Synthesis of Liquid-Crystalline Polyesters with (η^4-Cyclobutadiene)cobalt Moieties in the Main Chain

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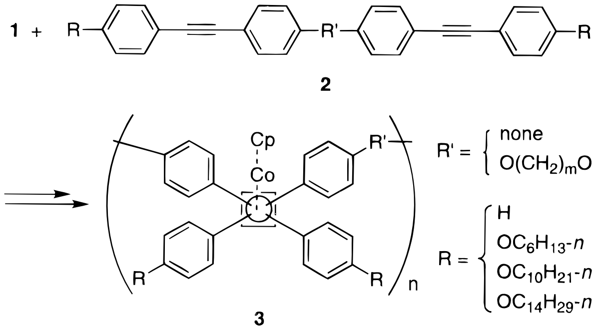
Organometallic polymers are very attractive because they offer plentiful possibilities in a macromolecular design, based on unique geometries and versatile synthetic methods of organometallic chemistry.[1] Metal-containing polymeric liquid crystals are of special interest as materials with potentially useful properties for applications to electro-optical devices and related fields.[2] Recently, we have reported the synthesis of novel organocobalt polymers by the reaction of (η^5-cyclopentadienyl)bis(triphenylphosphine)cobalt (**1**) with various diynes (**2**) (Scheme 1).[3] Organocobalt polymers with acetylene moieties in the main chains have been prepared independently by Bunz *et al.*[4] (η^4-Cyclobutadiene)cobalt-containing polymers **3** are both thermally and chemically stable and soluble in common organic solvents. Although they show good film-forming properties, these polymers do not form ordered phases. Apparently, the intrinsic irregularities in the backbone structures of **3** may suppress an ordering of polymeric chains.

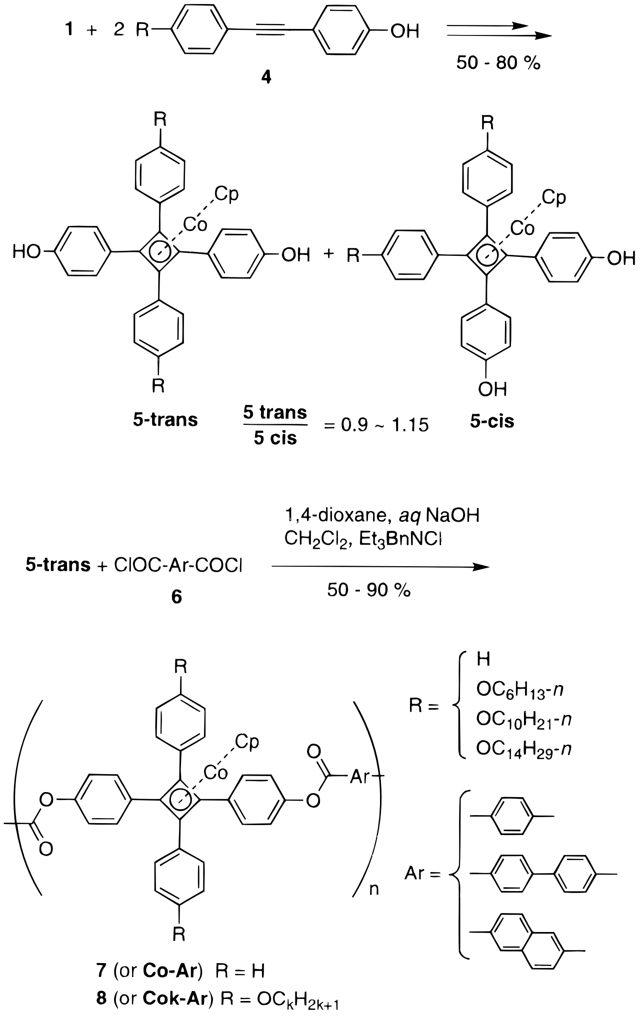
One of the possible ways to attain the desired structural regularity is to employ polycondensation reactions of bifunctional regioisomerically pure monomers. In this Communication, we describe the synthesis and properties of rigid-rod polyesters bearing (η^5-cyclopentadienyl)(η^4-tetraphenylcyclobutadiene)cobalt units and various aromatic linking groups in the main chain. A fully aromatic polyester (**7**), and a series of polymers with linear alkoxy lateral substituents (**8**) have been synthesized by the polycondensation reactions of organocobalt diols (**5**) with diacyl dichlorides (**6**) (Scheme 2).[5] According to literature data, an attachment of pendant flexible substituents improves processabilities and promotes thermotropic mesomorphism in linear stiff-chain polyesters,[6] polyamides,[7] polyimides,[8] and poly(p-phenylene)s[9] which are either lyotropic or completely intractable otherwise. It is expected that structurally similar polyesters **8** can also show liquid-crystalline properties.

Organocobalt diols (**5**) were synthesized by the reaction of **1** with corresponding phenylethynylphenols (**4**) and purified with the separation of isomers (**5-cis** and **5-trans**) by column chromatography on silica gel. Polyesters **7** and **8** were obtained by the interfacial polycondensations of **5-trans** with aromatic diacyl dichlorides (**6**) in the presence of a quaternary ammonium salt as a phase-transfer catalyst (Scheme 2, Table 1).[10] The polycondensations proceeded at room temperature within several minutes, to afford yellow fibrous flakes of polyesters (**7** or **8**) immediately after mixing of the monomers. **7** and **8** were successfully obtained from both dispersions and true solutions of reagents in good yields. In particular, polyesters with the highest degrees of polymerization (**Co10-Biph** and **Co14-Biph**) were obtained from suspensions of 4,4′-biphenyldicarbonyl dichloride in dichloromethane, since this acyl chloride was not soluble enough at room temperature.

Scheme 1



Scheme 2



Gel permeation chromatography analyses (GPC, HLC-8020) indicated an absence of low-molecular-weight admixtures in isolated products. The structure of polymers **8** was supported by their IR (JASCO FT/IR-5300) and NMR (JNM-EX400) spectra.[11] The representative ^{1}H NMR spectrum of **Co6-Biph** (Figure 1) manifests well-resolved fine structures in the region of aromatic protons that may be indicative of the high conformational uniformity of the main chains. On assuming that small peaks in this region, as well as the

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Table 1. Properties of Organocobalt Polyesters 7 (Entry 1) and 8 (Entries 2−8)

entry	Ar[a]	R	polymer designation	yield (%)[b]	$\bar{M}_n$[c]	$\bar{M}_w/\bar{M}_n$[c]	T_m (°C)[d]	T_g (°C)[e]	mesophase temperature range (°C)[f]
1	Biph	H	Co-Biph	77	7 200	1.86		no transitions	
2	Biph	OC_6H_{13}	Co6-Biph	75	10 700	1.73	73	145 (130)	140 to >250
3		$OC_{10}H_{21}$	Co10-Biph	77	22 500	3.08	73	115 (122)	125 to >250
4		$OC_{14}H_{29}$	Co14-Biph	89	19 700	5.45	82	100 (111)	110 to >250
5	Phen	$OC_{10}H_{21}$	Co10-Phen	62	13 300	1.93	72	90 (101)	115−175
6		$OC_{14}H_{29}$	Co14-Phen	69	12 500	2.36	68, 146	80 (n.o.)[g]	110−160
7	Naph	$OC_{10}H_{21}$	Co10-Naph	48	17 200	1.93	62, 224	103 (100)	120−225
8		$OC_{14}H_{29}$	Co14-Naph	77	17 800	2.19	71, 192	82 (105)	110−200

[a] Polymer structures according to Scheme 2: Biph = 1,1′-biphenyl-4,4′-diyl, Phen = *p*-phenylene, Naph = naphthalene-2,6-diyl. [b] Isolated yields. [c] Estimated from GPC, THF as an eluent, Tosoh TSK-G4000HXL and TSK-G5000HXL gels, polystyrene standard. [d] Determined by DSC in the first heating, 20 °C/min. [e] Determined by DSC in the second heating, 20 °C/min. Data of the first heating are given in parentheses. [f] Determined from polarizing microscope observations in the first heating, 10 °C/min. [g] n.o. = not observed.

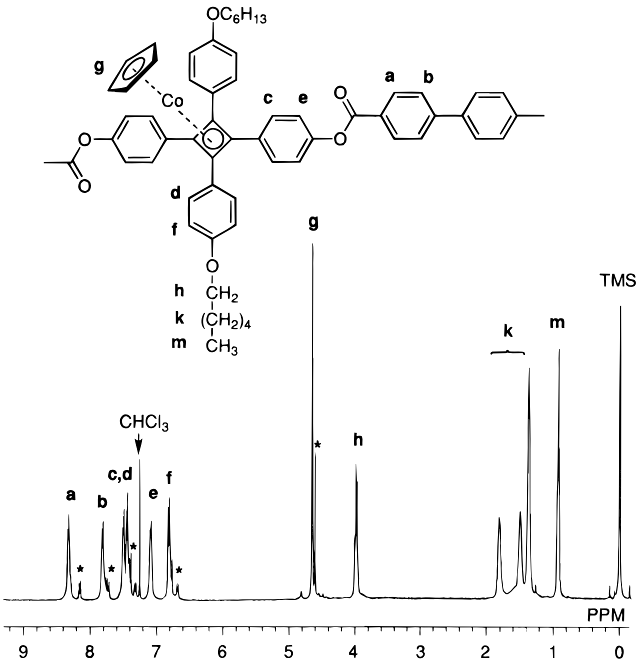

Figure 1. ^{1}H NMR spectrum of **Co6-Biph** (400 MHz, $CDCl_3$, TMS as a standard). Asterisks (*) mark bands of end groups.

band at 4.61 ppm (marked by asterisks), correspond to end groups, the number-averaged degree of polymerization ($\bar{DP}_n$) of **Co6-Biph** was estimated from relative intensities of these peaks, to be *ca.* 10, in good accordance with the results of GPC analyses ($DP_n \approx 11$).

Alkoxy-substituted polyesters **8** are readily soluble in THF, DMF, chloroform, and benzene at room temperature, forming flexible transparent films on casting. In general, these films are optically isotropic. In contrast, the wholly aromatic polyester **7** can be fully dissolved only in hot *o*-dichlorobenzene and nitrobenzene. Attempts to cast films were unsuccessful, because **7** was precipitated from concentrated solutions as a powder.

Thermogravimetric analyses (Seiko TG/DTA 220) revealed a higher thermal stability of **7**, compared with alkoxy-substituted polyesters **8** (**Co14-Biph**, as a representative example). Weight losses of 5% in N_2 took place at 410 and 355 °C in **7** and **8**, respectively. It is likely that thermally labile alkoxy moieties are responsible for the lower thermal stability of **8**.

According to differential scanning calorimetry measurements (DSC, DuPont 2000), polyesters **8** exhibited endothermic transitions at 60−80 °C ($\Delta H \approx 1{-}1.5$ kJ/mol) in the first heating. Transitions in this temperature range were observed also in other stiff-chain polymers, being commonly assigned to the melting of side chains.[6b,9a] **Co14-Phen**, **Co10-Naph**, and **Co14-Naph** exhibited additional melting endotherms at higher temperatures (Figure 2a). Only glass transitions were observed in the subsequent thermal cycles (Figure 2b). T_g's ranged from 80 to 145 °C, depending regularly on the content of aliphatic parts. No transitions were detected in the wholly aromatic **Co-Biph**.

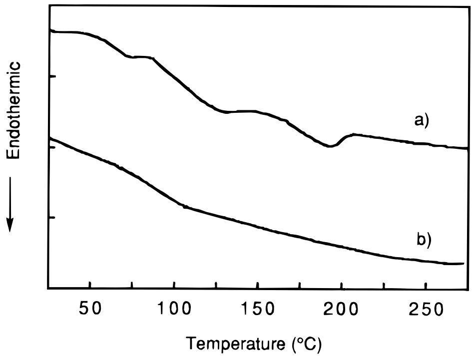

Figure 2. DSC traces of **Co14-Naph** (20 °C/min): (a) first heating; (b) second heating.

Thermotropic optically anisotropic phases were found in polyesters **8** by the polarizing microscope observations (Olympus BH-2, Mettler FP90 hot stage). When freshly prepared optically isotropic free-standing films were heated just above the corresponding T_g's, birefringent areas rapidly developed as uniformly colored domains, being accompanied also by homeotropic regions, dark arms, and Maltese crosses around defects (Figure 3a).[12] Shearing or twisting of the cover glass induced an in-plane orientation of local optical axes, as can be concluded from the corresponding bright fluid textures (Figure 3b). Polyesters of the **Biph** series retained these textures up to the onset of the decomposition (275−300 °C), showing only some decrease in their brightness at 220−250 °C. Polyesters with **Phen** and **Naph** linking groups exhibited distinct clearing points, which were close to higher-temperature melting endotherms, detected by DSC.[13] When the isotropic melts were cooled, as well as in subsequent thermal cycles, samples remained isotropic. Shearing of films at temperatures above their T_g's did not induce any optical anisotropy. These features are in good agreement with DSC, which did not detect recrystallization processes. For comparison, model (η^5-cyclopentadienyl)(η^4-tetrakis(4-alkoxyphenyl)cyclobutadiene)cobalt monomers exhibited multiple melting and a strong tendency to form glasses, with crystallization times ranging from hours to months. The similar irreversible thermotropic mesomorphism was also found in rigid-rod organocobalt poly(arylene ethynylenes)[4b] and in a number of low molar mass compounds with bulky mesogenes.[14] Probably, high melt viscosities and the bulkiness of the

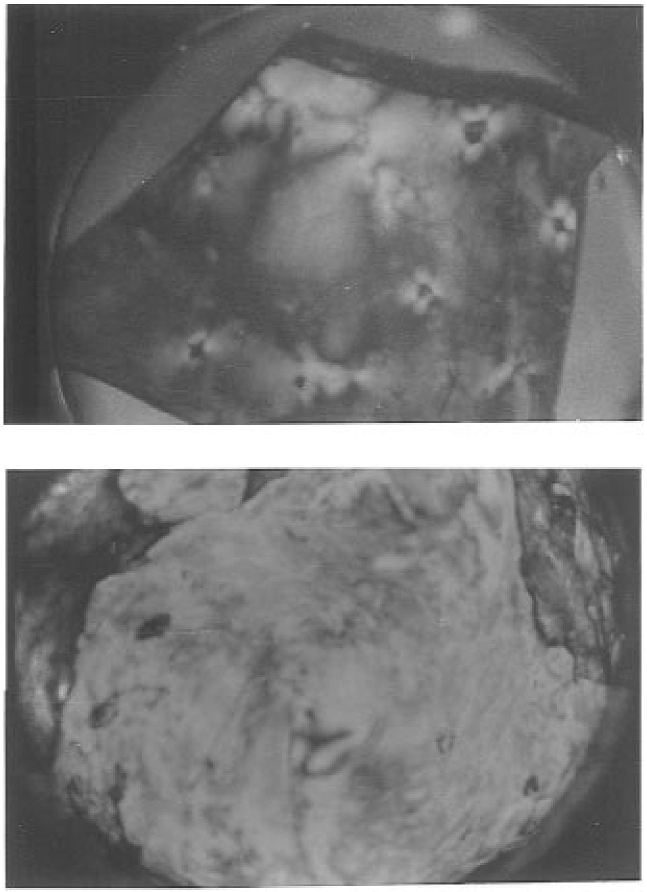

Figure 3. Optical textures of **Co14-Biph** at 200 °C (heating, crossed nicols, ×60): (a) noncovered film; (b) the same sample after imposing and twisting of the cover glass.

repeat units hinder the reordering of the corresponding stiff-chain polymers. The detailed study of the observed anisotropic phases is in progress.

In summary, several rigid-rod aromatic polyesters (**8**) with (η^4-cyclobutadiene)cobalt moieties in the main chain and flexible alkoxy groups in the side chains were synthesized by interfacial polycondensations of organometallic diols with aromatic diacyl dichlorides. Degrees of polymerization ranged from 10 to >50, which corresponds to 40−250 aromatic rings along the polymeric backbones. Polyesters **8** are soluble in common organic solvents, forming flexible transparent films on casting. Thermotropic mesophases were observed in the first thermal cycles of **8** in the temperature ranges above T_g, but they did not appear on cooling from the isotropic phase, probably due to kinetic reasons.

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Supporting Information Available: IR and ^{1}H NMR spectra of polyesters **7** and **8** (17 pp). Ordering information is given on any current masthead page.

References and Notes

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(5) In order to specify structures, each particular polyester **8** is denoted according to the number of carbon atoms in the side arm and the type of comonomer (e.g., **Co10-Biph**). Accordingly, **7** may be written as **Co-Biph**.

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(10) *The typical procedure.* Solutions of triethylbenzylammonium chloride (0.2 g, 0.88 mmol) and NaOH (1.0 g, 25 mmol) in water (25 mL) (solution I) and **5-trans** ($R = OC_6H_{13}$, 50 mg, 0.070 mmol) in 1,4-dioxane (0.5 mL) (solution II) were prepared in separate vessels. An aliquot of solution I (1 mL) was added to solution II, and the resulting emulsion was stirred for several minutes. When the homogeneous brown solution was formed, a suspension of 4,4′-biphenyldicarbonyl dichloride (20 mg, 0.070 mmol) in dichloromethane (1.5 mL) was added to it in one portion. Immediately, **Co6-Biph** started to form as yellow flakes. The reaction mixture was stirred vigorously for 20 min and then was poured into methanol (50 mL). The yellow precipitate was filtered off, washed repeatedly with water and then with methanol, and dried *in vacuo.* Yield: 48 mg (75%). IR (KBr, cm^{-1}): 1738 (COO), 1607, 1512 ($C{=}C$), 1244 ($={C}{-}O{-}$). ^{1}H NMR: Figure 1. See Supporting Information for more details.

(11) **7** (**Co-Biph**) was not soluble enough in NMR solvents. Its authenticity was established by the IR spectrum ((KBr, cm^{-1}): 1736 (COO), 1605, 1508 ($C{=}C$), 1260 ($={C}{-}O{-}$)), which was virtually identical to the spectrum of the soluble isomeric **Co-Biph-cis**, obtained from **5-cis**.

(12) The observed textures appeared spontaneously and showed an obvious temperature dependence. Special experiments ruled out their possible assignment to the stress birefringence. Bright birefringence colors could be stress-induced in the glassy state of polyesters **8** (e.g., by pushing the cover glass), but they rapidly disappeared in the vicinity of T_g's, not surviving in the fluid state.

(13) **Co10-Phen** is an exception, since it did not exhibit the distinct second melting endotherm. However, its isotropization proceeded more smoothly and in the broader temperature range (150−175 °C), compared with **Co14-Phen**.

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