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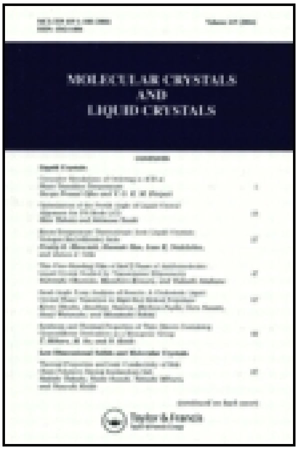

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Synthesis of Mesomorphic Polymers Having 1,3,2-Dioxaborinane Rings in the Main Chain

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Version of record first published: 24 Sep 2006.

To cite this article: Hiroshi Matsubara , Koji Seto & Shigetoshi Takahashi (1994): Synthesis of Mesomorphic Polymers Having 1,3,2-Dioxaborinane Rings in the Main Chain, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 241:1, 9-15

To link to this article: http://dx.doi.org/10.1080/10587259408029740

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Mol. Cryst. Liq. Cryst., 1994, Vol. 241, pp. 9–15
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Synthesis of Mesomorphic Polymers Having 1,3,2-Dioxaborinane Rings in the Main Chain

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(Received April 1, 1993; in final form May 25, 1993)

Two kinds of new polyesters having 1,3,2-dioxaborinane rings in the main chains were synthesized and it has been found that some of them show a nematic phase. The polymers provide the first thermotropic liquid crystalline materials which contain a metalloid atom, boron, arranged regularly in the main chain.

Keywords: dioxaborinane, mesomorphic polymer, liquid-crystalline polymer

INTRODUCTION

In recent years liquid crystalline polymers have attracted great interests in terms of their theoretical aspects, potential application and practical use.[1] There are three types of liquid crystalline polymers based on their structures; side-chain, main-chain and the combined liquid crystalline polymers. Liquid crystalline side-chain polymers have a principal structure consisting of a long main chain and a mesogenic side group attached to the main chain via a flexible spacer group, and liquid crystalline main-chain polymers contain mesogenic groups which are linked to each other with or without a flexible spacer group. Most of the side-chain polymers form thermotropic liquid crystals, whereas main-chain polymers such as polyamides and cellulose derivatives form lyotropic liquid crystals. Aromatic polyamides having a rod-like structure provide the representative example of lyotropic main-chain polymers, and a few examples of thermotropic main-chain liquid crystals include polyesters which have received attention in terms of high-performance structural materials. However, thermotropic liquid crystalline polymers containing heteroatoms except silicon are quite rare.

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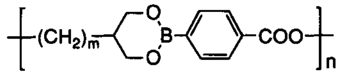
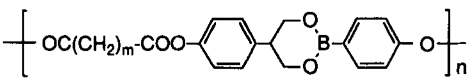
We have previously shown that 2,5-disubstituted-1,3,2-dioxaborinanes offer a suitable mesogenic group and form nematic and smectic A and C phases.[2] We also reported[3] a new family of thermotropic side-chain polymers which contain dioxaborinane derivatives as a mesogenic pendant group. Now we have attempted to synthesize a thermotropic main-chain polymer which is incorporated with a dioxaborinane ring in the polymer backbone. In this paper we wish to report the synthesis and thermal properties of new main chain polymers, **1** and **2**, some of which thermotropically form a nematic phase.



1 (a: m=6; b:m=8; c: m=11)



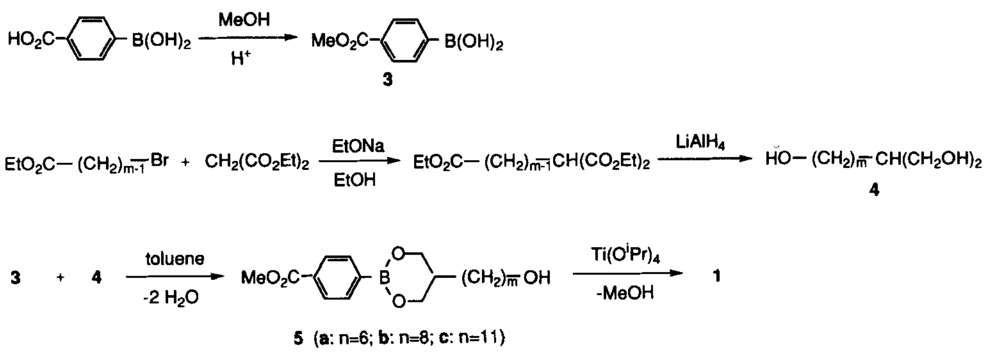
2 (a: m=4; b: m=5; c: m=6; d: m=7; e: m=8)

RESULTS AND DISCUSSION

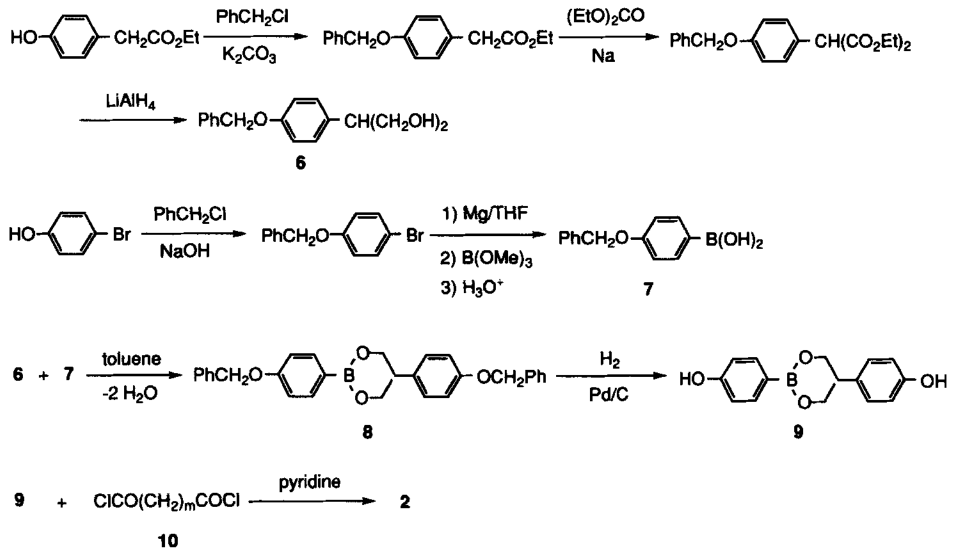
Synthesis and Characterization of Polymers 1 and 2

2-Aryl-1,3,2-dioxaborinane rings can be constructed by simple condensation between arylboronic acids and 1,3-diols.[2] The synthetic routes leading to the target polymers **1** and **2** are outlined in Schemes I and II, respectively.

Monomer **5** was prepared by the condensation of boronic acid **3** with triol **4** in a nearly quantitative yield. The triols are soluble in water when they bear a short alkyl group. Polymerization of monomer **5** was carried out by an ester interchange method in the presence of catalytic amounts of titanium tetraisopropoxide[4] to give polymer **1** in a good yield. Polymer **2** was synthesized by the polycondensation of bisphenol **9** with α,ω-alkanedicarbonyl chloride **10**. Both of polymers **1** and **2** did

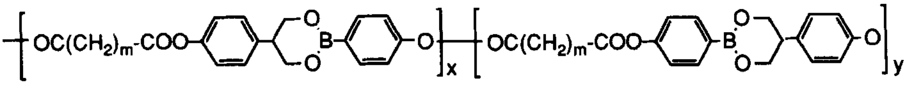


SCHEME I Synthesis of polymer 1



SCHEME II Synthesis of polymer 2

not dissolve in common organic solvents such as benzene, tetrahydrofuran, dimethylformamide and chloroform, but are sparingly soluble in hot 1,1,2,2-tetrachloroethane. Thus purification of the polymers was performed by reprecipitation from a tetrachloroethane solution with methanol. The molecular structure of the polymer was confirmed by NMR and IR spectra. ^{1}H-NMR spectrum of monomer **5a** ($m = 6$), for example, exhibited a peak as a singlet at 3.92 ppm due to the methyl proton, whereas in the spectrum of polymer **1a** the singlet completely disappeared though all other signals of the spectrum remained and considerably broadened. The IR spectrum of **5a** indicated the presence of hydroxy and ester groups at 3350 and, 1740 and 1270 cm^{-1}, respectively. In the spectrum of **1a**, however, the absorption due to the hydroxy group vanished while those of the ester group remained. A similar change of the NMR and IR spectra was observed on the transformation of **9** to polymer **2**, and the IR spectrum of **2** exhibited the absorptions due to the ester group at 1755 and 1245 cm^{-1}. These spectral data indicated that polymers **1** and **2** have the expected structure. In the case of polymer **2**, however, the main chain may contain repeating unit **B** in addition to **A** though we could not reveal the regularity of the sequence in the polymer backbone.



A **B**

Unfortunately the molecular weight of the polymers has not yet been determined because of their insolubility in solvents which are commonly used for the mobile phase of gel permeation chromatography.

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Thermal Behavior of Polymers 1 and 2

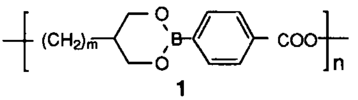
Thermal properties of polymers **1** and **2**, and monomer **5** were investigated with a polarizing microscope and a differential scanning calorimeter. The results obtained are summarized in Tables I and II.

Monomers **5a** ($m = 6$) and **5b** ($m = 8$) showed a nematic or smectic A phase, while polymer **1** did not show a stable mesophase though derivative **1b** having an octamethylene spacer ($m = 8$) exhibited a monotropic nematic phase which was, however, so unstable that we could not exactly determine the transition temperature.

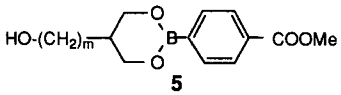
On the other hand, all of polymers **2** except **2e** ($m = 8$) formed a nematic phase which was identified by a characteristic schlieren texture though the phase transition was monotropic. Since their melting points were very high a partial decomposition of the polymers was observed when they melted to an isotropic liquid. Thermal analysis showed that gradual decomposition of the polymers began to start from ca. 260°C. Thus it was difficult to determine the exact temperature of transition from an isotropic phase to a nematic one by repeating runs of measurement because the second run showed a somewhat lower transition temperature than the first run due to partial decomposition. Transition temperatures obtained on the first run are listed in Table II. It may be noted that polymers **1** and **2** have a unique structure of polyesters in which boron atoms are regularly arranged in the main chain, and provide the first thermotropic liquid crystalline materials of main chain polymers which contain a metalloid atom, boron.

TABLE I

Transition temperature[a)] (°C) of polymer **1** and monomer **5**



1



5

	m			m	
1a	6	$K \xleftrightarrow{255} I$	**5a**	6	$K \xleftrightarrow{96.8} N \xleftrightarrow{104.7} I$
1b	8	$K \xrightarrow{239} I$ $I \xrightarrow{228^{b)}} N \xrightarrow{226^{b)}} K$	**5b**	8	$K \xleftrightarrow{84.4} S_A \xleftrightarrow{97.5} I$
1c	11	$K \xleftrightarrow{167} I$	**5c**	11	$K \xleftrightarrow{85.4} I$

K: crystal or solid; I: isotropic liquid; N: nematic; S_A: smectic A.

a) Measured using a differential scanning calorimeter.

b) Using a polarizing microscope with a heating stage.

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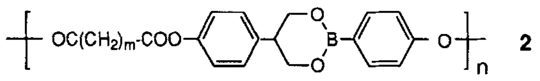
TABLE II

Transition temperature[a] (°C) polymer **2**



2

	m	
2a	4	$K \xrightarrow{306-309^{b)}} I$; $I \xrightarrow{287-291} N \xrightarrow{c)} K$
2b	5	$K \xrightarrow{263-264^{b)}} I$; $I \xrightarrow{246-248} N \xrightarrow{c)} K$
2c	6	$K \xrightarrow{273-275^{b)}} I$; $I \xrightarrow{250-253} N \xrightarrow{c)} K$
2d	7	$K \xrightarrow{248-250^{b)}} I$; $I \xrightarrow{235-239} N \xrightarrow{c)} K$
2e	8	$K \underset{c)}{\overset{276-278^{b)}}{\rightleftarrows}} I$

K: solid; N: nematic; I: isotropic liquid.

a) Measured using a polarizing microscope with a heating stage.

b) Melt with partial decomposition.

c) Transition temperatures could not be determined.

EXPERIMENTAL

Transition temperatures were measured using an Olympus BH-2 polarizing microscope in conjunction with a Mettler FP52 heating stage, FP5 control unit and a Shimadzu DSC-50 differential scanning calorimeter. The rate of heating or cooling was fixed at 5°C min^{-1}. IR spectra were obtained with a Hitachi 295 Infrared Spectrophotometer. ^{1}H NMR spectra were recorded on a Brucker WM-360 instrument with tetramethylsilane as an internal standard. Thermal analyses were performed on a Shimadzu TGA-50 thermogravimetric analyzer at a heating rate of 5°C min^{-1} under an argon atmosphere.

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Materials

2-(4-Methoxycarbonylphenyl)-5-(6-hydroxyhexyl)-1,3,2-dioxaborinane **5a**. A mixture of 4-methoxycarbonylphenylboronic acid (1.80 g, 10 mmol) and 2-(6-hydroxyhexyl)-1,3-propanediol (1.76 g, 10 mmol) in toluene (70 ml) was stirred under reflux for 2 h. During the reaction the water which formed was removed azeotropically using a Dean-Stark apparatus. After the reaction was completed, toluene was distilled off, and the resultant residue was purified by column chromatography on silica using dichloromethane-ether (9/1) as an eluent. Recrystallization from acetone-hexane gave colorless needles of **5a** (2.27 g) in 71% yield. IR (nujol) 3350 (OH), 1740 (C═O), 1325 (B—O), and 1270 cm^{-1} (C—O); NMR δ = 1.26–1.63 (10H, m, alkyl), 2.10 (1H, m, CH), 3.65 (2H, t, J = 6 Hz, $C\underline{H}_2OH$), 3.78 (2H, dd, J_{gem} = 10 and $J_{ax\text{-}ax}$ = 10 Hz, $CHC\underline{H}_2O$, ax), 3.92 (3H, s, CH_3), 4.18 (2H, dd, J_{gem} = 10 and $J_{ax\text{-}eq}$ = 4 Hz, $CHC\underline{H}_2O$, eq), 7.83 (2H, d, J = 8 Hz, Ar), and 8.00 (2H, d, J = 8 Hz, Ar). Anal. Calcd for $C_{17}H_{25}BO_5$: C, 63.77; H, 7.87%. Found: C, 65.36; H, 8.19%.

2,5-Bis(4-hydroxyphenyl)-1,3,2-dioxaborinane **9**. 4-Benzyloxyphenylboronic acid (2.28 g, 10 mmol) was reacted with 2-(4-benzyloxyphenyl)-1,3-propanediol (2.58 g, 10 mmol) in toluene (70 ml) under reflux for 2 h in the same manner as the preparation of **5a**. 2,5-Bis(4-benzyloxyphenyl)-1,3-propanediol **8** was obtained as colorless needles in 84% yield (m.p. 218–219°C). Then, compound **8** (2.20 g, 4.9 mmol) was treated with an atmospheric pressure of hydrogen in the presence of a 5% Pd/C catalyst in ethyl acetate (350 ml) at room temperature for 3 days. After the catalyst was filtered off, the solution was concentrated and poured into dichloromethane to give colorless solids. Recrystallization from hexane-ethyl acetate afforded colorless needles (1.21 g) of **9** in 91% yield. mp. 220–222°C. IR (nujol) 3350 (OH), 1600 (Ar), 1310 (B—O), and 1240 cm^{-1} (C—O); NMR (acetone-d_6) δ = 2.86 (1H, s, OH), 2.89 (1H, s, OH), 3.25 (1H, m, CH), 4.15–4.18 (4H, m, CH_2), 6.81 (2H, d, J = 8 Hz, Ar), 6.83 (2H, d, J = 9 Hz, Ar), 7.18 (2H, d, J = 9 Hz, Ar), and 7.63 (2H, d, J = 8 Hz, Ar). Anal. Calcd for $C_{15}H_{15}BO_4$: C, 66.70; H, 5.60%. Found: C, 66.22; H, 5.62%.

Other derivatives were prepared in the same manner described previously.[2a]

Synthesis of Polymer 1a

A mixture of 2-(4-methoxycarbonylphenyl)-5-(6-hydroxyhexyl)-1,3,2-dioxaborinane **5a** (1.28 g, 4 mml) and titanium tetraisopropoxide (23 mg, 80 μmol) was heated at 130°C for 3 h, then at 150°C for 2 h. During the reaction nitrogen was blown continuously through the mixture in order to remove the methanol which formed. Finally, the mixture was heated at 150°C under high vacuum for 2 h. After cooling, the reaction mixture was dissolved in hot 1,1,2,2-tetrachloroethane and the solution was poured into ethanol. The polymer which precipitated was isolated by centrifugation and reprecipitated three times from 1,1,2,2-tetrachloroethane-ethanol; yield 900 mg (78%). IR (nujol) 1730 (C═O), 1310 (B—O), and 1250 cm^{-1} (C—O); NMR (1,1,2,2-tetrachloroethane-d_2) δ = 1.31–1.77 (14H, m, alkyl), 2.05–2.08 (1H, m, CH), 3.75 (2H, dd, J_{gem} = 11 and $J_{ax\text{-}ax}$ = 11 Hz, $CH(C\underline{H}_2O—)_2$, ax), 4.16 (2H, dd, $J_{gem} = 11$ and $J_{ax\text{-}eq} = 4$ Hz, $CH(C\underline{H}_2O\text{—})_2$, eq), 4.29 (2H, t, $J = 7$ Hz, CO_2CH_2), 7.83 (2H, d, $J = 8$ Hz, Ar), and 7.97 (2H, d, $J = 8$ Hz, Ar). Anal. calcd for $C_{16}H_{21}BO_4$: C, 66.69; H, 7.35%. Found: C, 66.51; H, 7.20%.

Synthesis of Polymer 2c

To a solution of 2,5-bis(4-hydroxyphenyl)-1,3,2-dioxaborinane **9** (540 mg, 2 mmol) in dry pyridine (6 ml), siberoyl chloride **10** ($m = 6$) (422 mg, 2 mmol) in dichloromethane (6 ml) was added in one portion at 0°C. The reaction mixture was stirred at 0°C for 30 min and at room temperature for 20 h. Then the mixture was poured into methanol and the precipitate which formed was collected and washed with water and acetone.

Reprecipitation from 1,1,2,2-tetrachloroethane-ethanol gave polymer **2c**; yield 605 mg (74%). IR (nujol) 1755 (C═O), 1595 (Ar), 1310 (B—O), and 1245 cm^{-1} (C—O); NMR (1,1,2,2-tetrachloroethane-d_2) $\delta = 1.47$ (8H, m, γCH_2 from CO_2), 1.77 (4H, m, βCH_2 from CO_2), 2.57 (4H, m, CH_2CO_2), 3.33 (1H, m, CH), 4.12 (2H, dd, $J_{gem} = 11$ and $J_{ax\text{-}ax} = 11$ Hz, CH_2O, ax), 4.31 (2H, dd, $J_{gem} = 11$ and $J_{ax\text{-}eq} = 4$ Hz, CH_2O, eq), 7.07–7.09 (4H, m, Ar), 7.24 (2H, d, $J = 8$ Hz, Ar), and 7.83 (2H, d, $J = 8$ Hz, Ar). (Anal. calcd for $C_{23}H_{25}BO_6$: C, 67.67; H, 6.17%. Found: C, 66.08; H, 5.96%.)

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