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Synthesis and characterization of laterally substituted bis(alkoxybenzoyloxy)hydroquinones

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A new series of laterally substituted bis(alkoxybenzoyloxy)hydroquinone compounds has been synthesized and their mesomorphic properties studied. A number of hydroquinone compounds were synthesized with terminal *n*-alkoxy chains ranging from *n*-butyloxy to *n*-decyloxy. Additionally, lateral substituents ranging from *n*-butyl to *n*-octyl were incorporated through esterification at the remaining unsubstituted phenolic oxygen atoms. By optimizing the combination of the end group and lateral moieties we were able to tailor the molecular structure to form different liquid crystalline phases.

1. Introduction

In recent years, the rate of synthesis of new mesogenic materials has increased dramatically in an attempt to satisfy the growing range of industrial applications. One fascinating opportunity for the use of liquid crystals (LCs) is in the field of acoustography or acoustic wave imaging. The goal of using liquid crystals in acoustic imaging is being actively pursued because they have the potential to provide direct and inexpensive means for acoustic-to-optic image conversion [1–5]. Although the fundamental mechanism that dictates this coupling is still not known, recent experiments suggest that the attachment of lateral substituents to the molecular core of liquid crystalline materials increases the acoustic sensitivity [6–13].

The mesomorphic behaviour, and hence the suitability for different applications, has been shown to depend strongly on the relative positions and types of the lateral substituents incorporated into the materials [14]. Recently, 2,5-bis(4-alkoxybenzoyloxy)hydroquinone compounds were synthesized and incorporated in 'shish-kebab-type' chiral polymers [15]. The parent bis(alkoxybenzoyloxy)hydroquinone molecules have high melting points and small or non-existent mesogenic phases. By functionalizing the hydroquinones with different lateral substituents we hoped to tailor the mesogenic properties of the molecules [16]. Additional benefits of lateral substitution result from combinations of both steric and electronic effects [17, 18]. The steric effects caused by the protrusion of the substituents tend to disrupt the side-to-side intermolecular forces of attraction, thereby reducing the melting point and the tendency to form smectic mesophases. At the same time, these lateral substituents are less disruptive towards the formation of the non-lamellar nematic phase.

In this paper, we report the synthesis and characterization of novel, functionalized bis(alkoxybenzoyloxy)hydroquinone molecules. The hydroquinone derivatives were prepared in order to understand how changes and different combinations of lateral and end group substituents affect their mesomorphic properties.

2. Experimental

2.1. Characterization

¹H and ¹³C NMR spectra were recorded on a JEOL 400 MHz spectrometer. Chloroform-d (CDCl₃) was used as the solvent and tetramethylsilane (TMS) as the internal standard. DSC thermograms were recorded on a Perkin-Elmer DSC 7 instrument, at a scanning rate of 5° C min⁻¹. Textures were observed on a Nikon polarizing optical microscope equipped with a Mettler FP 82 heating stage attached to a Mettler FP 80 temperature controller.

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2.2. Synthesis

Purification by flash column chromatography was performed using silica gel 60, 230–400 mesh (Merck). 2,5-Dihydroxyquinone was prepared according to a literature procedure [19]. All other compounds were commercial products and used without further purification.

2.2.1. General synthesis of bis(alkoxybenzoyloxy)hydroquinones [15]

The bis(butyoxybenzoyloxy)hydroquinone 1 is given as an example. In a round bottom flask 6.0 ml (0.066 mol) of *n*-butanol was dissolved in 20 ml pyridine. Benzenesulphonyl chloride (10 ml, 0.078 mol) was added to the flask. The mixture was stirred at 0°C for 5 h then warmed to room temperature and stirred for 18 h. Water (50 ml) and hydrochloric acid (10 ml) were added to the flask. The organic layer was isolated and washed successively with water, sodium carbonate, dilute sulphuric acid, dilute hydrochloric acid and water. This solution was dried over magnesium sulfate, filtered and the solvent removed by rotatory evaporation. The *n*-butyl benzenesulphonylate was isolated as a clear liquid (6.6 g, 0.031 mol, 47% yield).

The *n*-butyl benzenesulphonylate (1.9 g, 8.9 mmol) was mixed with 4-hydroxybenzoic acid (2.4 g, 17 mmol), KOH (2.0 g, 36 mmol), ethanol (10 ml) and water (10 ml). The mixture was heated at reflux for 48 h then cooled to room temperature. Hydrochloric acid was added to the solution until the pH was 1–2 and a white precipitate was formed. The raw product was purified via recrystallization from ethanol (1.2 g, 6.2 mmol, 70% yield). The product was then added to an excess of thionyl chloride (4 ml, 54 mmol, *d* 1.631) and heated at reflux for 1 h. Excess thionyl chloride was removed via rotary evaporation, and the resulting acid chloride washed with petroleum ether (30 ml).

Tetrahydrofuran (8 ml) and pyridine (1 ml) were added to the acid chloride to make a solution, into which 2,5-dihydroxybenzoquinone (0.8 g, 5.7 mmol) dissolved in THF (10 ml) was added slowly. The solution was stirred for 20 h. The solvent was removed and the residue recrystallized from acetone to give a white solid. The quinone was reduced to the hydroquinone product (0.23 g, 0.42 mmol, 15% yield) using an aqueous solution of ammonium chloride and sodium hydrosulfite. Melting point 211°C. ¹H NMR (CDCl₃, TMS) δ 0.8 (t, 6H, CH3-CH2), 1.0 (t, 6H, CH3-CH2), 1.3 (sextet, 4H, (CH₂-CH₂), 1.6 (m, 4H, (CH₂-CH₂), 1.8 (m, 4H, (CH₂-CH₂), 2.4 (t, 4H, (CH₂-C(O)), 4.0 (t, 4H, (CH_2-O) , 7.0 (d, 4H, (ArH)), 7.3 (s, 2H, (ArH)), 8.1 (d, 4H, (ArH)). ¹³C NMR (CDCl₃, TMS) δ 13.7, 19.3, 27.0, 31.2, 68.1, 114.4, 118.5, 120.6, 132.5, 140.0, 163.5, 170.8.

2.2.2. General synthesis of laterally substituted hydroquinone compounds

Hydroquinone derivative 7 is given as an example. In a nitrogen-flushed flask, hydroquinone 1 (0.1 g, 0.2 mmol), pyridine (0.05 ml, 0.6 mmol, d 0.978), butanoyl chloride (0.1 ml, 0.9 mmol, d 1.026) and DMAP (10 mg) were dissolved in 10 ml dichloromethane and stirred at room temperature for 48 h. The solution was acidified with 1N HCl then washed with a Na₂CO₃ saturated aqueous solution and brine. The aqueous layer was extracted with two 50 ml portions of dichloromethane; the organic layers were isolated, dried over MgSO₄ and the solvent removed by rotatory evaporation. The residue was purified using column chromatography (silica gel, dichloromethane) to give the product as a white solid (0.12 g, 0.2 mmol, 97% yield). ¹H NMR (CDCl₃, TMS) δ 0.8 (t, 6H, CH3-CH2), 1.0 (t, 6H, CH3-CH2), 1.3 (sextet, 4H, (CH₂-CH₂), 1.6 (m, 4H, (CH₂-CH₂), 1.8 (m, 4H, (CH_2-CH_2) , 2.4 (t, 4H, $(CH_2-C(O))$, 4.0 (t, 4H, (CH₂-O)), 7.0 (d, 4H, (ArH)), 7.3 (s, 2H, (ArH)), 8.1 (d, 4H, (ArH)). ¹³C NMR (CDCl₃, TMS) δ 13.7, 13.9, 19.3, 22.2, 27.0, 31.2, 33.8, 68.1, 114.4, 118.5, 120.6, 132.5, 140.0, 163.5, 163.9, 170.8. Anal: calcd for C₃₆H₄₂O₁₀ C 68.12, H 6.67; found C 68.30, H 6.85%.

3. Results and discussion 3.1. Synthesis

We synthesized six different parent hydroquinone compounds (1-6) possessing end chain alkoxy groups with lengths ranging from four to ten carbons (table 1) [15]. Hydroquinones 1-6 are all high melting solids and show no significant mesogenic behaviour; they are white solids that decompose rapidly at temperatures above their melting points to red solids.

Table 1. Structures and melting points of parent (alkoxybenzoyloxy)hydroquinones.

R.O-	O OH O OH HO O	→
Compound	R	Melting point
1 2 3 4 5 6	$\begin{array}{c} n\text{-}C_{4}H_{9} \\ n\text{-}C_{5}H_{11} \\ n\text{-}C_{6}H_{13} \\ n\text{-}C_{8}H_{17} \\ n\text{-}C_{10}H_{21} \\ \hline \end{array}$	211 196 190 197 188 181

Table 2.	Structures	and	phase	transition	temperatures	of	laterally	substituted	(alkoxybenzoyloxy)hydroquinones.	Cr = crystal
N = nematic $I = isotropic phase$										

Hydroquinone	R	R'	Phase transitions
7	$n-C_4H_9$	n-C ₄ H ₉	Cr 87 N 137 I
8	$n-C_6H_{13}$	$n-C_4H_9$	Cr 106 N 123 I
9	$n - C_8 H_{17}$	$n-C_4H_9$	Cr 118 N 130 I
10	$n - C_{10} H_{21}$	$n-C_4H_9$	Cr 118 I
11		<i>n</i> -C ₄ H ₉	Cr 110 N* 130 I
12	$n - C_8 H_{17}$	CH ₂ -CH ₂ -CH ₂ -CH=CH ₂	Cr 110 N 125 I
13	$n - C_{10} H_{21}$	CH ₂ -CH ₂ -CH ₂ -CH=CH ₂	Cr 110 I
14	$n - C_8 H_{17}$	$n-C_8H_{17}$	Cr 85 N 99 I
15	$n - C_{10} H_{21}$	$n-C_8H_{17}^{-1}$	Cr 96 N 107 I
16	$n-C_5H_{11}$	$n-C_8H_{17}$	Cr 120 I
17	$n-C_5H_{11}$	CH ₂ -CH ₂ -CH ₂ -CH=CH ₂	Cr 94 I
18	$n-C_5H_{11}^{11}$	$CF_2 - CF_2 - CF_3$	Cr 58 I
19	$n-C_5H_{11}^{11}$	$n-\tilde{C_4}H_9$	Cr 102 I

The parent hydroquinone compounds were functionalized with lateral alkoxy substituents via an esterification reaction with the corresponding acid chloride. Hydroquinones 1-6 were systematically reacted to give different chain lengths in the two lateral positions in the central core of the molecules. Table 2 shows the thirteen derivatives synthesized (7-19).[†] We were able to incorporate n-butyl, n-pentyl, and n-octyl alkoxy groups into the lateral positions. The pentyl substituents include a terminal unsaturation unit that allows for further chemical modification. We also incorporated a highly hydrophobic group in the lateral side chain positions with a -CF₂- CF₂-CF₃ moiety. The fluorinated compound 18 allowed us to probe the effect of non-lipophilic intermolecular interactions on the formation of liquid crystalline phases.

Compound 7: 97% yield. ¹H NMR (CDCl₃, 400 MHz) δ 0.8 (t, 6H, CH₃-CH₂), 1.0 (t, 6H, CH₃-CH₂), 1.3 (sextet, 4H, (CH₂-CH₂), 1.6 (m, 4H, (CH₂-CH₂), 1.8 (m, 4H, (CH₂-CH₂), 2.4 (t, 4H, (CH₂-C(O)), 4.0 (t, 4H, (CH₂-O)), 7.0 (d, 4H, (ArH)), 7.3 (s, 2H, (ArH)),

[†]For textual simplicity, the alkoxy end groups and ester-linked lateral substituents are denoted *n*-butyl, *n*-octyl, etc., the exact linkage being understood.

8.1 (d, 4H, (ArH)). $^{13}\mathrm{C}$ NMR (CDCl₃, 400 MHz) δ 13.7, 13.9, 19.3, 22.2, 27.0, 31.2, 33.8, 68.1, 114.4, 118.5, 120.6, 132.5, 140.0, 163.5, 163.9, 170.8. Anal: calcd for $\mathrm{C_{36}H_{42}O_{10}}$ C 68.12, H 6.67; found C 68.30, H 6.85%.

Compound 8: 95% yield. ¹H NMR (CDCl₃, 400 MHz) δ 0.8 (t, 6H, CH₃-CH₂), 1.0 (t, 6H, CH₃-CH₂), 1.3-1.6 (m, 8H, (CH₂-CH₂), 1.6 (m, 4H, (CH₂-CH₂), 1.8 (m, 4H, (CH₂-CH₂), 2.4 (t, 4H, (CH₂-C(O)), 4.0 (t, 4H, (CH₂-O)), 7.0 (d, 4H, (ArH)), 7.3 (s, 2H, (ArH)), 8.1 (d, 4H, (ArH)). Anal: calcd for C₄₀H₅₀O₁₀ C 69.54, H 7.30; found C 69.6, H 7.29%.

Compound **9**: 99% yield. ¹H NMR (CDCl₃, 400 MHz) δ 0.8 (t, 6H, CH₃-CH₂), 1.0 (t, 6H, CH₃-CH₂), 1.3-1.6 (m, 12H, (CH₂-CH₂), 1.6 (m, 4H, (CH₂-CH₂), 1.8 (m, 4H, (CH₂-CH₂), 2.4 (t, 4H, (CH₂-C(O)), 4.0 (t, 4H, (CH₂-O)), 7.0 (d, 4H, (ArH)), 7.3 (s, 2H, (ArH)), 8.1 (d, 4H, (ArH)). Anal: calcd for C₄₄H₅₈O₁₀ C 70.75, H 7.83; found C 70.83, H 7.85%.

Compound **10**: 99% yield. ¹H NMR (CDCl₃, 400 MHz) δ 0.8 (t, 6H, CH₃-CH₂), 1.0 (t, 6H, CH₃-CH₂), 1.3–1.6 (m, 16H, (CH₂-CH₂), 1.6 (m, 4H, (CH₂-CH₂), 1.8 (m, 4H, (CH₂-CH₂), 2.4 (t, 4H, (CH₂-C(O)), 4.0 (t, 4H, (CH₂-O)), 7.0 (d, 4H, (ArH)), 7.3 (s, 2H, (ArH)), 8.1 (d, 4H, (ArH)). Anal: calcd for C₄₈H₆₆O₁₀ C 71.79, H 8.28; found C 71.60, H 8.39%.

Compound 11: 54% yield. ¹H NMR (CDCl₃, 400 MHz) δ 0.8 (t, 3H, CH₃–CH₂), 0.9 (t, 3H, CH₃–CH₂), 1.0 (t, 6H, CH₃–CH₂), 1.3 (sextet, 8H, (CH₂–CH₂), 1.6 (m, 4H, (CH₂–CH₂), 1.8 (m, 4H, (CH₂–CH₂), 2.4 (t, 4H, (CH₂–C(O)), 3.8 (m, 4H, (CH₂–(O)), 7.0 (d, 4H, (ArH)), 7.3 (s, 2H, (ArH)), 8.1 (d, 4H, (ArH)). Anal: calcd for C₃₈H₄₆O₁₀ C 68.86, H 7.0; found C 68.69, H 7.28%.

Compound **12**: 92% yield. ¹H NMR (CDCl₃, 400 MHz) δ 0.8 (t, 6H, CH₃-CH₂), 1.0 (t, 6H, CH₃-CH₂), 1.3-1.6 (m, 12H, (CH₂-CH₂), 1.6 (m, 4H, (CH₂-CH₂), 1.8 (m, 4H, (CH₂-CH₂), 2.4 (t, 4H, (CH₂-C(O)), 4.0 (t, 4H, (CH₂-O)), 5.0 (dd, 4H, (CH₂=CH)), 5.7 (m, 2H, (CH=CH₂)), 7.0 (d, 4H, (ArH)), 7.3 (s, 2H, (ArH)), 8.1 (d, 4H, (ArH)). Anal: calcd for C₄₆H₆₂O₁₀ C 71.29, H 8.06; found C 71.43, H 7.90%.

Compound **13**: 68% yield. ¹H NMR (CDCl₃, 400 MHz) δ 0.8 (t, 6H, CH₃-CH₂), 1.0 (t, 6H, CH₃-CH₂), 1.3-1.6 (m, 16H, (CH₂-CH₂), 1.6 (m, 4H, (CH₂-CH₂), 1.8 (m, 4H, (CH₂-CH₂), 2.4 (t, 4H, (CH₂-C(O)), 4.0 (t, 4H, (CH₂-O)), 5.0 (dd, 4H, (CH₂-CH)), 5.7 (m, 2H, (CH=CH₂)), 7.0 (d, 4H, (ArH)), 7.3 (s, 2H, (ArH)), 8.1 (d, 4H, (ArH)). Anal: calcd for C₅₀H₇₀O₁₀ C 72.26, H 8.49; found C 72.45, H 8.25%.

Compound 14: 98% yield. ¹H NMR (CDCl₃, 400 MHz) δ 0.8 (t, 6H, CH₃-CH₂), 1.0 (m, 6H, CH₃-CH₂), 1.3-1.6 (m, 12H, (CH₂-CH₂), 1.6 (m, 12H, (CH₂-CH₂), 1.8 (m, 4H, (CH₂-CH₂), 2.4 (t, 4H, (CH₂-C(O)), 4.0 (t, 4H, (CH₂-O)), 7.0 (d, 4H, (ArH)), 7.3 (s, 2H, (ArH)), 8.1 (d, 4H, (ArH)). Anal: calcd for C₅₂H₇₄O₁₀ C 72.70, H 8.68; found C 72.60, H 8.55%.

Compound **15**: 95% yield. ¹H NMR (CDCl₃, 400 MHz) δ 0.8 (t, 6H, CH₃-CH₂), 1.0 (m, 6H, CH₃-CH₂), 1.3-1.6 (m, 16H, (CH₂-CH₂), 1.6 (m, 12H, (CH₂-CH₂), 1.8 (m, 4H, (CH₂-CH₂), 2.4 (t, 4H, (CH₂-C(O)), 4.0 (t, 4H, (CH₂-O)), 7.0 (d, 4H, (ArH)), 7.3 (s, 2H, (ArH)), 8.1 (d, 4H, (ArH)). Anal: calcd for C₅₆H₈₂O₁₀ C 73.49, H 9.03; found C 73.45, H 8.90%.

Compound **16**: 90% yield. ¹H NMR (CDCl₃, 400 MHz) δ 0.8 (t, 6H, CH₃-CH₂), 1.0 (t, 6H, CH₃-CH₂), 1.1–1.3 (m, 14H, (CH₂-CH₂), 1.6 (m, 4H, (CH₂-CH₂), 1.8 (m, 4H, (CH₂-CH₂), 2.4 (t, 4H, (CH₂-C(O)), 4.0 (t, 4H, (CH₂-O)), 7.0 (d, 4H, (ArH)), 7.3 (s, 2H, (ArH)), 8.1 (d, 4H, (ArH)). Anal: calcd for C₄₆H₆₂O₁₀ C 71.29, H 8.06; found C 71.01, H 7.97%.

Compound 17: 96% yield. ¹H NMR (CDCl₃, 400 MHz) δ 0.8 (t, 6H, CH₃-CH₂), 1.0 (t, 6H, CH₃-CH₂), 1.3-1.5 (sextet, 6H, (CH₂-CH₂), 1.6 (m, 4H, (CH₂-CH₂), 1.8 (m, 4H, (CH₂-CH₂), 2.4 (t, 4H, (CH₂-C(O)), 4.0 (t, 4H, (CH₂-O)), 5.0 (dd, 4H, (CH₂-C(O)), 5.7 (m, 2H, (CH=CH₂)), 7.0 (d, 4H, (ArH)), 7.3 (s, 2H, (ArH)), 8.1 (d, 4H, (ArH)). Anal: calcd for C₄₀H₄₆O₁₀ C 69.95, H 6.75; found C 69.78, H 6.72%.

Compound **18**: 46% yield. ¹H NMR (CDCl₃, 400 MHz) δ 0.8 (t, 6H, CH₃-CH₂), 1.3–1.5 (m, 8H, (CH₂-CH₂),

1.6 (m, 4H, (CH_2-CH_2) , 1.8 (m, 4H, (CH_2-CH_2) , 4.0 (t, 4H, (CH_2-O)), 7.0 (d, 4H, (ArH)), 7.3 (s, 2H, (ArH)), 8.1 (d, 4H, (ArH)). Anal: calcd for $C_{38}H_{32}O_{10}$ C 49.90, H 3.53; found C 50.10, H 3.40%.

Compound **19**: 87% yield. ¹H NMR (CDCl₃, 400 MHz) δ 0.8 (t, 6H, CH₃-CH₂), 1.0 (t, 6H, CH₃-CH₂), 1.3-1.6 (m, 8H, (CH₂-CH₂), 1.6 (m, 4H, (CH₂-CH₂), 1.8 (m, 4H, (CH₂-CH₂), 2.4 (t, 4H, (CH₂-C(O)), 4.0 (t, 4H, (CH₂-O)), 7.0 (d, 4H, (ArH)), 7.3 (s, 2H, (ArH)), 8.1 (d, 4H, (ArH)). Anal: calcd for C₃₉H₄₈O₁₀ C 69.21, H 7.15; found C 69.59, H 7.21%.

3.2. Mesomorphic behaviour

The thermal behaviour of the compounds was examined by DSC and the phase assignments were carried out by means of polarizing optical microscopy. We were able to identify the nematic phases by their textures, and to differentiate a nematic from smectic A and smectic C phases. The phase transitions for all the substituted hydroquinone derivatives (7-19) are listed in table 2. In every hydroquinone, the addition of lateral substituents caused a large reduction in the melting point when compared with the parent hydroquinones 1-6. The series of compounds with butyl side groups (7-10) showed an interesting trend in their ability to form liquid crystalline phases. As the length of the end groups increased from butyl to decyl the temperature at which melting to the nematic phase occurred increased dramatically and the range decreased or disappeared completely. Hydroquinones 7-9 show nematic phases starting at 87, 106, and 118°C, respectively, and are isotropic at 137, 123, and 130°C, respectively. Compound 10 shows no liquid crystalline phase and a melting point of 118°C.

We found a similar trend in liquid crystalline behaviour for the compounds with pentyl and octyl lateral substituents (12-15). As the length of the end-groups is increased from octyl to decyl the range of the liquid crystalline phase decreased or completely disappeared. Interestingly, none of the compounds possessing the n-pentyl end groups (16-19) had nematic liquid crystal phases. We are currently studying other n-pentyl derivatives to understand why their behaviour is not consistent with the rest of the hydroquinone family. One interesting result from hydroquinones 16-19 is that as the lateral substituents were changed from octyl, butyl, pentyl, and $-CF_2-CF_2-CF_3$ the melting points decreased dramatically from 120 to 58°C. By using the -CF₂-CF₂-CF₃ lateral substituent in hydroquinone compounds we were able to create liquid crystalline phases with progressively lower melting points.

4. Conclusions

In conclusion, a new family of laterally substituted bis(alkoxybenzoyloxy)hydroquinone molecules has been

synthesized and their mesomorphic properties studied. The mesomorphic behaviour of the hydroquinone materials depends strongly on the length and type of lateral substituent. Attaching lateral substituents to the hydroquinone central core through ester bonds consistently lowered the melting points of the compounds and allowed the formation of nematic liquid crystal phases. By optimizing the combination of lateral and end group substituents on the hydroquinones we are able to tailor the formation of mesogenic phases.

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References

- [1] KAPUSTINA, O. A., 1984, Mol. Cryst. liq. Cryst., 112, 1.
 [2] SANDHU, J. S., WANG, H., and POPEK, W. J., 2000, Proc
- SPIE, **3955**, 94.
- [3] SANDHU, J. S., and WANG, H., 1997, SBIR, Phase II Report to NSF, Grant No. DMI-9407745.
- SANDHU, J. S., 1988, Mater. Eval., 46, 608.
- [5] DENIS, R., 1978, Ultrasonics, 37.

- [6] NAGAI, S., PETERS, A., and CANDAU, S., 1997, Rev. Phys. Appl., **12**, 21.
- SANDHU, J. S., WANG, H., and POPEK, W. J., 1996, [7] Proceedings on Nondestructive Evaluation Techniques for
- Aging Infrastructure and Manufacturing.
 [8] SANDHU, J. S., 1995, Acoustography, 2nd Edn, Vol. 9, edited by P. O. Moore, and P. McIntire.
 [9] DION, J. L., and JACOB, A. D., 1977, Appl. Phys. Lett.,
- 31, 490.
- [10] COATES, D., 1987, *Liq. Cryst.*, 2, 423.
 [11] HIRD, M., GRAY, G. W., and TOYNE, K. J., 1992, *Liq. Cryst.*, 11, 531.
- [12] BALKWILL, P., BISHOP, D., PEARSON, A., and SAGE, I. C.,
- [12] BALKWILL, P., BISHOP, D., PEARSON, A., and SAGE, I. C., Mol. Cryst. liq. Cryst., 123, 1.
 [13] REIFFENRATH, V., DRAUSE, J., PLACH, H. J., and WEBER, G., 1989, Liq. Cryst., 5, 159.
 [14] HIRD, M., TOYNE, K. J., GRAY, G. W., MCDONNELL, D. G., and SAGE, I. C., 1995, Liq. Cryst., 18, 1.
 [15] LI, Z., NING, C., ZHENG, S., ZHANG, S., CAO, S., ZHANG, D., and ZHOU, Q.-F., 1999, Macromolecules, 32, 7040 **32,** 7040.
- [16] NACIRI, J., RUTH, J., CRAWFORD, G., SHASHIDHAR, R.,
- [10] INACIRI, J., KUTH, J., CRAWFORD, G., SHASHIDHAR, R., and RATNA, B. R., 1995, *Chem. Mater.*, **7**, 1397.
 [17] SASAKI, M., TAKEUCHI, K., SATO, H., and TAKATSU, H., 1984, *Mol. Cryst. lig. Cryst.*, **109**, 169.
 [18] KELLY, S. M., 1984, *Helv. Chim. Acta*, **67**, 1572.
 [19] REUBEN, G. J., and SHONLE, H. A., 1946, *J. Am. chem. Soc.*, **67**, 1034.