

Synthesis of novel organocobalt poly(arylene-vinylene)s containing (cyclobutadiene)cobalt moieties in the main chain

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Summary

Organocobalt poly(arylene-vinylene)s composed of 1,2- or 1,3- linkage at their cyclobutadiene moieties (**3** and **4**, respectively) were prepared by the Heck reaction of *p*-divinylbenzene with (cyclobutadiene)cobalt-containing monomers having two aryl bromide moieties (**1** and **2**, respectively). The number average molecular weights (M_n) of the obtained organocobalt poly(arylene-vinylene)s (**3** and **4**) were 4,100 and 4,000, respectively (GPC, on the basis of polystyrene). UV-vis spectra of **3** and **4** exhibited main π - π^* absorption peaks at 362 and 397 nm, respectively, which were ca. 60 nm bathochromically shifted from those of the corresponding monomeric units. Both polymers were found to show thermotropic liquid crystallinity in the range of room temperature to ca. 80 °C by employing differential scanning calorimetry (DSC and the optical measurement using crossed polarizers).

Introduction

On the basis of a variety of geometries of organometallic complexes and their potential for revealing unique physical properties, organometallic polymers are attractive candidates for novel functional materials (1). For example, metal-containing liquid crystalline polymers, or metallomesogenic polymers have attracted much attention. Owing to the features of organometallic cores such as redox-active and $d\pi$ - π electron delocalizations, these polymers are expected to serve as anisotropic materials with excellent properties suitable for advanced electro-optical devices. However, studies on such metallomesogenic polymers have been still limited so far (2).

We have reported the synthesis of a variety of polymers having cobaltacyclopentadiene or (cyclobutadiene)cobalt cores and suggested the potentials for various applications (3). In the case of polyesters having 1, 3-linked (cyclobutadiene)cobalt moieties in the main chain, for instance, thermotropic liquid crystalline phase was observed (3e, 3f). Poly(arylene)s containing (cyclobutadiene)cobalt units were also found to form lyotropic as well as thermotropic liquid crystalline phase in the presence of appropriate lateral alkyl side chains (3g, 3h). Bunz *et al.* have independently reported the synthesis of conformationally linear and stiff polymers containing cyclobutadiene and alkyne units and their mesophase properties (4). So as to investigate another possibility of a new class of organometallic polymers and to compare the properties, we report herein the synthesis and properties of novel organocobalt poly(arylene-vinylene)s bearing (cyclobutadiene)cobalt and vinylene moieties in the main chain.

Experimental

Materials and instruments

Monomers (**1** and **2**) were prepared by modification of the reported procedure for cyclobutadienecobalt derivatives (3e-h,5). That is, (cyclobutadiene)cobalt dibromide bisphenols were obtained by the reaction of 2 equiv of (4-bromophenyl)(4'-

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hydroxyphenyl)acetylene with (η^5 -cyclopentadienyl)bis(triphenylphosphine)cobalt (**1**) (CpCo(PPh₃)₂). Chromatography on SiO₂ easily led to the isolation of 1,2- and 1,3-bisphenols. Alkylation of the hydroxy groups with 1-bromotetradecane resulted in 1,2- and 1,3-organocobalt monomers (**1** and **2**). *p*-Divinylbenzene was prepared according to the literature procedure (6). Dimethylformamide (DMF) and tri-*n*-butylamine were dried over CaH₂, distilled, and stored under N₂. Toluene and tetrahydrofuran (THF) were dried over sodium and distilled under N₂. Other reagents were used as received.

The purification of products was carried out on a JAI LC-908 recycling preparative high-performance liquid chromatography (HPLC using chloroform as eluent (JAIGEL-1H and JAIGEL-2H). ¹H- and ¹³C-NMR spectra were recorded on a JEOL JNM-EX400 spectrometer in CDCl₃ (400 MHz and 100 MHz, respectively). Gel permeation chromatographic (GPC) analyses were performed on a Tosoh HLC-8020 (TSK gel G2500HXL, G3000HXL, G4000HXL, and G5000HXL, THF as eluent) on the basis of polystyrene standards. IR spectra were obtained on a JASCO FT/IR-5300 spectrometer from KBr pellets. UV-vis spectra were recorded on a Shimadzu UV-2100 spectrometer in CHCl₃. Thermogravimetric analyses (TGA) were carried out on a Shimadzu TGA-50 instrument at a heating rate of 20 °C/min under N₂. Anisotropic textures were observed by use of the polarizing microscope (Olympus BH-2, Mettler FP90 hot stage).

Synthesis of an organocobalt polymer.

The following representative procedure for **3** is presented. To a DMF solution (0.6 ml) of Pd(OAc)₂ (0.42 mg, 0.0019 mmol), tri(*o*-tolyl)phosphine (1.1 mg, 0.0038 mmol), and **1** (100 mg, 0.094 mmol) were added *p*-divinylbenzene (12 mg, 0.094 mmol) and tri-*n*-butylamine (70 mg, 0.38 mmol) under N₂ atmosphere. Stirred for 10 h at 100 °C, the reaction mixture was poured into 100 ml of methanol. The resulting yellow powder was filtered, washed with methanol, and then dried *in vacuo* to give 77 mg of the polymer: yield 74 %; ¹H-NMR (δ , ppm) 0.81 (t, -CH₃, 6H), 1.20-1.39 (m, -CH₂-, 48H), 3.90 (t, -OCH₂-, 4H), 4.54 (s, C₅H₅, 5H), 6.51-6.76 (br, -CH=CH-, 2H); ¹³C-NMR (δ , ppm) 14.2 (-CH₃), 22.7, 25.1, 26.1, 29.4, 29.5, 29.7, 31.9 (-(CH₂)₁₂-), 68.0 (-CH₂-O-), 83.0 (C₅H₅), 114.1, 119.5, 126.1, 126.6, 128.8, 128.9, 129.9, 130.0, 130.1, 130.2, 131.1, 131.2, 136.5, 157.8 (-CH=CH-, -C₅H₅-, C₄); IR (KBr, cm⁻¹) 2924, 2853, 1607, 1514, 1466, 1383, 1244, 1175, 1074, 1009, 808, 743.

Results and Discussion

The polycondensation of an organocobalt monomer bearing two aryl bromide moieties at 1,2- position of the cyclobutadiene moieties (**1**) with *p*-divinylbenzene by means of the Heck reaction process (7) gave a poly(arylene-vinylene) (**3**) in 74 % yield (Scheme 1). GPC analysis suggested that the number average molecular weight (M_n) of **3** was 4,100 ($M_w/M_n = 1.17$) (8). Likewise, the isomeric monomer (**2**) gave a polymer (M_n ($M_w/M_n = 4,000$ (1.15)) in 82 % yield. From the ¹H-NMR spectra, both **3** and **4** were found to have cis:trans=10:90 vinylene units (9). Both the polymers obtained were yellow and soluble in common organic solvents such as chloroform, tetrahydrofuran (THF), and dichloromethane. Despite these similarities, the form of polymers is apparently different: **3** is sticky while **4** is powdery, similar to those of 1,2- and 1,3-type poly(arylene)s described previously (3g, 3h). The difference is most probably originated from their structures. That is, **3** has a softer main chain microstructure than **4** owing to its zigzag linkage.

In the UV-vis spectra of **3** and **4**, the absorption maxima were observed at 362 and 397 nm, respectively. So as to estimate the effect of the number of repeating unit on the absorption spectra, model compounds (**3a** and **4a**) were prepared by the reaction of styrene with **1** and **2**, respectively. Oligomeric fractions of the polymers (**3** and **4**) were also separated into dimeric (**3b** and **4b**), trimeric (**3c** and **4c**), and tetrameric (**3d** and **4d**) species by HPLC.

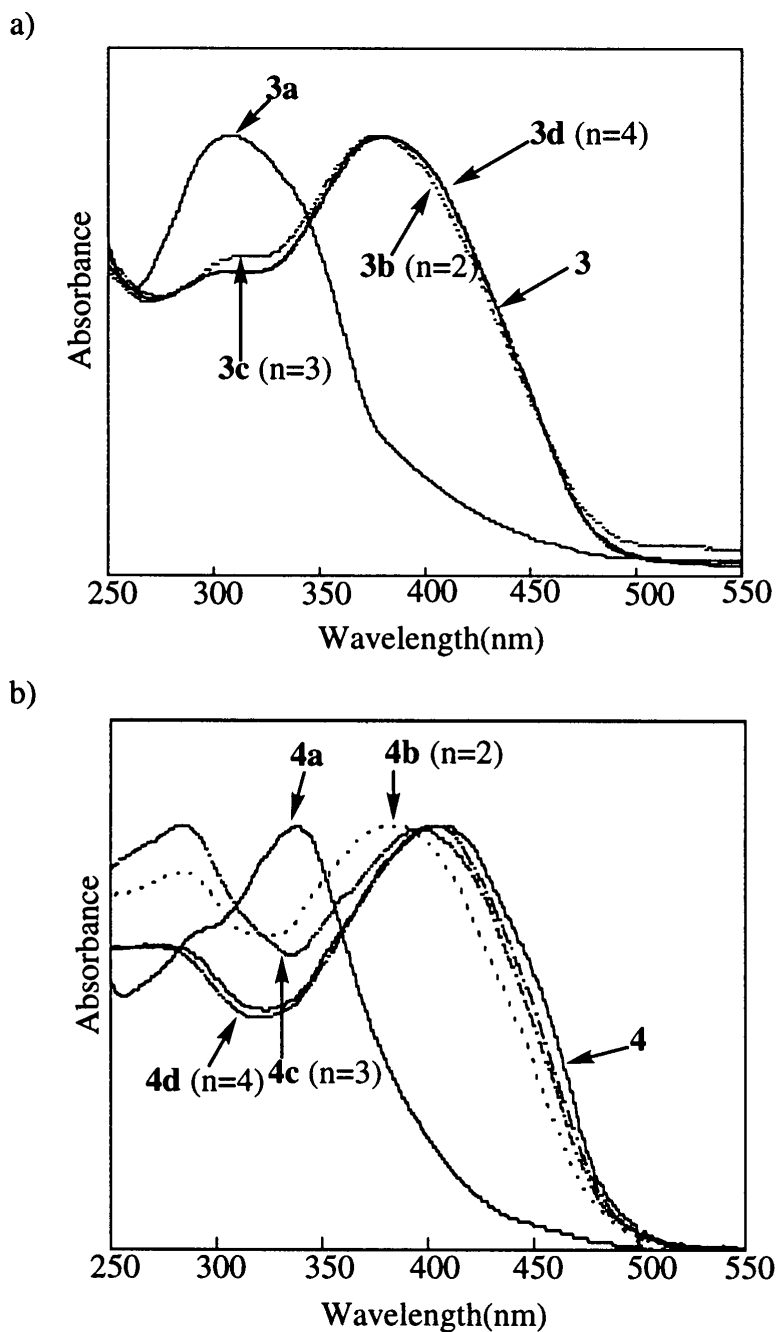


Figure 1 UV-vis absorption spectra of a monomeric model compound, oligomeric fractions (dimer, trimer, tetramer), and a polymeric fraction for **3** (a) and **4** (b) series.

Liquid crystallinity of the 1,2- and 1,3-type monomeric model compounds (**3a** and **4a**), the polymers (**3** and **4**), and oligomeric fractions (**3b-d** and **4b-d**) were examined by differential scanning calorimetry (DSC and the optical measurement using crossed polarizers. All oligomers and polymers except for **3a** and **4a** showed enantiotropic liquid crystallinity (10). Since we were unable to find any substantial thermal transitions in the DSC traces, the phase transitions listed in Table 2 were determined by the optical observation. A typical optical micrograph of 1,2-type polymers measured at 35 °C is shown in Figure 2. In the cases of **3b-3d**, glassy state - mesophase transitions were observed near room temperature and mesophase -

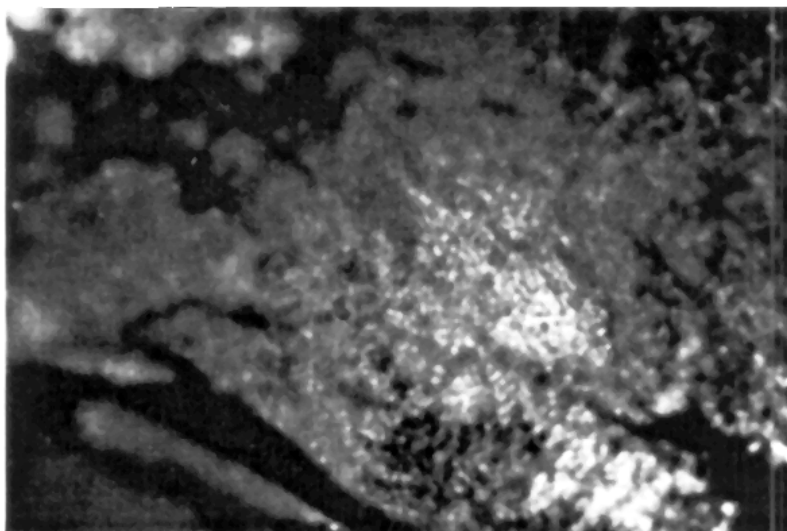


Figure 2 A typical optical texture of the organocobalt poly(arylene-vinylene)s under crossed polarizers (3, measured at 35 °C).

Table 2. Phase Transition Temperatures of 3a-3e and 4a-4e.^{a)}

	$T_{k-m}^{b)}$	$T_{m-i}^{c)}$
3a	d)	d)
3b	35	59
3c	<rt	72
3d	<rt	78
3	33	82

4a	d)	d)
4b	34	54
4c	53	92
4d	43	92
4	54	106

- a) Anisotropic textures of the polymers were observed by the optical measurement using crossed polarizers.
 b) Temperature of crystalline-mesophase transition.
 c) Temperature of mesophase-isotropic phase transition.
 d) Not observed.

isotropic phase transitions occurred between 59 and 82 °C. Table 2 suggested that the isotropization temperature (T_{m-i}) exhibited an increase with the degree of polymerization.

Another series (**4b-4d**) showed a similar thermal transition behavior to **3b-3d**, in which, however, the isotropic melt was observed at higher temperature. The results are likely due to the backbone structures of **3** and **4** where **4** is more rigid than **3**.

Because the repeating unit of **3** and **4** is supposed to be conjugated along the main chain and they reveal thermotropic liquid crystallinity, further studies leading to novel functional materials are now under investigation.

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8. The reason for the relatively low molecular weights of the resulting polymers has not been sufficiently clarified yet.
9. ¹H-NMR spectra of model compounds (**3a** and **4a**) were analogous to those of polymers in the cis/trans ratio as well as their constitution.
10. Both **3a** and **4a** were amorphous during both heating and cooling processes.
11. Thermogravimetric analysis (TGA) showed that the polymers had good thermal stability. For example, heating **3** to 400 °C (20 °C/min) gave a weight retention of 83 % with the onset of weight loss at approximately 350 °C.