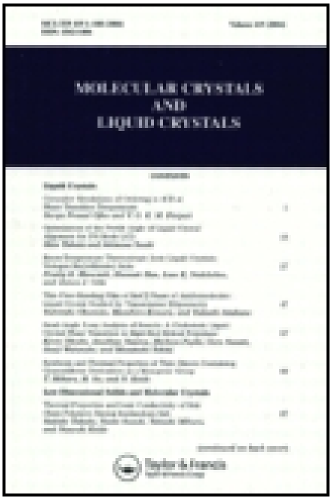

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Liquid Crystalline Behavior of Poly(*m*-Phenylenebutadiynylene)s Having a Mesogenic Substituent

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Poly(*m*-phenylenebutadiynylene)s having a side chain with *p*-(4-pentylcyclohexyl)phenyl and cyanobiphenylyl mesogenic core were synthesized from corresponding *m*-diethynylbenzene by oxidative polycondensation with a Cu-amine catalyst under O_2. These polymers showed an enantiotropic nematic phase that was confirmed by polarizing optical microscopy and XRD. Uniaxial alignment of these polymers was carried out by a rubbing technique. Polarizing IR results of the aligned samples suggested that the main chain and the mesogenic side chain were aligned in parallel to the rubbing direction.

Keywords: liquid crystalline conjugated polymer; rubbing alignment; poly(*m*-phenylenebutadiynylene)s

INTRODUCTION

Alignment of rigid main chains of conjugated polymers has been a growing demand for elucidation of their electrical, optical and optoelectronic anisotropies. Poly(2,5-dialkoxy-*p*-phenylenebutadiynylene)s (**PDAPB**) have received much attention as a novel conjugated polymer with a butadiynylene linkage showing a main-chain type thermotropic liquid crystalline property with an intense

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fluorescence[1]. However, the polymers have a low solubility in common organic solvents and a narrow temperature range of the liquid crystalline state that results in poor processability for making homogeneous film on substrates. Recently we found that introduction of a bent moiety such as a *m*-phenylene in the rigid rod-like **PDAPB** greatly enhanced the solubility[2]. In addition, poly(4-dodecyloxy-*m*-phenylenebutadiynylene) was found to have a good solubility but no liquid crystalline behaviors in our recent preliminary results. Thus a probable way for synthesis of a poly(phenylenebutadiynylene) with a good solubility and a liquid crystalline property is introduction of a liquid crystalline side chains into the poly(*m*-phenylenebutadiynylene).

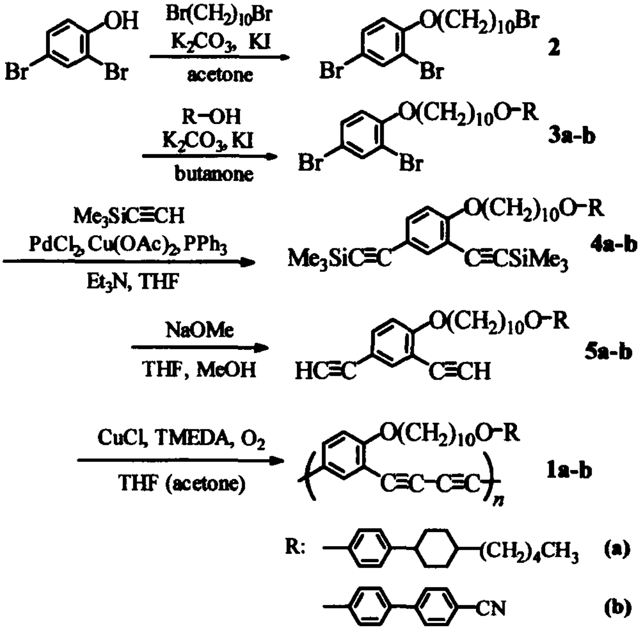
In this report, we synthesized poly(*m*-phenylenebutadiynylene)s having a mesogenic substituent at the phenylene moiety, and investigated their liquid crystalline properties.

EXPERIMENTALS

Synthesis

Synthetic route of **1a-b** was summarized in Scheme 1. Reaction of 2,4-dibromophenol (50 mmol) with excess 1,10-dibromodecane (400 mmol) by a general reaction[3] using K_2CO_3 in presence of KI in acetone, gave **2** as a white powder in 52 % yield. Similarly, **2** (11 mmol) was reacted with equimolar *p*-(*trans*-4-pentylcyclohexyl)phenol and 4-cyano-4'-hydroxybiphenyl in butanone, affording **3a-b** as a white powder in 55 % and 79 % yields, respectively. According to the reported method[3], trimethylsilylacetylene (26 mmol) in triethylamine (80 ml) and THF (80 ml) was reacted with **3a-b** (8 mmol) in the presence of $PdCl_2$ (0.8 mmol), $Cu(OAc)_2$ (0.8 mmol) and triphenylposphine (26 mmol), affording **4a-b** as a white powder in 62 % and 70 % yields. Alkali treatment[1] of **4a-b** (5 mmol) using NaOMe (11 mmol) in THF (20 ml) and methanol (4 ml) gave **5a-b** as a white powder in 54 % and 94 % yields, respectively.

Polymers **1a-b** were synthesized by oxidative polycondensation of **5a-b** in the presence of CuCl and *N*, *N*, *N'*, *N'*-tetramethylethylenediamine (TMEDA) at room temperature under O_2. The polymers **1a-b** were soluble in common organic solvents such as $CHCl_3$, THF and benzene, and were identified by NMR, IR, Raman and elemental analyses. The number average molecular weight (M_n) were determined by gel permeation chromatography (GPC) versus polystyrene standard.



TMEDA: *N*, *N*, *N'*, *N'*-tetramethylethylenediamine

SCHEME 1

TABLE I Polymerization results[a]

entry	polymer	yield (%)	M_n	M_w/M_n	D.P.
1	**1a**	90	15700	1.5	30
2	**1b**	75	23700	1.6	50
3	**1b**[b]	80	5000	1.3	10

[a] Conditions: [monomer, 5] = 2.5 x 10^{-2} mmol/dm^{-3}, [CuCl] = [TMEDA] = 6.2 x 10^{-3} mmol/dm^{-3} in THF at r. t. for 12 h.

[b] Polymerization was carried out in THF-acetone (1:1) solvents for 12 h.

RESULTS AND DISCUSSION

Syntheses and general properties of polymers 1a-b

Poly(*m*-phenylenebutadiynylene)s having a mesogenic substisuent at 4-position of the 1,3-phenylene moiety **1a-b** are synthesized according to the Scheme 1. Polymerization results were summarized in Table I. The M_ns observed for **1a-b** were larger than those of **PDAPB**, which might be due to an improved solubility of **1a-b** with a reduced rigidity of the polymer backbones. It is possible to decrease the M_n by using a poor solvent such as acetone (entry 3 in Table I).

In the UV-Vis spectra, absorption maximum (λ_{max}) of **1a** and **1b** in $CHCl_3$ was observed at 351 and 350 nm, respectively. These values are shifted longer in wavelength than those of monomers, **5a** (316 nm) and **5b** (299 nm), which is ascribed to an extension of π-conjugation by the polymerization. However the shifted values (30~50 nm) are smaller than the cases observed for **PDAPB** (70~80 nm). In the fluorescence spectra, the emission maxima (em_{max}) of **1a-b** in solution and solid states were observed at about 406 nm. The em_{max}s are shifted shorter in wavelength with weaker intensities than those of **PDAPB**.

Phase transition behaviors

The phase transition behaviors of **1a-b** were investigated by thermocontrolled polarizing optical microscopy (POM) and differential scanning calorimetry (DSC). The phase transition behaviors are summarized in Table II. An enantiotropic mesophase is observed for **1a** with a POM texture as shown in Figure 1(a). In case of **1b** with a high M_n (entry 2 in Table I), decomposition is occurred at over 170 °C, which is due to a high reactivity of the C≡C–C≡C and C≡N bonds. Contrary to this, phase transition temperatures are low enough to behave as liquid crystal without the decomposition for **1b** with the low M_n (entry3 in Table I), that is, the polymer shows an enantiotropic mesophase with a schlieren texture as shown in Figure 1(b).

In order to determine the mesophase, X-ray diffraction (XRD) analyses of **1a-b** were carried out. Only broad peak in range of 17-25° in 2θ is observed for **1a-b**. Therefore these mesophases are determined as nematic.

DSC thermograms of **1a** and **1b** (entry 3) were shown in Figure 2. Both show one exothermic peak in the heating process and one endothermic peak in the cooling process, which is due to phase

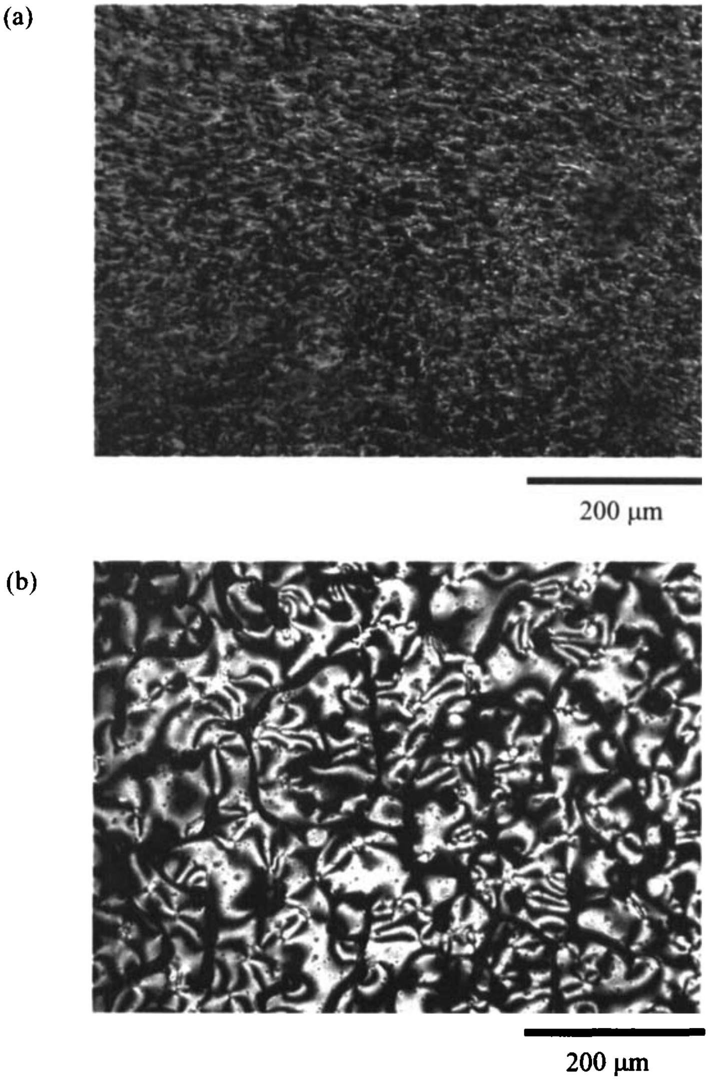


FIGURE 1 Polarizing optical micrographs of **1a** at 120 °C (a) and **1b** at 145 °C (b) in cooling processes
See Color Plate VI at the back of this issue.

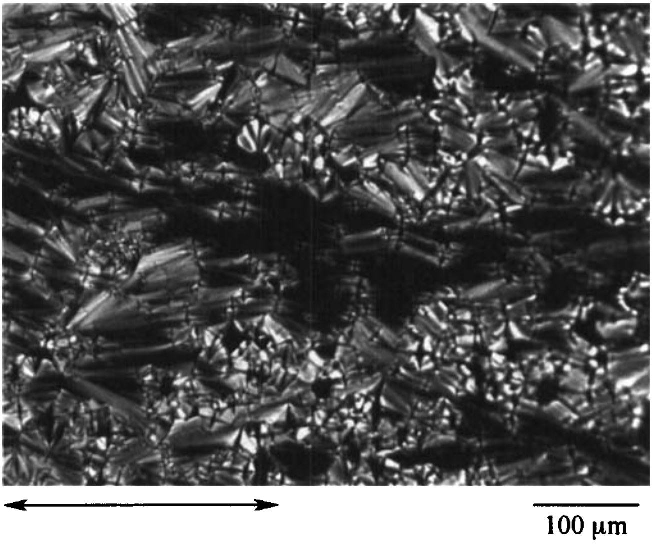


FIGURE 1 Polarizing optical micrograph of **OB6** after rubbing treatment See Color Plate VII at the back of this issue

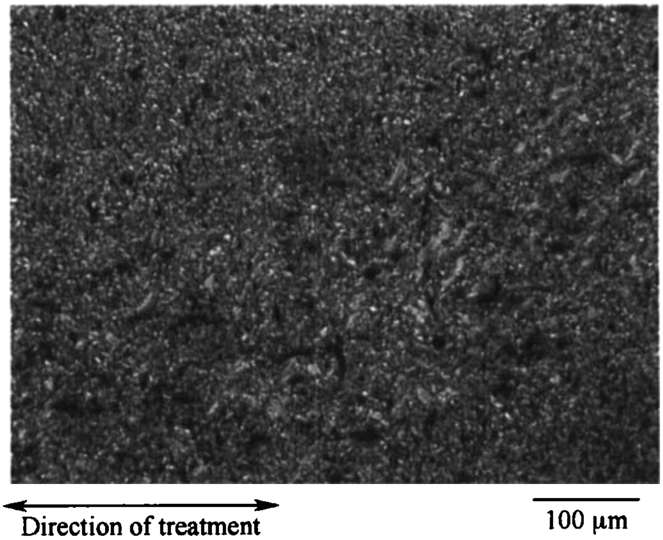


FIGURE 2 Polarizing optical micrograph of **CB10**. See Color Plate VIII at the back of this issue.

TABLE II **Thermal properties of polymers 1a-b**

	phase transitions (°C) and corresponding enthalpy changes[a] (J /g)	
Polymer	**heating**	**cooling**
1a	G • 110 • N • 138(9.8) • I	I • 136(-8.2) • N • 100 • G
1b[c]	G • 150 • N [~dec.[b]]	N • 140 • G
1b[d]	G • 110 • N • 160(8.8) • I	I • 153(-9.6) • N • 109 • G

[a] Enthalpy changes were shown in ( ).
[b] Decomposition occurred over 170 °C.
[c] High molecular weight **1b** in entry 2 in Table I.
[d] Low molecular weight **1b** in entry 3 in Table I.
Abbreviations: G: glassy phase, N: nematic phase I: isotropic phase

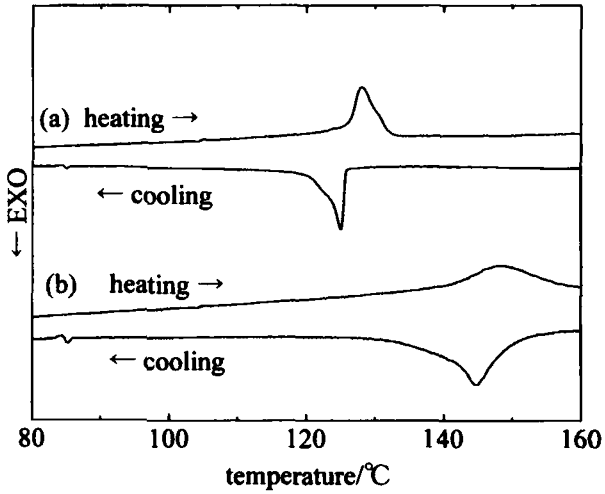


FIGURE 2 DSC thermograms of **1a** (a) and **1b** (b) at a scan rate of 10 °C min $^{-1}$

transitions between liquid crystalline and isotropic phases. The values of enthalpy changes of these phase transitions are about 9 J / g, which are rather smaller than those of **PDAPB** (about 80 J / g). This result is ascribed to phase transition behaviors of side-chain type liquid crystalline polymers.

Characterizations of aligned polymers

Characterizations of aligned polymers in glassy state were carried out by polarizing IR measurement. Polymers on a KBr substrate are cooled from isotropic temperature to a temperature in liquid crystalline state near the glassy transition temperature. At this temperature, the samples are rubbed with teflon in one direction on the substrates. Polarizing parallel and perpendicular IR spectra of aligned **1b** are shown in Figure 3 with a difference spectrum. Dichroic ratios ($R = A_{//} / A_{\perp}$) of stretching vibrations; $\nu_{C\text{-}H}$ of terminal acetylene (3288 cm^{-1}, R = 1.71), $\nu_{C\equiv N}$ (2223

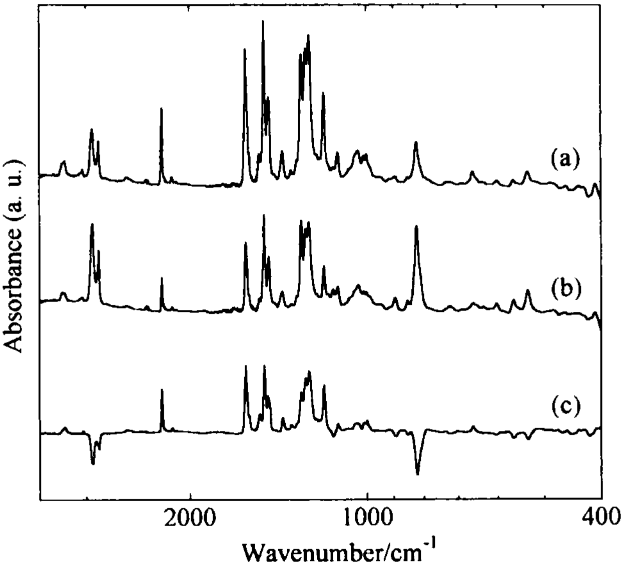


FIGURE 3 Polarizing parallel (a), perpendicular (b) and difference (c) IR spectra of aligned **1b**.

$\mathrm{cm^{-1}}$, $R = 2.26$), $\nu_{C\equiv C}$ (2142 $\mathrm{cm^{-1}}$, $R = 1.99$), ν_{ring} of phenylene (1601 $\mathrm{cm^{-1}}$, $R = 1.90$) and $\nu_{C\text{–}O\text{–}C}$ (1251 $\mathrm{cm^{-1}}$, $R = 1.69$), are larger than unity. Contrastively, the R values of $\nu_{C\text{–}H}$ of methylene at side chains (2925 $\mathrm{cm^{-1}}$, $R = 0.61$) and out-of-plane bending of the phenyl ring C–H (821 $\mathrm{cm^{-1}}$, $R = 0.49$) are smaller than unity. These results suggest that the main chains and the side chains are aligned in the direction of the rubbing. Similar tendency is observed for the aligned **1a**.

CONCLUSION

We synthesized novel poly(*m*-phenylenebutadiynylene)s having a mesogenic substituent **1a-b**. These polymers were well soluble in common organic solvents compared with **PDAPB**. These polymers showed a stable enantiotropic nematic phase with a high fluidity. When these polymers were rubbed on the substrate, the main chain and the mesogenic side chain of the polymers could be easily aligned in parallel to the rubbing direction. Therefore we expect that the other useful methods are applicable to effective alignment of these polymers.

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