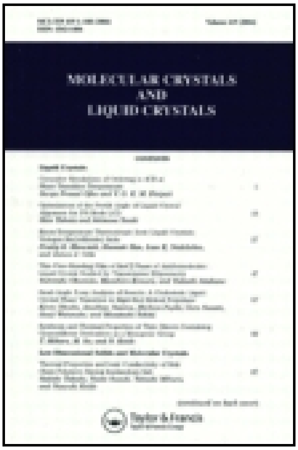

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Transformation of Liquid-Crystalline Diaryldiacetylenes to Liquid-Crystalline 2,5-Diarylthiophenes

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Transformation of Liquid-Crystalline Diaryldiacetylenes to Liquid-Crystalline 2, 5-Diarylthiophenes

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Liquid-crystalline 2, 5-diarylthiophene derivatives were prepared directly by the reaction of liquid-crystalline diaryldiacetylene derivatives derived from the coupling reaction of alkynyliodonium salts with organocopper reagents. The 2, 5-diarylthiophene derivaties prepared in the present study exhibit the nematic phase.

Keywords: Coupling reaction; alkynyliodonium salts; diaryldiacetylenes; 2, 5-diarylthiophene; liquid crystals; nematic phase

INTRODUCTION

Recently much attention has been paid to synthesis and properties of liquid-crystalline compounds containing thiophene units [1–3], since there is significant improvement of solubility and fusibility resulting from the grafting of flexible hydrocarbon chains on their conjugated thiophene backbones [2]. However, despite their high potential utility for the liquid-crystalline units, liquid-crystalline diarylthiophene derivatives are rare [4].

We have recently developed the synthesis of liquid-crystalline diaryldiacetylenes by the coupling reaction of alkynyliodonium salts **1** with organocopper

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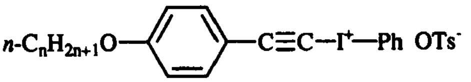
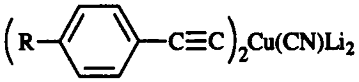
[*] Corresponding author.

reagents **2** [5, 6]. This coupling reaction using alkynyliodonium salts has been found to be also useful for preparation of diaryldiacetylene liquid crystals.



1 : n = 8, 10, 12, and 14



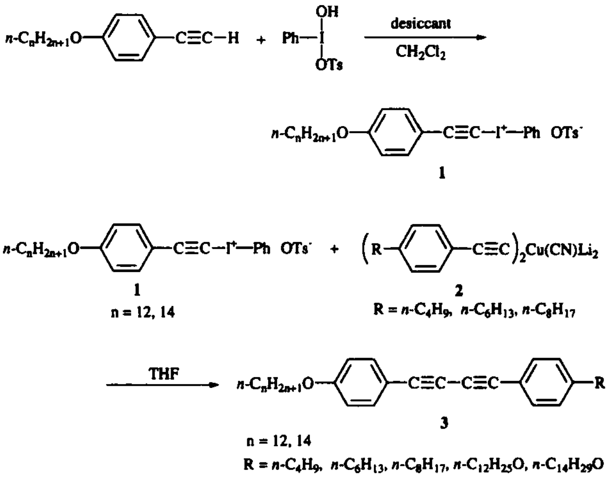
2 : R = OMe, Me, CN, NO_2, n-C_4H_9, n-C_6H_{13}, n-C_8H_{17}

COMPOUNDS 1 & 2

Conjugated 1, 3-butadiynes are also useful for mesogens and non-linear optics. Long-chained alkyl groups play an important role in the generation of such properties and are also essential for molecular assembly which is applied to crystal engineering and molecular devices [7]. In particular, it is expected that such compounds with 1, 3-diyne units create new functionality upon reactions with various reagents. The transformation of 1, 3-diynes to thiophenes [8] is suitable for synthesis of thiophene liquid crystals using liquid-crystalline diaryldiacetylenes. Thus we have examined direct synthesis of liquid-crystalline, 2, 5-diarylthiophene derivatives using liquid-crystalline diaryldiacetylenes which are readily prepared by the coupling reaction of alkynyliodonium salts with organocopper reagents [5, 6]. Here we report a new route to liquid-crystalline diarylthiophenes and their properties.

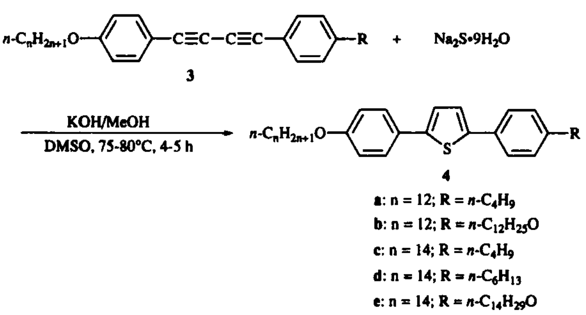
RESULTS AND DISCUSSION

Long-chained alkynyl(phenyl)iodonium tosylates (**1**: $n = 12$ and 14) were prepared by reaction of arylacetylenes with hydroxy(tosyloxy)iodobenzene according to our previous paper [5]. The substrates, liquid-crystalline diaryldiacetylenes **3**, were readily prepared by the coupling reaction of alkynyl(phenyl)iodonium tosylate **1** ($n = 12$ and 14) with alkynylcopper reagents **2** ($R = n$-C_4H_9, n-C_6H_{13} and n-C_8H_{17}) as shown in Scheme 1.



SCHEME 1

The transformation of diaryldiacetylene **3** into diarylthiophenes **4** was first performed according to the literature [3]. When diaryldiacetylenes **3** were treated with Na_2S in a refluxing DMF or in DMSO at 55°C, diarylthiophenes **4** were obtained only in 10–13% yields.



SCHEME 2

Then, we conducted the transformation reaction with Na_2S under basic conditions (KOH/DMSO) [9]. When a solution of diaryldiacetylene **3a** in DMSO was treated with a solution of KOH and $Na_2S{\bullet}9H_2O$ in MeOH and the reaction mixture was heated at 75–80°C for 5 h, 2, 5-diarylthiophene **4a** was formed in a 52% yield. Other 2, 5-diarylthiophenes **4b**–**e** were obtained by this procedure in 52–58% yields.

The results are summarized in Table I. Table I indicates that the direct synthesis of the 2, 5-diarylthiophene derivatives proceeds well even in the case of the substrates bearing long-chained alkyl and alkoxy groups and is not affected in the yield of the 2,5-diarylthiophene derivatives. Accordingly, the present procedure is useful for synthesis of mesogenic diarylthiophene derivatives.

Mesogenic Properties of 2,5-Diarylthiophene Derivatives

The liquid crystal phase transition temperatures and the phase types of the 2,5-diarylthiophene derivatives **6** newly prepared in the present work have been examined by optical microscopy and confirmed by differential scanning calorimetry (DSC). The results are given in Table II. The 2,5-diarylthiophene derivatives having long alkyl- and alkoxy chains are all enantiotropic liquid crystals and show mesogenic regions at 120–155°C. All the

TABLE I 2,5-Diarylthiophene derivatives using diaryldiacetylenes **4**[a]

diaryldiacetylene **3** *n*	*R*	*2,5-diarylthiophene* **4** *(isolated yield, %)*
12	n-C_4H_9	52
	n-$C_{12}H_{25}O$	58
14	n-C_4H_9	56
	n-C_6H_{13}	52
	n-$C_{14}H_{29}O$	58

[a] Typical conditions: diaryldiacetylene **3** (0.1 mmol), $Na_2S \bullet 9H_2O$ (0.11 mmol), KOH (0.2 mmol), MeOH (1 ml), DMSO (5 ml), 75–80°C, 4–5 h.

TABLE II Liquid crystal phase and transition temperatures of 2,5-diarylthiophene derivatives **4**[a]

$n = 12$	$R = n$-C_4H_9	**4a**	$K \underset{136.7}{\overset{136.0}{\rightleftharpoons}} N \underset{151.0}{\overset{147.5}{\rightleftharpoons}} I$
	$R = n$-$C_{12}H_{25}O$	**4b**	$K \underset{143.1}{\overset{140.8}{\rightleftharpoons}} N \underset{154.4}{\overset{151.5}{\rightleftharpoons}} I$
$n = 14$	$R = n$-C_4H_9	**4c**	$K \underset{127.0}{\overset{124.0}{\rightleftharpoons}} N \underset{140.5}{\overset{136.0}{\rightleftharpoons}} I$
	$R = n$-C_6H_{13}	**4d**	$K \underset{119.3}{\overset{118.5}{\rightleftharpoons}} N \underset{131.5}{\overset{129.5}{\rightleftharpoons}} I$
	$R = n$-$C_{14}H_{29}O$	**4e**	$K \underset{141.9}{\overset{138.0}{\rightleftharpoons}} N \underset{155.2}{\overset{151.0}{\rightleftharpoons}} I$

[a] Key; *K*: crystal, *N*: nematic, and *I*: isotropic.

2,5-diarylthiophene derivatives exhibit only the nematic phase, showing marbled textures. Therefore, the mesogenic property is somewhat different from the long-chained diaryldiacetylenes **3** which exhibit both smectic and nematic phases [6, 10].

CONCLUSION

We have developed a direct synthesis of liquid-crystalline 2,5-diarylthiophene derivatives **4** from diaryldiacetylene **3**. The long-chained alkyl groups do not affect the yield of the 2,5-diarylthiophene derivatives. The utility of long alkyl and alkoxy groups as the terminal groups of liquid crystals is generally recognized. Therefore, the present direct procedure using liquid-crystalline diaryldiacetylenes **4** provides a new route to the 2,5-diarylthiophene derivatives which have liquid-crystalline properties. All the 2,5-diarylthiophene derivatives **4** prepared in the present study show only nematic phases suitable for use in liquid crystal display devices. Therefore, the present one-pot synthesis of the 2,5-diarylthiophene derivatives using diaryldiacetylenes possesses possible wide applications for liquid crystals, electronics, and non-linear optical materials.

EXPERIMENTAL

General

^{1}H NMR spectra were obtained with a BRUKER AC-250P (250 MHz) spectrometer. Chemical shifts are given in ppm. Microanalyses were performed by the Service Center of the Elementary Analysis of Organic Compound, Faculty of Science, Kyushu University. The transition temperatures were determined by a polarizing microscope (OLYMPUS, BHSP) equipped with a hot stage and a controller (JAPAN HYTECH, TH-600RH) and also on the basis of the thermograms recorded on a differential scanning calorimeter (RIGAKU, THERMOFLEX DSC 8230).

General Procedure for Synthesis of the 2,5-Diarylthiophene Derivatives 4

To a solution of the diaryldiacetylenes (0.1 mmol) in DMSO (5 ml) was treated with solution of KOH (11.22 mg, 0.2 mmol) in MeOH (1 ml) and

$Na_2S{\bullet}9H_2O$ (26.41 mg, 0.11 mmol). After the reaction mixture was heated at 75–80°C for 5 h, it was allowed to reach to room temperature and subsequently the whole mixture was stirred continuously for 2 h. The whole mixture was extracted with CH_2Cl_2, and the extract was washed with brine, dried over Na_2SO_4, and concentrated. The products were separated by CH_2Cl_2. The 2, 5-diarylthiophene derivatives were not dissolved in CH_2Cl_2. The ^1H NMR chemical shifts and elemental analyses for the 2, 5-diarylthiophene liquid crystals **4a–e** are given below.

2-[4-(Dodecyloxy)phenyl]-5-(4-Butylphenyl)thiophene (4a)

^1H NMR (250 MHz, Benzene-d_6): $\delta = 0.88$ (t, *J* 7.2 Hz, 3 H, Me), 1.25–1.41 (m, 26 H, CH_2), 1.70 (quint, *J* 6.2 Hz, 2 H, CH_2), 2.50 (t, *J* 7.2 Hz, 2 H, $ArCH_2$), 3.77 (t, *J* 6.4 Hz, 2 H, OCH_2), 6.85 (d, *J* 7.1 Hz, 4 H, ArH), 7.04 (s, 2 H, CH), 7.54 (quart, *J* 5.5 Hz, 4 H, ArH). Anal. Found: C, 80.55; H, 9.09. Calcd for $C_{32}H_{44}OS$: C, 80.68; H, 9.24%.

2, 5-Bis[4-(Dodecyloxy)phenyl]thiophene (4b)

^1H NMR (250 MHz, Benzene-d_6): $\delta = 0.92$ (t, *J* 6.2 Hz, 6 H, Me), 1.27–1.41 (m, 36 H, CH_2), 1.66 (quint, *J* 6.8 Hz, 4 H, CH_2), 3.72 (t, *J* 6.4 Hz, 4 H, OCH_2), 6.86 (d, *J* 8.5 Hz, 4 H, ArH), 7.05 (s, 2 H, CH), 7.54 (d, *J* 8.5 Hz, 4 H, ArH). Anal. Found: C, 79.24; H, 9.78. Calcd for $C_{40}H_{60}OS_2$: C, 79.47; H, 9.93%.

2-[4-(Tetradecyloxy)phenyl]-5-(4-Butylphenyl)thiophene (4c)

^1H NMR (250 MHz, Benzene-d_6): $\delta = 0.88$ (t, *J* 7.2 Hz, 3 H, Me), 1.25–1.41 (m, 30 H, CH_2), 1.71 (quint, *J* 6.2 Hz, 2 H, CH_2), 2.50 (t, *J* 7.3 Hz, 2 H, $ArCH_2$), 3.77 (t, *J* 6.4 Hz, 2 H, OCH_2), 6.85 (d, *J* 7.1 Hz, 4 H, ArH), 7.04 (s, 2 H, CH), 7.54 (quart, *J* 5.5 Hz, 4 H, ArH). Anal. Found: C, 79.83; H, 9.60. Calcd for $C_{34}H_{48}OS$: C, 80.96; H, 9.52%.

2-[4-(Tetradecyloxy)phenyl]-5-(4-Hexylphenyl)thiophene (4d)

^1H NMR (250 MHz, Benzene-d_6): $\delta = 0.89$ (t, *J* 7.2 Hz, 3 H, Me), 1.27–1.41 (m, 34 H, CH_2), 1.66 (quint, *J* 7.4 Hz, 2 H, CH_2), 2.52 (t, *J* 7.2 Hz, 2 H, $ArCH_2$), 3.77 (t, *J* 6.5 Hz, 2 H, OCH_2), 6.85 (d, *J* 7.2 Hz, 4 H, ArH), 7.04 (s, 2 H, CH), 7.54 (quart, *J* 5.5 Hz, 4 H, ArH). Anal. Found: C, 81.02; H, 9.70. Calcd for $C_{36}H_{52}OS$: C, 81.21; H, 9.77%.

2,5-Bis[4-(Tetradecyloxy)phenyl]thiophene (4e)

^{1}H NMR (250 MHz, Benzene-d_6): $\delta = 0.91$ (t, J 6.2 Hz, 6 H, Me), 1.27–1.41 (m, 44 H, CH_2), 1.65 (quint, J 6.8 Hz, 4 H, CH_2), 3.71 (t, J 6.4 Hz, 4 H, OCH_2), 6.86 (d, J 8.4 Hz, 4 H, ArH), 7.06 (s, 2 H, CH), 7.54 (d, J 8.4 Hz, 4 H, ArH). Anal. Found: C, 79.89; H, 10.12. Calcd for $C_{44}H_{68}OS_2$: C, 80.01; H, 10.29%.

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