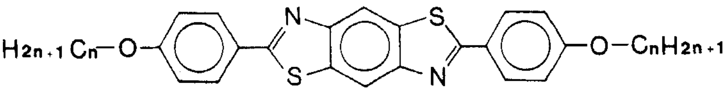
2.1. *Synthesis of materials*

2,6-Di(4-alkyloxyphenyl)benzo[1,2-d:4,5-d′]bisthiazoles (**I**-C_8, **I**-C_{12} and **I**-C_{16}) were synthesized by condensing 2,5-diamino-1,4-benzenedithiol dihydrochloride (DADT) [1], with the respective 4-alkyloxybenzoic acid in methanesulphonic acid (MSA) containing phosphorus pentoxide (4 per cent by weight based on MSA) at 90°C

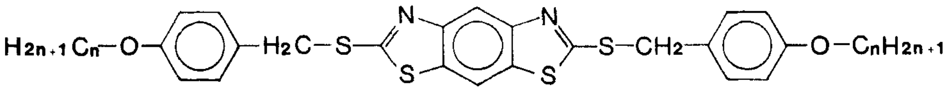
---

* Author for correspondence.

§ Present address: Geo-Centers, Inc., 10904 Indian Head Highway, Fort Washington, Maryland 20744, U.S.A.



I



II

n structure	8	12	16
I	I-8	I-12	I-16
II	II-8	II-12	II-16

Figure 1. Chemical structures (**I** and **II**) of the two series of compounds synthesized.

for 1 h and then 80°C for another 5 h. The resulting reaction mixture was filtered and the precipitate washed thoroughly with water and dried *in vacuo*. It was recrystallized repeatedly from *N*-methylpyrrolidone. Calc. for $C_{52}H_{76}N_2S_2O_2$(**I**-C_{16}): C, 75·73 per cent; H, 9·22 per cent; N, 3·40 per cent; S, 7·77 per cent. Found: C, 75·24 per cent, H, 9·07 per cent; N, 3·99 per cent; S, 8·43 per cent. Analytical results of **I**-C_8 and **I**-C_{12} were also satisfactory.

2,6-Di(4-alkyloxybenzylthio)benzo[1,2-d : 5,4-d′]bisthiazoles (**II**-C_8, **II**-C_{12} and **II**-C_{16}) were synthesized by heating a mixture of 1 mmole of 2,6-dimercaptobenzo[1,2-d : 5,4-d′] bisthiazole (DMBT) [6] and 2 mmoles of 4-alkyloxybenzyl chloride in 15 ml of *N*-methylpyrrolidone in which was dissolved 1·2 g of anhydrous potassium carbonate at 75°C for 3 h. The reaction mixture was treated with water to precipitate the product which, after filtration, was then washed thoroughly with water, methanol and chloroform. The solid was recrystallized from benzene. Calc. for $C_{54}H_{80}N_2S_4O_2$ (**II**-C_{16}): C, 70·74 per cent; H, 8·73 per cent; N, 3·05 per cent; S, 13·97 per cent. Found: C, 70·69 per cent; H, 8·99 per cent; N, 2·78 per cent; S, 14·26 per cent. Analytical results of **II**-C_8 and **II**-C_{12} were also satisfactory.

2.2. *Optical and thermal characterization*

The phase transitions were observed with a Zeiss microscope in conjunction with a Linkam THM 600 hot stage and PR 600 controller. Differential scanning calorimetry (DSC) results were recorded at a scan rate of 5°C min^{-1} with a Perkin–Elmer DSC 7 instrument. The transition temperatures and the enthalpy changes were taken from the cooling cycle of the thermogram.

3. Results and discussion

The results obtained by optical microscopy and DSC are given in the table and figures 2–5. It is observed that there is a distinct difference in the thermal behaviour between compounds with structure **I** and **II** depending on the linkage between the BBT and alkyloxyphenyl moieties. Liquid-crystallinity is seen when there is a direct linkage while a thiomethylene linkage does not promote mesomorphism. This behaviour is seen for alkyl chain lengths, $n = 8$, 12 or 16. While the marked difference in the thermal behaviour of compounds with structures **I** and **II** might be attributed to the isomeric BBT structures themselves, this is unlikely because the differences in steric and ring dipolar forces between them are too small to give rise to intermolecular force changes. It is more likely that the thiomethylene linkage creates a notable flexibility between the rigid moieties. This hypothesis is supported by their isotropic temperatures, which are greatly lowered for compounds with structure **II** as compared with those of structure **I**. When the linking unit is thioester (–S–CO–), liquid-crystalline mesophases are observed [7] at relatively higher temperatures. It is known [8–10] that a flexible linking unit such as $-CH_2CH-$ between mesogens and residues shows very weak or no nematic tendencies while the ester function has a role of conjugative interaction within the ester group and with the rings, leading to a double bond character.

Since BBT is a flat and elongated fused ring structure, when it is used as a mesogenic core a high transition temperature will result. By the same token, molecules incorporating a BBT moiety in their structures have a high melting point and a poor solubility. Therefore, it is not surprising that when the BBT core and the phenyl ring are directly linked and kept free of steric hindrance, the melting point will increase further. For this reason, structure **I** derivatives exhibit very high transition temperatures, the isotropic transition temperatures being significantly lowered with increasing terminal alkyl chain length. All of these directly linked rigid rod mesogenic compounds exhibit tilted smectic phases. As commonly observed, only the shortest compound, namely **I**-C_8, exhibits the nematic phase over a narrow temperature range. The nematic phase is absent in the longer **I**-C_{12} and **I**-C_{16} compounds. This may be due to the combination

Transition temperatures and enthalpy changes of benzenebisthiazole derivatives.

Compound	Transition temperature	ΔH/ kJ mol^{-1}
I-C_{16}	S_C 290°C I	16·8
	S_F 272°C S_C	1·13
	S_H 229°C S_F	13·5
I-C_{12}	S_C 308°C I	16·2
	S_H 235°C S_C	13·4
I-C_8	N 344°C I	2·68
	S_C 339·5°C N	8·28
	S_G 259°C S_C	14·6
II-C_{16}	C 139°C I	65·3
II-C_{12}	C 145°C I	57·4
II-C_8	C 150°C I	43·9

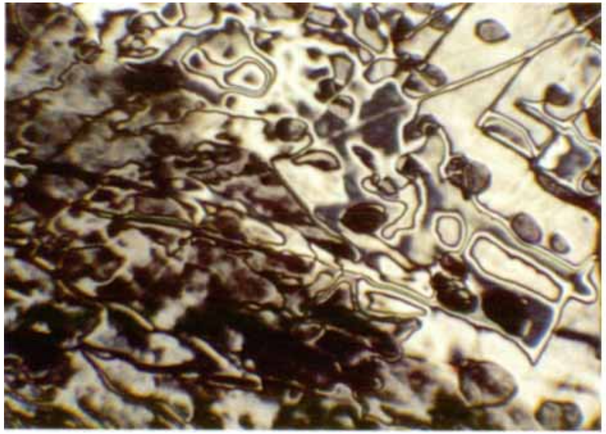


Figure 2. Schlieren texture of the nematic phase transforming to the schlieren texture of the smectic C phase for the I-C_8 compound ($T = 340°C$).

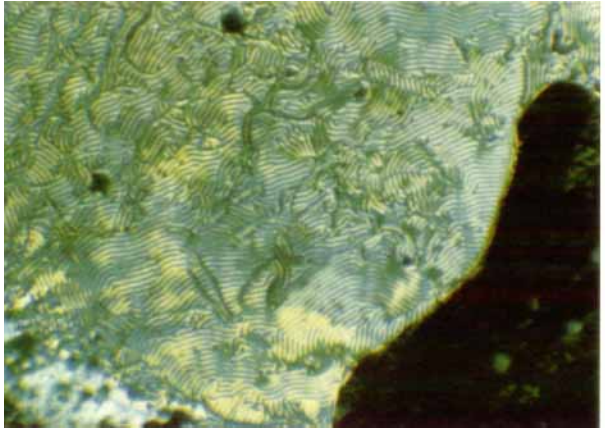


Figure 3. Another area of compound **I-C_8** showing a banded texture at the smectic C–nematic transition.

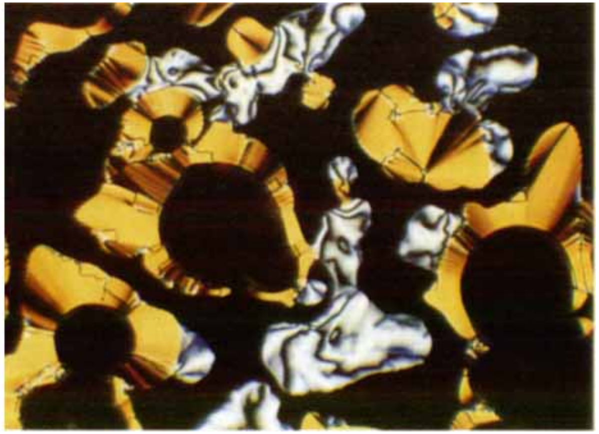


Figure 4. Smectic C phase of **I-C_{16}** emerging from the isotropic phase ($T = 290°C$).

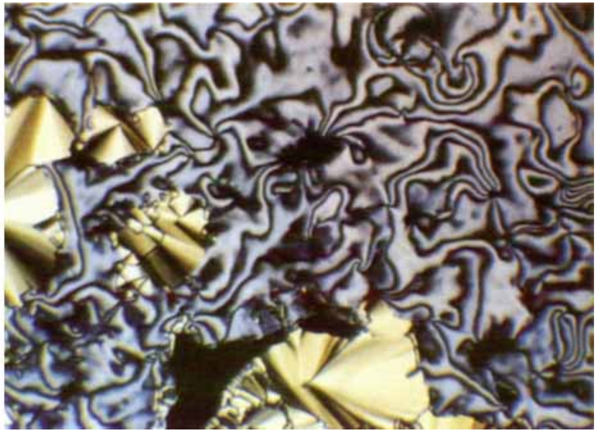


Figure 5. Schlieren texture of the smectic F phase of **I-C_{16}**. ($T = 230°C$).

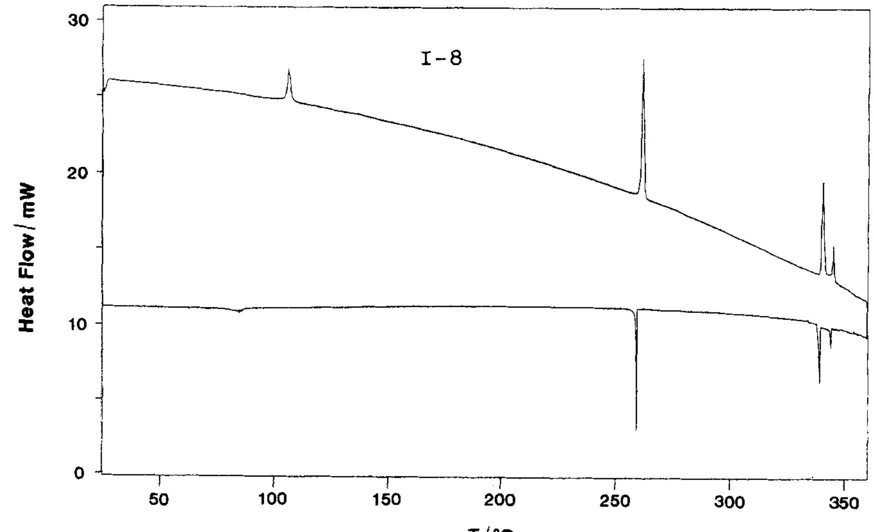


Figure 6. DSC trace for I-C_8 showing the transitions in both heating and cooling modes (scanning rate = 5°C min^{-1}).

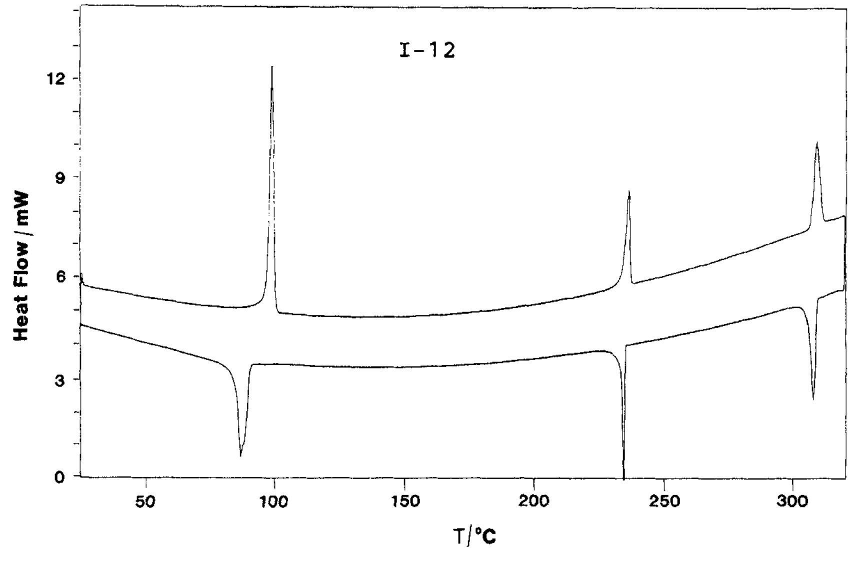


Figure 7. DSC trace for I-C_{12} recorded for both the heating and cooling cycles (scanning rate = 5°C min^{-1}).

of a longer rigid segment with a short flexible segment. For the I-C_8 compound, upon transformation of the nematic phase (340°C) into the smectic C (S_C) phase, a schlieren texture appears (see figure 2). Sometimes a banded texture is observable at the smectic C–nematic transition (see figure 3). On further cooling, the schlieren texture turns into the mosaic texture of the smectic G (S_G) phase. The phase behaviour of I-C_{12} and I-C_{16} compounds is similar except for the smectic F (S_F) phase which is not present for the I-C_{12} compound. The S_C phase is characterized by a schlieren texture which coexists with a focal conic texture observed at the periphery of air bubbles trapped in the sample (see figure 4). At the onset of the S_F phase, the schlieren texture becomes sharper while

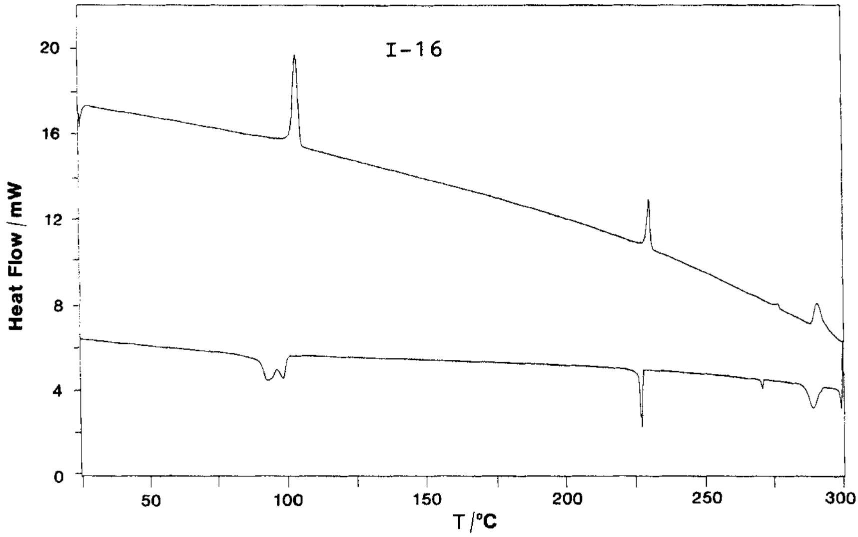


Figure 8. DSC trace for I-C_{16} recorded for both the heating and cooling cycles (scanning rate = 5°C min^{-1}).

there is also a change in the focal conic texture (see figure 5). On further cooling, a mosaic texture characteristic of the higher order smectic is seen.

The DSC traces for the structure **I** series are shown in figures 6–8. Of particular interest is a sharp peak seen for the smectic F–smectic C transition (see figure 8). These two phases have the same macroscopic symmetry and hence the transition between them has to be first order. There can also exist a continuous evolution from one phase to the other. Recent high resolution X-ray studies [11] on a material exhibiting an apparent S_F–S_C transition have failed to produce evidence of the existence of such a transition. Considering that I-C_{12} does show a sharp peak, a high resolution X-ray study of this material would be of interest.

The occurrence of the smectic C phase in structure **I** molecules with highly rigid cores is interesting. It has been argued on theoretical grounds that the smectic C phase is due to dipolar forces [12–14] or to molecular packing driven by zig-zag shaped molecules with a rigid core [15]. In the present systems we have incorporated a new type of mesogenic core, BBT. This moiety is a planar rigid core free of steric hindrance. Compounds with structure **I** which have no significant transverse central dipole moment, exhibit the S_C phase. This is reminiscent of square planar metal complexes as mesogenic cores in which bidentate coordination of ligands to a metal ion produces an anti-symmetry and leads to cancellation of the dipole moment. Compounds consisting of such a metal complex in the rigid core and flexible alkyloxy terminal groups have been recently reported [16, 17]; they exhibit S_C phases that are sensitive to the steric hindrance in the core. On the other hand, compounds with structure **II** possess a significantly higher dipole moment in the rigid core, but they do not show any smectic phases. This is probably due to the presence of flexible linking groups between BBT and the alkyloxyphenyl moieties. This flexible linkage induces a molecular distortion from the planar configuration required for the molecular packing that leads to a S_C phase. It is likely, therefore, that the exhibition of a S_C phase by the compounds comprising the rigid BBT core is dictated by the molecular geometry.

The partial support of the Office of Naval Research is gratefully acknowledged.

References

[1] Wolfe, J. F., and Arnold, F. E., 1981, *Macromolecules*, **14**, 909.

[2] Allen, S. R., Farris, R. J., and Thomas, E. L., 1985, *J. Mater. Sci.*, **20**, 2727.

[3] Wolfe, J. F., 1988, *Encyclopedia of Polymer Science and Engineering*, Vol. 11, 2nd edn (Wiley), pp, 601–635.

[4] Jenekhe, S. A., Johnson, P. O., and Agarawal, A. K., 1989, *Macromolecules*, **22**, 3216.

[5] Ballauf, M., 1989, *Angew. Chem., Int. Ed.*, **28**, 253.

[6] Grandolini, G., 1960, *Gazz. chim. Ital.*, **90**, 122.

[7] Kim, O.-K., Lee, H. S., Yoon, T. H., and Shashidhar, R. (unpublished data).

[8] Gray, G. W., and McDonnell, D. G., 1986, *Molec. Crystals liq. Crystals*, **37**, 189.

[9] Gray, G. W., 1979, *The Molecular Physics of Liquid Crystals*, edited by G. R. Luckhurst and G. W. Gray (Academic Press), pp, 1–29, 263–284.

[10] He, G.-X., Wada, F., Kikukawa, K., and Matsuda, T., 1987, *J. chem. Soc. Chem. Commun.*, 1294.

[11] Brock, J. D., Birgeneau, R. J., Evans-Lutterodt, K. W., Litster, J. D., Horn, P. M., Stephensen, G. B., and Tajbaksh, A. R., 1986, *Phys. Rev. Lett.*, **57**, 98.

[12] McMilan, W. L., 1973, *Phys. Rev.* A, **8**, 1921.

[13] Cabib, D., and Benguigui, L., 1977, *J. Phys. Paris*, **38**, 419.

[14] Van der Meer, B., and Vertogen, G., 1979, *J. Phys. Colloq., Paris*, **40**, C3.

[15] Wulf, A., 1975, *Phys. Rev.* A, **11**, 365.

[16] Marcos, M., Romero, P., Serrano, J. L., Barbera, J., and Levelut, A. M., 1990, *Liq. Crystals*, **7**, 251.

[17] Ohta, K., Ema, H., Morizumi, Y., Watanabe, T., Fujimoto, T., and Yamamoto, I., 1990, *Liq. Crystals*, **8**, 311.