# Synthesis of Conjugated Rigid-Rod Polyarylenes with ($\eta^4$-Cyclobutadiene)cobalt Moieties in the Main Chain

Igor L. Rozhanskii, Ikuyoshi Tomita, and Takeshi Endo*
*Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226*

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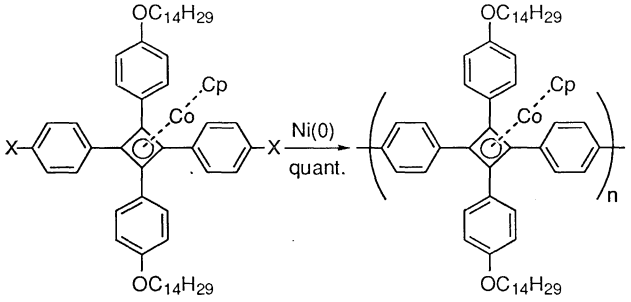
Ni(0)-promoted dehalogenation polycondensation of bifunctional ($\eta^5$-cyclopentadienyl)($\eta^4$-cylobutadiene)cobalt complexes yields rigid-rod π-conjugated polyarylenes, which exhibit the liquid-crystalline behavior both in melts and in solutions.

Metal-containing polymers offer plentiful possibilities in a macromolecular design, based on their unique properties and versatile synthetic methods of organometallic chemistry.[1] In particular, polymers bearing extended π-conjugated backbones with incorporated 2,2'-dipyridyl transition metal complexes exhibited interesting luminescent, electroconductive and catalytic properties.[2] Their specific features would be attributed in part to the interactions of metal complexes and conjugated main chains. Apparently, conjugated polymers with other organometallic moieties may be also of interest. Recently, novel organocobalt polymers have been synthesized by our[3] and Bunz[4] groups. Facile methods of introduction ($\eta^5$-cyclopentadienyl)($\eta^4$-cyclobutadiene)cobalt moieties into polymeric backbones have been established. These units would be regarded as convenient building blocks for the construction of desired organometallic π-conjugated polymers.

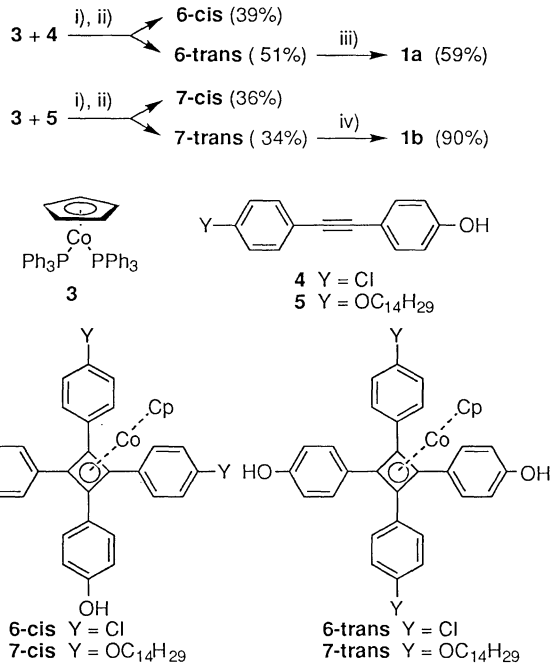
In this communication, we wish to describe the synthesis of novel rigid-rod oligo- and polyarylenes bearing ($\eta^5$-cyclopentadienyl)($\eta^4$-tetraphenylcyclobutadiene)cobalt units in the main chain and *n*-tetradecyloxy groups in side chains (**2**) by the Ni(0)-promoted aryl-aryl coupling of bifunctional cobalt complexes (**1**) (Scheme 1). Analogous stiff-chain polymers bearing flexible side chains often exhibit good mechanical properties, combined with enhanced solubilities and decreased melting points. In many instances, they can form liquid crystalline phases.[5]

The monomers (**1a** and **1b**) were synthesized in two steps (Scheme 2), starting from ($\eta^5$-cyclopentadienyl)bis(triphenylphosphine)cobalt (**3**), which was obtained by the procedure of Yamazaki,[6] and corresponding ethynylphenols (**4**, **5**).[7] *Cis* and *trans* isomers of organocobalt bis-phenols (**6**, **7**) were easily separated by the chromatography on silica gel. In a typical polycondensation procedure, which is a modification of Yamamoto method,[2a] **1a** (164 mg, 0.17 mmol) was mixed with $Ni(cod)_2$ (cod=1,5-cyclooctadiene), cod and 2,2'-dipyridyl (2 equivalents each) under dry nitrogen, benzene (1 $cm^3$) was added, and the reaction mixture was stirred at 80 °C. After 2.5 h stirring became impossible because of formation of gel. Two fractions of **2a** have been collected. The first one (32 mg, 20%) was isolated after Soxhlet extraction of the reaction mixture with benzene, followed by the precipitation of the concentrated extract into methanol. An acidic workup of an insoluble residue (aimed to remove inorganic admixtures) gave the main fraction as a yellow powder (127 mg, 82%). Although soluble products were obtained by the condensation of **1b** under similar conditions, the fine black precipitate (presumably, Ni) was formed after 5 - 6 h, indicating the decomposition of Ni(0) complex and the premature termination of the reaction.

**Scheme 1.**




**Scheme 2.**




i) THF, 45 °C, 20 h; ii) THF/DMF, 125 °C, 2 h; iii) $C_{14}H_{29}Br$, $K_2CO_3$, DMF, 125 °C, 24 h; iv) $(CF_3SO_2)_2O$, Py, 20 °C, 12 h.

According to gel permeation chromatography (GPC) analyses, **2b** and a benzene-soluble fraction of **2a** (19.5% of the isolated product) consisted of oligomers ($DP_n \approx 3$ - 5). The benzene-insoluble fraction of **2a** (80.5%) was estimated to have $DP_n > 15$ ($M_n \approx 22000$ by the polystyrene standard).[8] Probably, **1b** is not reactive enough in the present reaction system and does not form a high polymer before the decomposition of the relatively unstable

$Ni(cod)_2$. On the contrary, the degree of polymerization of **2a** seems to depend mostly on its solubility. IR, $^1H$ and $^{13}C$ NMR spectra of soluble oligomers supported the proposed structures and were in excellent agreement with spectra of model compounds.[9] IR spectra of oligomeric and polymeric fractions of **2a** exhibited the same features.

UV spectra of **2** revealed the new band ($\lambda_{max}$ = 340 nm), which may be assigned to a $\pi$–$\pi^*$ transition of the delocalized $\pi$-electron system (Figure 1).[10] Judging from the convergence limit of UV spectra of oligomers (separated by the preparative HPLC), an average conjugation length of **2** may be estimated as 12 - 15 aromatic rings. A bandgap of 2.56 eV can be determined from the onset of the UV absorption.

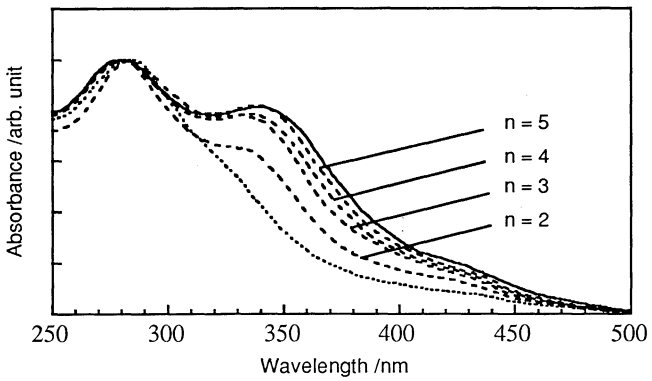



**Figure 1.** UV spectra of **1a** (dotted line) and **2a**: oligomers (dashed lines) and polymeric fraction (solid line). Solvent $CHCl_3$, concentration *ca.* $10^{-5}$ *M* per repeat unit. Spectra are normalized to the band of 280 nm.

The polymeric fraction of **2a** ($DP_n$ > 15) is soluble in *o*-dichlorobenzene and nitrobenzene. Homogeneous and optically isotropic solutions were observed above 100 °C (concentration of polymer *ca.* 5%). With decreasing the temperature, the solution separated into optically isotropic and anisotropic phases, starting from 60 °C. The single gel-like anisotropic phase was obtained on slow evaporation of solutions. Being observed between crossed polarizers, this phase exhibited 'Maltese cross' patterns, and might be preliminary assigned as the nematic physical gel.[11] The cast films of **2a** retained anisotropic textures of the preceding lyotropic phase. These textures became more bright and fluid above the glass transition temperature ($T_g$ = 160 °C, measured by DSC), that may indicate the formation of the thermotropic mesophase. Shearing of the cover glass led to bright birefringence colors and marbled textures. The examined samples did not exhibit transitions to isotropic melts, being anisotropic up to *ca.* 350 °C, when an appreciable darkening occurred.

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8 The rough estimation of $DP_n$ is based on the retention times of the resolved peaks of oligomers (up to heptamer).

9 Spectral data of **2a** (i) fraction $DP_n$ > 15: $\nu_{max}$ (KBr)/ $cm^{-1}$ 3034 ($CH_{ar}$), 2924, 2853 ($CH_{al}$), 1607, 1512 (C=C), 1244 (C-O), 831, 806 (C=C-H, out-of-plane); (ii) fraction $DP_n \approx 4$: $\nu_{max}$ (neat)/$cm^{-1}$ 3038 ($CH_{ar}$), 2924, 2855 ($CH_{al}$), 1607, 1514 (C=C), 1242 (C-O), 825, 804 (C=C-H, out-of-plane); $\delta_H$ (400 MHz; $C_6D_6$; $Me_4Si$) 0.92 (6H, br, Me), 1.33(br, 44H, -$CH_2$-), 1.66 (br, 4H, -$CH_2$-, $\beta$ to -O-) 3.99 (4H, br, -$OCH_2$-), 4.60 (2.5H, s, $C_5H_5$ end group), 4.62 (2.5H, s, $C_5H_5$), 6.81-6.87 (4H, $C_6H_4$, *ortho* to -OAlk), 7.10 - 7.12 (~1H, $C_6H_4$, *ortho* to end groups), 7.59-7.77 (11H, $C_6H_4$, main chain and side chain, *meta* to -OAlk).

10 $\lambda_{max} \approx$ 280 nm may be attributed to an absorption of non-conjugated pendant phenoxy groups.

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