Synthesis of Novel Organocobalt Polymers with Flexible Aliphatic Spacers in the Main Chain

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ABSTRACT: A series of polymers **3** bearing (η^5-cyclopentadienyl)cobaltacyclopentadiene moieties in the main chain and flexible aliphatic alkoxy groups in both the main and side chains has been synthesized. Polymers **4** having (η^5-cyclopentadienyl)(η^4-cyclobutadiene)cobalt moieties were obtained by the thermolysis of toluene solutions of the corresponding polymers **3**. The resulting polymers of both series were soluble in common organic solvents. According to the thermal analysis data, polymers **3** underwent rearrangement to produce **4** upon heating (155−175 °C), while polymers **4** were stable before 410−425 °C. Glass transitions of polymers **4** were observed in the range −10 to +120 °C, depending regularly on the size of the aliphatic segments.

Introduction

Organometallic polymers may be of interest because of their possible applications in molecular electronics, nonlinear optics, and potential new optical devices.[1] Recently, we have described the synthesis of the organocobalt polymer **3a** with rigid main chains by the reaction of CpCo(PPh$_3$)$_2$ (**1**) with 4,4′-bis(phenylethynyl)biphenyl (**2a**).[2] The chemical structure of the backbone of **3a** can be modified in various ways on the basis of the specific reactivity of the cobaltacycle units.[3] For instance, a thermally stable (η^4-cyclobutadiene)cobalt-containing polymer **4a** can be obtained by the thermal rearrangement of **3a**.[4] Since these polymers are built from aromatic rigid statistic chains, they are deep-colored stiff glasses, showing neither ordered phases nor glass transitions below their decomposition temperatures. Because of this intractability, there are limitations on the possible applications of organocobalt polymers.

In this paper, we report the synthesis of polymers containing aromatic organocobalt moieties and linear aliphatic alkoxy substituents in the main chains (**3b**,**c** and **4b**,**c**). Likewise, flexible groups can additionally be inserted into lateral positions in a number of polymers (**3d**−**h** and **4d**−**j**). By varying the content of the aliphatic part, one can expect a corresponding shift in the glass transition temperature (T_g), the appearance of ordered phases, and an increase in solubility.

Experimental Section

(η^5-Cyclopentadienyl)bis(triphenylphosphine)cobalt complex (**1**) was obtained according to the literature procedure.[5] A detailed account of the synthesis and properties of α,ω-bis[4-(phenylethynyl)phenoxy]alkanes (**2b**,**2c**) and α,ω-bis[4-[(4-alkoxyphenyl)ethynyl]phenoxy]alkanes (**2d**−**j**) will be reported elsewhere.[6] Toluene was dried over sodium and distilled under nitrogen. Other reagents were used as received.

The fractionation of polymers was carried out on a JAI LC-908 recycling preparative high-performance liquid chromatograph (HPLC) with tetrahydrofuran (THF) as eluent. ^{1}H NMR spectra were recorded on JEOL JNM-PMX60SI and JNM-EX400 spectrometers (60 and 400 MHz, respectively) in CDCl$_3$ (tetramethylsilane as internal standard). IR spectra were obtained on a Jacso FT/IR-5300 spectrometer in KBr disks. UV spectra were recorded on a Shimadzu UV-2100 spectrophotometer in THF. Gel permeation chromatographic (GPC) analyses were performed on a Tosoh CCPD (TSK gel G3000, THF as eluent) on the basis of polystyrene standards. Thermogravimetric (TG) and differential thermal analyses (DTA) were carried out on a Seiko TG/DTA 220 instrument at a heating rate of 10 °C/min under nitrogen. Differential scanning calorimetry (DSC) analyses were carried out on a Seiko Instruments SSC/220C calorimeter at scanning rates of 20 and 10 °C/min (first and second heatings, respectively).

Synthesis of (η^5-Cyclopentadienyl)cobaltacyclopentadiene-Containing Polymers 3b−h. Typical Procedure for the Synthesis of 3b. To a test tube containing **1** (140 mg, 0.22 mmol) was added 2 mL of a toluene solution of **2b** (102 mg, 0.22 mmol) under nitrogen, and the reaction mixture was kept stirring for 3 days at 50 °C. After filtration and reduction of the volume under vacuum, the condensed solution was poured dropwise into *n*-hexane (50 mL). The resulting orange-brown powder was filtered, washed successively with methanol and then with *n*-hexane, and dried *in vacuo*. According to IR, NMR, and GPC data, triphenylphosphine was quantitatively removed by this procedure. Thus, **3b** was characterized without additional purification. **3b**: yield, 143 mg (77%); ^{1}H NMR δ 1.33−1.75 (CH$_2$, 8H), 3.55−4.00 (br, OCH$_2$, 4H), 4.74 (s, C$_5$H$_5$, 5H),[7] 6.32−7.67 (C$_6$H$_4$, C$_6$H$_5$, 33H); IR (KBr, cm^{-1}) 3054, 2926, 2857, 1597, 1499, 1466, 1435, 1236, 1173, 1090, 1071, 1026, 1013, 831, 810, 748, 698, 527.

Similarly, all of the polymers **3b**−**h** were prepared under the same conditions. Polymers with lateral substituents **3d**−**h** were precipitated into methanol because of their higher solubility in *n*-hexane. Polymers **3i** and **3j** were converted into their (η^4-cyclobutadiene)cobalt analogs **4i** and **4j** without isolation.

3c: yield, 58%; ^{1}H NMR δ 1.28−1.75 (CH$_2$, 16H), 3.55−4.00 (br, OCH$_2$, 4H), 4.59 (s), 4.74 (s, both C$_5$H$_5$, 5H), 6.32−7.67 (C$_6$H$_4$, C$_6$H$_5$, 33H); IR (KBr, cm^{-1}) 3054, 2926, 2857, 1597, 1499, 1479, 1435, 1238, 1173, 1090, 1071, 1026, 1011, 831, 810, 748, 698, 527.

3d: yield, 48%; ^{1}H NMR δ 0.88 (t, CH$_3$, 6H), 1.35−1.72 (CH$_2$, 24H), 3.60−3.95 (br, OCH$_2$, 8H), 4.72 (s, C$_5$H$_5$, 5H),[7] 6.30−7.60 (C$_6$H$_4$, C$_6$H$_5$, 31H); IR (KBr, cm^{-1}) 3057, 2932, 2861, 1605, 1516, 1495, 1472, 1240, 1171, 1107, 1088, 1024, 829, 806, 747, 696, 527.

3e: yield, 60%; ^{1}H NMR δ 0.88 (t, CH$_3$, 6H), 1.28−1.72 (CH$_2$, 30H), 3.60−3.95 (br, OCH$_2$, 8H), 4.72 (s, C$_5$H$_5$, 5H),[7] 6.30−7.60 (C$_6$H$_4$, C$_6$H$_5$, 31H); IR (KBr, cm^{-1}) 3057, 2930, 2857, 1605, 1516, 1495, 1472, 1240, 1171, 1107, 1088, 1030, 831, 808, 747, 696, 527.

3f: yield, 52%; ^{1}H NMR δ 0.88 (t, CH$_3$, 6H), 1.28−1.72 (CH$_2$, 40H), 3.60−3.95 (br, OCH$_2$, 8H), 4.72 (s, C$_5$H$_5$, 5H),[7] 6.30−7.60 (C$_6$H$_4$, C$_6$H$_5$, 31H); IR (KBr, cm^{-1}) 3057, 2926, 2855, 1603, 1516, 1495, 1470, 1238, 1171, 1107, 1088, 1028, 829, 808, 747, 696, 527.

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3g: yield, 43%; ^{1}H NMR δ 0.88 (t, CH_3, 6H), 1.28−1.72 (CH_2, 46H), 3.60−3.95 (br, OCH_2, 8H), 4.72 (s, C_5H_5, 5H),[7] 6.30−7.60 (C_6H_4, C_6H_5, 31H); IR (KBr, cm^{-1}) 3057, 2926, 2855, 1605, 1516, 1497, 1470, 1240, 1173, 1107, 1090, 1028, 829, 808, 747, 696, 527.

3h: yield, 48%; ^{1}H NMR δ 0.88 (t, CH_3, 6H), 1.28−1.72 (CH_2, 48H), 3.60−3.95 (br, OCH_2, 8H), 4.72 (s, C_5H_5, 5H),[7] 6.30−7.60 (C_6H_4, C_6H_5, 31H); IR (KBr, cm^{-1}) 3057, 2926, 2855, 1605, 1514, 1495, 1470, 1240, 1173, 1107, 1090, 1030, 829, 810, 747, 696, 527.

Synthesis of (η^5-Cyclopentadienyl)(η^4-cyclobutadiene)cobalt-Containing Polymers 4b−j. Typical Procedure for the Synthesis of 4b. A portion of **3b** (100 mg, 0.11 mmol, recalculated per repeating unit) was dissolved in toluene (10 mL) under nitrogen and stirred at 110 °C for 2 h. After filtration and reduction of the volume, the final polymer was precipitated into *n*-hexane (30 mL). The resulting yellow powder was filtered, washed successively with methanol and then with *n*-hexane, and dried *in vacuo*. **4b**: yield, 74%; ^{1}H NMR δ 1.35−1.80 (CH_2, 8H), 3.95 (t, OCH_2, 4H), 4.59 (s, C_5H_5, 5H), 6.75−7.43 (C_6H_5, C_6H_4, 18H); IR (KBr, cm^{-1}) 3057, 2926, 2855, 1605, 1512, 1464, 1242, 1173, 1107, 1067, 1024, 1003, 833, 808, 760, 696, 588, 567.

4c was prepared and purified in a similar manner. Polymers **4d−j** with lateral substituents could not be efficiently purified by the corresponding technique, since they formed adhesive viscous precipitates. Thus, **4d−j** were isolated and fractionated by preparative HPLC after filtration and the removal of solvent.[8]

4c: yield, 84%; ^{1}H NMR δ 1.28−1.80 (CH_2, 16H), 3.95 (t, OCH_2, 4H), 4.59 (s, C_5H_5, 5H), 6.75−7.43 (C_6H_5, C_6H_4, 18H); IR (KBr, cm^{-1}) 3057, 2926, 2855, 1607, 1512, 1242, 1173, 1107, 1067, 1026, 1003, 833, 806, 758, 696, 588, 565.

4d: yield, 88%; ^{1}H NMR δ 0.88 (t, CH_3, 6H), 1.35−1.80 (CH_2, 24H), 3.96 (t, OCH_2, 8H), 4.58 (s, C_5H_5, 5H), 6.65−7.43 (C_6H_4, 16H); IR (KBr, cm^{-1}) 2928, 2859, 1607, 1514, 1468, 1244, 1173, 1107, 1096, 1028, 833, 804, 586, 569.

4e: yield, 77%; ^{1}H NMR δ 0.88 (t, CH_3, 6H), 1.28−1.80 (CH_2, 30H), 3.95 (t, OCH_2, 8H), 4.58 (s, C_5H_5, 5H), 6.65−7.43 (C_6H_4, 16H); IR (KBr, cm^{-1}) 2930, 2857, 1601, 1510, 1468, 1248, 1167, 1113, 1024, 833, 806, 579.

4f: yield, 90%; ^{1}H NMR δ 0.88 (t, CH_3, 6H), 1.28−1.80 (CH_2, 40H), 3.97 (t, OCH_2, 8H), 4.58 (s, C_5H_5, 5H), 6.65−7.45 (C_6H_4, 16H); IR (KBr, cm^{-1}) 2926, 2855, 1607, 1514, 1468, 1244, 1173, 1107, 1096, 1026, 831, 806, 586, 571.

4g: yield, 81%; ^{1}H NMR δ 0.88 (t, CH_3, 6H), 1.28−1.80 (CH_2, 46H), 3.95 (t, OCH_2, 8H), 4.58 (s, C_5H_5, 5H), 6.65−7.43 (C_6H_4, 16H); IR (KBr, cm^{-1}) 2926, 2855, 1609, 1514, 1468, 1244, 1173, 1109, 1096, 1032, 831, 804, 586, 569.

4h: yield, 90%; ^{1}H NMR δ 0.88 (t, CH_3, 6H), 1.28−1.80 (CH_2, 48H), 3.95 (t, OCH_2, 8H), 4.58 (s, C_5H_5, 5H), 6.65−7.43 (C_6H_4, 16H); IR (KBr, cm^{-1}) 2926, 2855, 1601, 1512, 1468, 1246, 1169, 1109, 1095, 1028, 833, 806, 577.

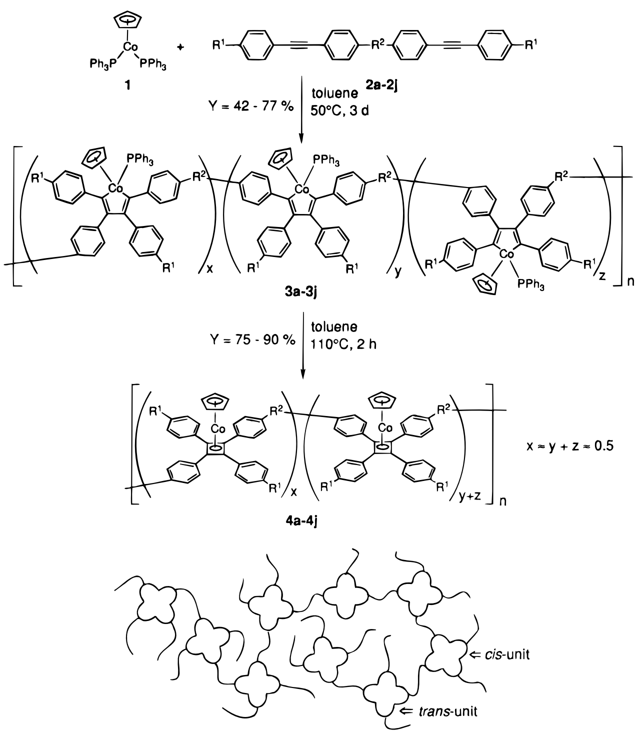
4i: yield, 33% (based on the starting diyne); ^{1}H NMR δ 0.88 (t, CH_3, 6H), 1.28−1.80 (CH_2, 56H), 3.95 (t, OCH_2, 8H), 4.58 (s, C_5H_5, 5H), 6.68−7.43 (C_6H_4, 16H); IR (KBr, cm^{-1}) 2924, 2855, 1601, 1514, 1468, 1258, 1169, 1107, 1020, 831, 804, 576.

4j: yield, 45% (based on the starting diyne); ^{1}H NMR δ 0.88 (t, CH_3, 6H), 1.28−1.80 (CH_2, 62H), 3.95 (t, OCH_2, 8H), 4.58 (s, C_5H_5, 5H), 6.65−7.43 (C_6H_4, 16H); IR (KBr, cm^{-1}) 2926, 2855, 1607, 1514, 1462, 1244, 1171, 1099, 1030, 831, 804, 586, 571.

Results and Discussion

Synthesis. For the synthesis of polymers **3b−j**, a previously established method[2] was used. Polymerization reactions of (η^5-cyclopentadienyl)cobalt complex **1**[5] and a series of alkoxy-substituted diynes **2b−j** were carried out at 50 °C in toluene under nitrogen. Relatively low concentrations of monomers (0.10−0.15 M) were used because of the poor solubility of diynes **2b−j** in organic solvents.

Scheme 1



	R^1	R^2
a	H	none
b	H	$O(CH_2)_6O$
c	H	$O(CH_2)_{10}O$
d	*n*-OC_6H_{13}	$O(CH_2)_6O$
e	*n*-OC_6H_{13}	$O(CH_2)_9O$
f	*n*-$OC_{10}H_{21}$	$O(CH_2)_6O$
g	*n*-$OC_{10}H_{21}$	$O(CH_2)_9O$
h	*n*-$OC_{10}H_{21}$	$O(CH_2)_{10}O$
i	*n*-$OC_{14}H_{29}$	$O(CH_2)_6O$
j	*n*-$OC_{14}H_{29}$	$O(CH_2)_9O$

Thermal treatment of toluene solutions of polymers **3b−j** gave their (η^4-cyclobutadiene)cobalt analogs **4b−j** in high yields. The rearrangement reaction proceeded quantitatively within several minutes, which could be easily recognized by the change in the color of the solution from dark red-brown to light-brown (yellow in dilute solutions). From GPC analyses of the reaction mixture, only triphenylphosphine was found in the low molecular weight region (M < 800), thereby indicating an absence of side reactions. In the cases of **4b** and **4c**, good separations of the polymers from the eliminated triphenylphosphine were attained by precipitation with *n*-hexane, while **4d−j** formed adhesive viscous precipitates under similar isolation conditions. Accordingly, these samples were purified by HPLC.

Structure. ^{1}H NMR spectra of polymers of both rows (**3** and **4**) were in good agreement with the proposed formulae (Figures 1 and 2). Complicated spectra were observed for cobaltacycle-containing polymers **3b−h** because of the unsymmetric structure of the organometallic cores. Two magnetically nonequivalent groups of protons for CH_2O units were determined. The same effect was also found for methylene groups in β-positions to the phenoxy moieties. The peaks at 4.59 and 3.96 ppm (e and f in Figure 1, respectively) indicated the presence of (η^4-cyclobutadiene)cobalt moieties.[9] Therefore, a partial rearrangement (*ca.* 10%, estimated by NMR) occurred at the reaction conditions (50 °C). In contrast, polymer **3a** did not undergo any rearrangement reactions at this temperature. Perhaps the electron-donating alkoxy groups destabilize the cobaltacycle units compared with the unsubstituted species **3a**. According to the literature data, the reactivity of cobaltacyclopentadiene complexes is dependent on the electronegativity of the substituents, with increasing

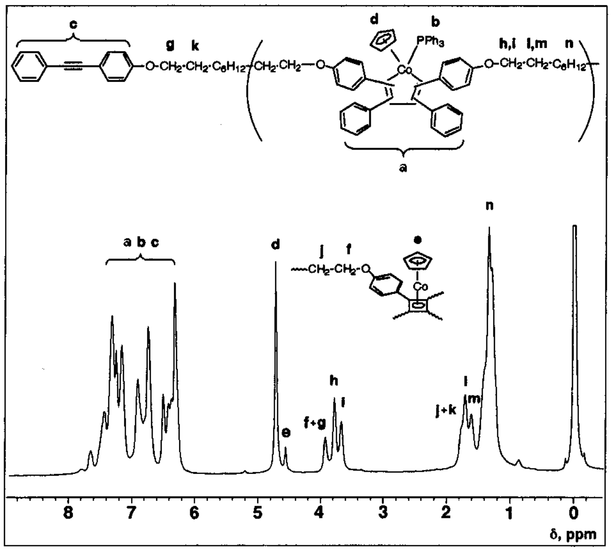


Figure 1. ^{1}H NMR spectrum of **3c** (400 MHz, CDCl$_3$).

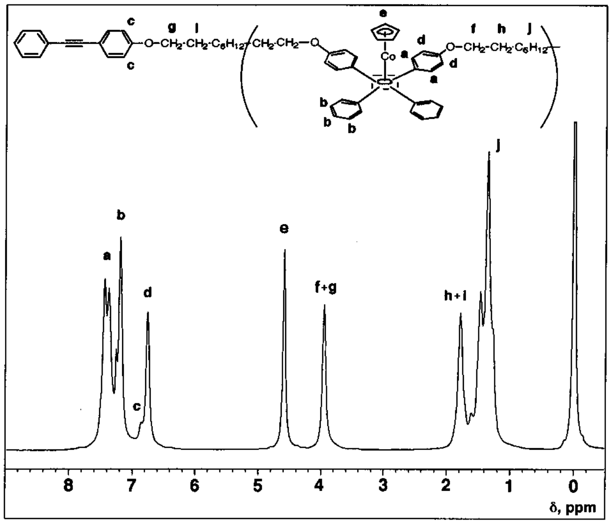


Figure 2. ^{1}H NMR spectrum of **4c** (400 MHz, CDCl$_3$).

stability of compounds with electron-withdrawing groups and *vice versa*.[5] As a result of the study of model monomers **5** and **6**, it was found that 1,2- and 1,3-isomers of **6** were obtained in approximately equal amounts (54:46, respectively, after separation by column chromatography). One can conclude that the corresponding polymerization reactions proceed without the preferred formation of either isomer, with randomly distributed *cis* and *trans* isomers of organometallic units.

The structural changes can be illustrated by UV spectra (Figure 3). Compared with the fully aromatic polymers **3a** and **4a**, those with flexible spacers (**3c** and **4c**, as representative examples) showed a systematic blue shift of the band of $\pi-\pi^*$ transition, indicating the breaking off of conjugation due to the insertion of alkoxy groups in the main chain. The spectra of **3c** and **4c** were in fact identical to those of the model monomers (**5** and **6**, respectively). An essential increase (~1.5 times) in the extinction coefficients for polymers **3c** and **4c** could be explained by the influence of oxygen atoms from alkoxy groups. Rearrangement of organometallic cores led to the red shift of $\pi-\pi^*$ bands (311→331 nm and 274→285 nm for **3a**→**4a** and **3c**→**4c**, respectively) and an increase in their absorbance. In considering the conformations of organocobalt moieties, these changes

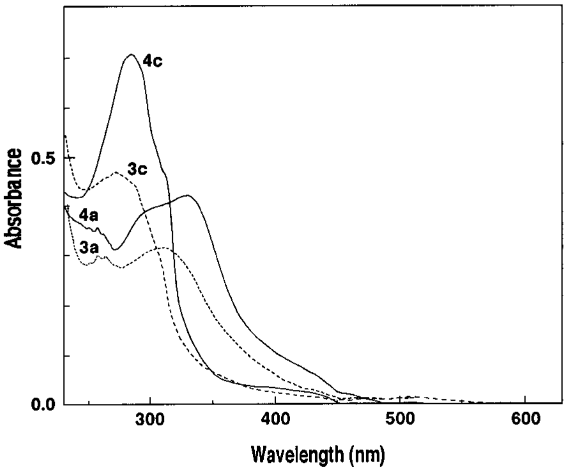
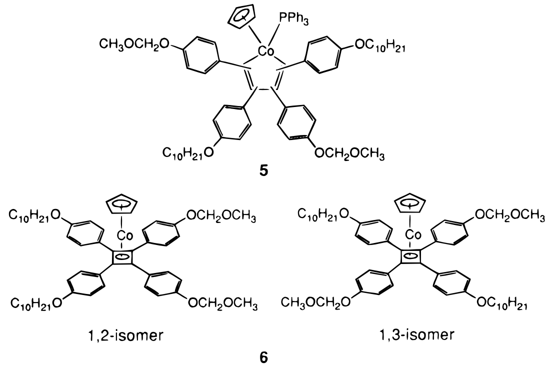


Figure 3. UV spectra of cobaltacycle-containing (**3a** and **3c**, dashed lines) and (η^4-cyclobutadiene)cobalt-containing polymers (**4a** and **4c**, solid lines) (THF, $c = 10^{-5}$ mol/L, recalculated per repeating unit).

Scheme 2



could be caused by the transition from sterically hindered metallacycle structures **3** to the symmetric complexes **4** with higher degrees of conjugation within their cores. Changes in the visible region (disappearance of the band at 510 nm and increase in the shoulder at ~425 nm in **4** compared with **3**) are likely to be related to the d-electron shells of the Co ion.

Physical Properties. As expected, the insertion of aliphatic spacers into polymeric backbones gave the corresponding increase in solubility. Polymers of both series (**3b**–**h** and **4b**–**j**) were highly soluble in benzene, diethyl ether, THF, *N*,*N*-dimethylformamide, chloroform, and chlorobenzene. Those with flexible lateral groups (**3d**–**h**, **4d**–**j**) were also soluble in *n*-hexane. Uniform flexible films were obtained by the casting of concentrated solutions.

The thermal stability of organocobalt polymers was studied by TG and DTA methods. Cobaltacycle-containing polymers **3b**–**h** showed two exothermic peaks on DTA curves and the corresponding weight losses on TG traces (Figure 4). The first 27% weight loss at 150–175 °C for **3b** corresponds to the elimination of triphenylphosphine (calculated, 31%) that may accompany the rearrangement of organometallic cores. The second one at 410–420 °C was assigned to the degradation of polymeric chains (weight loss varied from one polymer to another and was approximately equal to the content of aliphatic alkoxy groups). Accordingly, polymers **4b**–**j** exhibited only the latter decomposition at 410–420 °C, with the corresponding weight losses.

In contrast to the polymers with rigid backbones (**3a** and **4a**), glass transitions were observed for most of the

Table 1. Properties of Organocobalt Polymers 3 and 4

		transition temperatures (°C)					transition temperatures (°C)		
sample	$\bar{M}_n$ ($\bar{M}_w/\bar{M}_n$)[a]	fresh sample	annealed sample[b]	T_r[c] (°C)	sample	$\bar{M}_n$ ($\bar{M}_w/\bar{M}_n$)[a]	fresh sample	annealed sample[d]	T_d[e] (°C)
3b	8400 (1.32)	$T_m = 105$	no transitions	172	**4b**	7800 (1.27)	$T_{m1} = 60$, $T_g = 128$	$T_g = 119$	415
3c	11100 (1.48)	no transitions	no transitions	157	**4c**	9800 (1.41)	$T_{m1} = 75$, $T_{m2} = 128$	$T_g = 65$	423
3d	6700 (1.35)	$T_g = 41$	$T_g = 10$, $T_m = 69$	nd[f]	**4d**	8100 (1.37)[g]	$T_g = 50$	$T_g = 44$	nd
3e	7000 (1.33)	$T_g = 60$	$T_g = 48$, $T_m = 105$	156	**4e**	7100 (1.47)[g]	$T_g = 24$, $T_m = 69$	$T_g = 16$	nd
3f	11000 (1.46)	$T_{m1} = 45$, $T_{m2} = 85$	$T_g = 31$	153	**4f**	12800 (1.31)[g]	$T_g = 19$	$T_g = 17$	420
3g	10000 (1.34)	$T_{m1} = 55$, $T_{m2} = 97$	$T_g = 32$, $T_m = 89$	nd	**4g**	12900 (1.36)[g]	$T_g = 20$	$T_g = 18$	nd
3h	11300 (1.41)	$T_g = 43$	$T_g = 22$, $T_m = 95$	152	**4h**	14600 (2.09)[g]	$T_g = -8$	$T_g = -4$	410
						5300 (1.57)[h]	$T_g = -4$	$T_g = 0$	
3i	not isolated				**4i**	6300 (1.16)	$T_m = 25$	$T_g = 0$	420
3j	not isolated				**4j**	12800 (1.50)	$T_g = -7$	$T_g = -11$	nd

[a] Estimated by GPC in THF (polystyrene standard). [b] Annealed at 125 °C for 30 min. [c] Temperature of rearrangement to cyclobutadiene-containing polymer **4**, determined by the exothermic peak on DTA charts. [d] Annealed at 175−200 °C for 30 min. [e] Degradation temperature, determined by the exothermic peak on DTA charts. [f] Not determined. [g] Higher molecular weight fraction. [h] Lower molecular weight fraction (separated by HPLC).

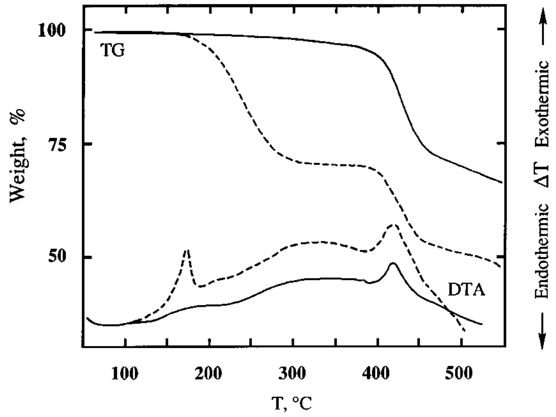


Figure 4. TG and DTA traces of **3b** (dashed lines) and **4b** (solid lines) under N_2 (10 °C/min).

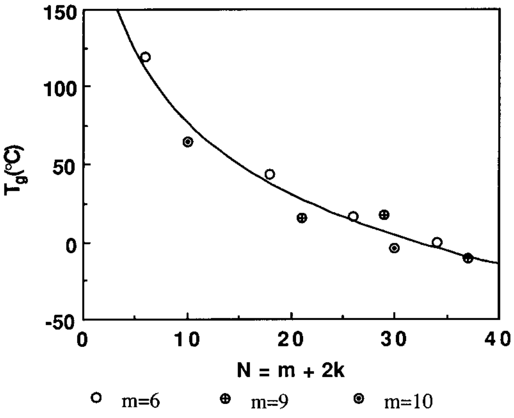


Figure 5. Glass transition temperatures of (η^4-cyclobutadiene)cobalt-containing polymers **4b**−**j** as a function of the number of carbon atoms in alkoxy substituents in bridging (*m*) and lateral (*k*) positions (annealed samples, heating rate 10 °C/min).

polymers with flexible spacers (**3d**−**h** and **4b**−**j**). Cobaltacycle-containing polymers **3d**−**h** also exhibited endothermic peaks above their T_g's. The presence of the anisotropic phase was detected by polarizing microscope observations, although its origin is not clearly understood. Essential shifts of transition temperatures were registered for annealed samples of polymers **3d**−**h** compared with freshly prepared ones. Except for the changes in morphology, annealed specimens could differ in their chemical structure because of the partial uncontrolled rearrangement of these polymers at the annealing temperature (125 °C), with the formation of (η^4-cyclobutadiene)cobalt moieties and the elimination of triphenylphosphine. Thermally stable polymers **4b**−**j** showed more regular behavior. The single glass transitions were detected for annealed samples. Glass transition temperatures showed a regular dependence on the number of aliphatic carbon atoms per repeating unit, decreasing with increasing content of the aliphatic part (Figure 5). Moreover, T_g's were almost independent of the molecular weight of the polymers, as can be illustrated by the typical example **4h**. In spite of the triple difference in molecular weight and the low degree of polymerization for the fraction with $\bar{M}_n$ = 5300 (*n* = 3−6), the samples examined show almost equal T_g's. It is likely that the thermal properties of polymers **4b**−**j** are defined mostly by the short-range interactions between bulky aromatic cores and flexible aliphatic moieties, with the length of the main chain being of secondary importance.

Conclusions

Two series of polymers bearing phenyl-substituted (η^5-cyclopentadienyl)cobaltacyclopentadiene or (η^5-cyclopentadienyl)(η^4-cyclobutadiene)cobalt moieties in the main chain and flexible aliphatic alkoxy groups in both the main and side chains have been synthesized and studied. Cobaltacyclopentadiene-containing polymers could be converted to their (η^4-cyclobutadiene)cobalt-containing analogs in high yields. Polymers with (η^4-cyclobutadiene)cobalt moieties were thermally stable before 410−420 °C, were soluble in organic solvents, and showed glass transitions in the range −10 to +120 °C, depending on the content of the aliphatic part.

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Supporting Information Available: Methods for the synthesis of diynes **2b**−**j** and model organocobalt complexes **5** and **6** and IR, ^{1}H NMR, and thermal data for **2b**−**j**, **5**, and **6**, as well as for intermediate compounds (10 pages). Ordering information is given on any current masthead page.

References and Notes

(1) For recent reviews, see: (a) Chisholm, M. H. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 673. (b) Allcock, H. R. *Adv. Mater.* **1994**, *6*, 106. (c) Oriol, L.; Serrano., J. L. *Adv. Mater.* **1995**, *7*, 348.

(2) Tomita, I.; Nishio, A.; Igarashi, T.; Endo, T. *Polym. Bull.* **1993**, *30*, 179−186.

(3) Tomita, I.; Nishio, A.; Endo, T. *Macromolecules* **1995**, *28*, 3042.

(4) Tomita, I.; Nishio, A.; Endo, T. *Macromolecules* **1994**, *27*, 7009.

(5) Yamazaki, H.; Wakatsuki, Y. *J. Organomet. Chem.* **1977**, *139*, 157.

(6) Rozhanskii, I. L.; Tomita, I.; Endo, T. Manuscript in preparation.

(7) The shoulder peak at *ca.* 4.60 ppm was also detected. It was assigned to the protons of the cyclopentadienyl group from the (η^4-cyclobutadiene)cobalt moiety.

(8) As a rule, three fractions were isolated, namely, low molecular weight products (PPh_3), oligomers (∼15% from the total amount of the product), and the main fraction (∼85%). Accordingly, the latter fraction provided the main contribution to the molecular weight distributions, and nonfractionated samples essentially did not differ from those of the higher molecular weight fraction.

(9) The band 3.96 ppm is overlapped by the peak of the methylene protons of end groups (diphenylacetylene units).

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