

Synthesis and monomer reactivity ratio of cobalt-containing hybrid polysilanes

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Abstract: Dichloromethylsilylcobaltcarbonyl (DCMSC) was synthesized by the reaction of dichloromethylsilane (DCMS) with dicobaltoctacarbonyl (DCOC) and used to prepare metal-containing polysilanes. Copolymers of DCMSC with dichlorodimethyl- (DCDMS), dichlorodiethyl- (DCDES), dichloromethylphenyl- (DCMPS) silane were obtained using reductive coupling polymerization. The molecular weight of the copolymers increased regularly in the initial stage of the reaction but approached equilibrium values as the reaction proceeded. Depending on the monomer reactivity ratios, copolymers 2, 3 and 4 could have either alternating or block-like copolymer structures. Increasing amounts of carbons in the side-chain of the copolymers leads to block-like composition.

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Keywords: cobalt containing polysilanes; hybrid; reductive coupling; copolymerization; monomer reactivity ratio

INTRODUCTION

Polysilanes are polymers containing linear Si–Si units in the main chain with two organic substituents on each silicon atom.^{1–3} The organic substituents are usually alkyl or aromatic groups.^{4,5} Several interesting properties of polysilanes have been attributed to the σ electron-conjugation and have led to the current intensive research work. In addition, the chemistry of transition metal–silicon complexes has become a significant domain of the general chemistry of silicon, as in catalytic processes in the preparation of organometallic precursors of advanced materials.^{6,7} Organosilicon–cobalt complexes, in particular, have been widely investigated, since $\text{Co}_2(\text{CO})_8$ is known as a hydrosilylation catalyst.⁸ The first series of reports on a transition metal complex either activating or containing a silicon–silicon bond appeared in the 1960s.^{9–12} Transition metal-containing, as well as general, polysilanes have been used as precursors for fibers, ceramics and conducting materials. In particular, Seyferth and coworkers^{13,14} prepared pre-ceramic organosilicon–metal carbonyl polymers by mixing an organosilicon polymer containing multiple Si–H/Si–Si functional groups with a sufficient quantity of a metal carbonyl. In addition, organosilicon–transition metal compounds vary widely in their resistance to thermal degradation.^{15,16}

In this paper, we synthesized cobalt-containing polysilanes and investigated the effect of monomer composition. Synthesis of dichloromethylsilylcobaltcarbonyl [DCMSC; $\text{Cl}_2\text{MeSiCo}(\text{CO})_4$], 1, which has

been used as a starting material for polysilanes, was accomplished by the direct reaction of silicon hydride with dicobaltoctacarbonyl [DCOC; $(\text{Co}_2(\text{CO})_8)$] as shown in Scheme 1.^{10,17} Copolymers (2, 3 and 4) of DCMSC with dichlorodimethyl- (DCDMS; Cl_2SiMe_2), dichlorodiethyl- (DCDES; Cl_2SiEt_2) and dichloromethylphenyl- (DCMPS; Cl_2SiMePh) silane, by the reductive coupling shown in Scheme 2, were also investigated *versus* reaction time. A tendency toward alternating or block-like copolymerization could be explained through the monomer reactivity ratios of the Fineman–Ross¹⁸ and Kelen–Tudos methods.¹⁹

EXPERIMENTAL

Materials

Dichloromethylsilane (DCMS; Cl_2SiMeH), DCDMS, DCDES and DCMPS were purchased from Aldrich. DCOC was purchased from Strem Chemicals Inc. Hexane (Mallinckrodt) and toluene (Mallinckrodt) were distilled over a Na–benzophenone system. Na (99.9 % purity) was purchased from Samchun Pure Chemicals. All materials were stored under an inert atmosphere prior to use. All reactions were performed under an inert atmosphere using standard Schlenk techniques.

Measurements

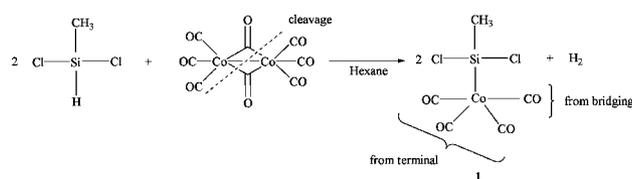
The FTIR spectra were obtained with the KBr pellet technique on a Nicolet Magna-IR 760 spectrometer.

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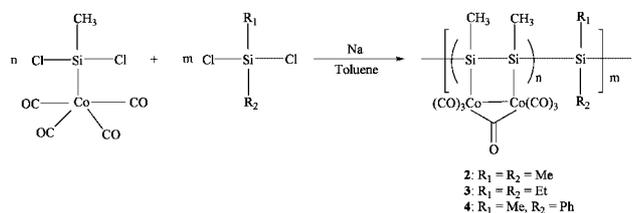
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Scheme 1. The preparation of organosilicon–cobalt complex **1**.



Scheme 2. The preparation of copolymers with complex **1** and $R_1R_2SiCl_2$.

The NMR spectra were recorded with a Varian Gemini 300 spectrometer. All spectra were obtained using $CDCl_3$ as a solvent and tetramethylsilane (TMS) was used as an external standard. Elemental analysis was performed with a Thermoquest EA-1110 CHNS analyzer. GC/MS analysis was performed by using a JEOL JMS-DX303 mass spectrometer, a Hewlett-Packard 5890A gas chromatograph, and a JEOL DA 5000 computer system. Molecular weights and molecular weight distributions were determined by gel-permeation chromatography (GPC) using a Waters 410 RI detector, 616 pump, and a Waters Styragel[®] column set (HR 1, 4, 5). The system was calibrated using polystyrene standards and toluene was used as an eluent at a flow rate of 0.3 ml min^{-1} . Thermogravimetric analysis (TGA) measurements were performed on a TA Instruments SDT 2960 in a nitrogen atmosphere with a gas flow rate of 70 ml min^{-1} . The temperature was scanned from room temperature to 900°C at a heating rate of $10^\circ\text{C min}^{-1}$. Differential scanning calorimetry (DSC), TA Instrument DSC 2910, was used to monitor the thermal transitions at a scan rate of 5°C min^{-1} (cooling-heating two-cycle system) and in a nitrogen atmosphere with a gas flow rate of 60 ml min^{-1} .

Synthesis of $Cl_2SiMeCo(CO)_4$ (**1**)

To a 100-ml Schlenk flask charged with DCOC (1 g, 2.9 mmol) and distilled hexane (15 ml) was added an excess of DCMS (0.67 ml, 2.2 equiv). The reaction mixture was stirred under static vacuum for 6 h at room temperature, filtered, and then trap-to-trap distilled under reduced pressure. The reaction product was purified by sublimation *in vacuo* to give a pale yellow crystalline solid which was soluble in hydrocarbon solvents. The final product was analyzed by IR, NMR, GC/MS and elemental analysis; IR (neat, KBr, cm^{-1}): 2960 (*v* C–H), 1265 (*v* CH_3), 722 (*v* Si–Cl), 2124 (*v* bridging CO), 2034 (*v* terminal CO); 1H NMR ($CDCl_3$, ppm): 1.32 (s, Si– CH_3); ^{13}C NMR ($CDCl_3$,

ppm): 17.16 (s, Si– CH_3), 195.67 (s, CO); ^{29}Si NMR ($CDCl_3$, ppm): 66.38 (s, CH_3SiCo); MS: $m/z = 284$ (M^+), 256 ($M^+ - CO$), 228 ($M^+ - 2CO$), 200 ($M^+ - 3CO$), 172 ($M^+ - 4CO$), 157 ($M^+ - 4CO - CH_3$), 137 ($M^+ - 4CO - Cl$), 115 ($M^+ - Co(CO)_4$), 102 ($M^+ - 4CO - Cl_2$); Anal: Calcd C, 21.05, H, 1.05 %; Found C, 20.65, H, 1.17 %.

Preparation of poly(methylcobaltcarbonyl-co-dimethyl)silane (**2**)

A 150-ml three-necked, round-bottomed flask was fitted with a reflux condenser and charged with 0.31 g (14.0 mmol) of Na metal in 20 ml of toluene. The flask was kept in an ultrasonic bath at 60°C for 1.5 h. After termination of the ultrasound treatment, a solution (1:1 mixture) of $Cl_2SiMeCo(CO)_4$, **1** (1.0 g, 3.5 mmol) with DCDMS (0.42 ml, 3.5 mmol) in 10 ml of toluene was added to the flask. The mixture was stirred while purging with dry nitrogen at 60°C for 24 h. The reaction mixture turned gradually from yellow to purple. The reaction was quenched in an ice-bath and the solids were filtered off. The resulting polymer was precipitated by pouring the filtrate into distilled hexane. The solvent and volatile unreacted monomers were then distilled off under vacuum to isolate the purple powdery product. Molecular weights and polydispersities of the resulting copolymer were determined by GPC and further chemical characterization was performed with IR and NMR spectroscopy; IR (neat, KBr, cm^{-1}): 2960 (*v* C–H), 1259 and 730 (*v* CH_3), 2054 (*v* terminal CO), 1860 (*v* bridging CO), 460 (*v* Si–Si); 1H NMR ($CDCl_3$, ppm): 1.33 (b, Si– CH_3), 0.07 (b, Si–(CH_3)₂); ^{13}C NMR ($CDCl_3$, ppm): 16.22 (s, Si–(CH_3)₂), 5.10 (s, Si– CH_3), 194.82 (b, CO); ^{29}Si NMR ($CDCl_3$, ppm): -24.09 (b, $Si(CH_3)_2$) and 66.35 (b, CH_3SiCo).

Preparation of poly(methylcobaltcarbonyl-co-diethyl)silane (**3**)

A synthetic procedure similar to that used in the preparation of **2** with DCDES as a comonomer; IR (neat, KBr, cm^{-1}): 1494 and 726 (*v* CH_2CH_3), 1259 (*v* CH_3), 2054 (*v* terminal CO), 1860 (*v* bridging CO), 464 (*v* Si–Si); 1H NMR ($CDCl_3$, ppm): 1.33 (b, Si– CH_3), 0.95 (b, Si– CH_2CH_3), 0.54 (b, Si– CH_2CH_3); ^{13}C NMR ($CDCl_3$, ppm): 16.22 (s, Si– CH_2CH_3) and 6.87 ~ 6.04 (d, Si– CH_2CH_3), 5.92 ~ 5.57 (t, Si– CH_3), 194.56 (b, CO); ^{29}Si NMR ($CDCl_3$, ppm): -22.61 (b, SiC_2H_5) and 66.20 (b, CH_3SiCo).

Preparation of poly(methylcobalttetracarbonyl-co-methylphenyl)silane (**4**)

A synthetic procedure similar to that used in the preparation of **2** with DCMPS as a co-monomer; IR (neat, KBr, cm^{-1}): 3030 (*v* C–H, aromatic), 2959 (*v* C–H, methyl), 1428 (*v* Si– C_6H_5), 1262 (*v* Si– CH_3), 2055 (*v* terminal CO), 1860 (*v* bridging CO), 484 (*v* Si–Si); 1H NMR ($CDCl_3$, ppm): -0.11 (b, Si– $CH_3C_6H_5$), 1.05 (b, Si– CH_3), 7.07 (t, C_6H_5);

^{13}C NMR (CDCl_3 , ppm): 14.06 (s, $\text{Si}-\text{CH}_3\text{C}_6\text{H}_5$), 5.10 (s, $\text{Si}-\text{CH}_3$), 133.34 ~ 127.86 (q, C_6H_5), 195.22 (b, CO); ^{29}Si NMR (CDCl_3 , ppm): -33.16 (b, $\text{CH}_3\text{SiC}_6\text{H}_5$) and 66.15 (CH_3SiCo).

RESULTS AND DISCUSSION

Monomer synthesis

Harrod *et al.*¹⁰ synthesized silane molecules containing cobalt carbonyls by direct reaction of trichlorosilane with DCOC in the 1960s. The crystal and molecular structure of $\text{Co}(\text{SiCl}_3)(\text{CO})_4$ were determined by Robinson and Ibers.⁹

The organosilicon-cobalt complex, **1**, was obtained as pale yellow crystals after sublimation from hexane solution by the method analogous to that of Chalk and Harrod.^{8,10} The reaction of DCOC with DCMS proceeded rapidly at room temperature and the principal products of the reaction were silylcobalt carbonyls and hydrogen (Scheme 1). Yields were generally high (*ca* 90 %). The completion of reaction was confirmed by the disappearance of the IR bands from the $\text{Si}-\text{H}$ stretching vibrational mode (2215 cm^{-1}) and the bridging CO (1860 cm^{-1}) of DCOC as well as by a slight shift of the 2124 cm^{-1} bridging CO band. The ^{13}C NMR spectrum also showed a $\text{Si}-\text{Co}(\text{CO})_4$ signal (singlet at 195.67 ppm) in agreement with Weinmann's data.²⁰ The analysis from GC/MS and elemental analysis indicated that complex **1** was a monomeric unit. The yellow crystalline materials obtained exhibited some stability (duration of 24 h) in the solid state towards atmospheric oxidation when held at low temperature in the absence of light, however, in solution (THF, ether and acetonitrile), complex **1** quickly decomposed.

Copolymerization of complex **1** with $\text{R}_1\text{R}_2\text{SiCl}_2$

We also investigated the copolymerization of organosilicon-cobalt complex, **1**, with alkyl or aromatic substituted dichlorosilanes by Wurtz coupling at ambient temperature (Scheme 2). In the IR spectrum of the copolymers, stretching vibrational bands from terminal CO ligands were observed (2054 cm^{-1}) and the absorption band from bridging CO appeared (1860 cm^{-1}) again, which indicated that the polymer had dimeric cobalt-containing silane units in its main chain. The IR spectroscopic data were similar to those of the dimeric complex which had been synthesized by Bourg *et al.*²¹ Unfortunately, we did not find any difference between the terminal CO and the bridging CO by ^{13}C NMR and found just a broad peak extending from 194 to 195 ppm.

Using ^{29}Si NMR, two singlet peaks were present at -24.09, 66.35 ppm (32.90, 66.30 ppm in monomer) for copolymer **2**, at -22.61, 66.20 ppm (36.10, 66.30 ppm in monomer) for copolymer **3** and at -33.16, 66.15 ppm (10.30, 66.30 ppm in monomer) for copolymer **4**, respectively (Fig 1). The upfield shift of silicon for copolymers **2** and **3** was mainly due to

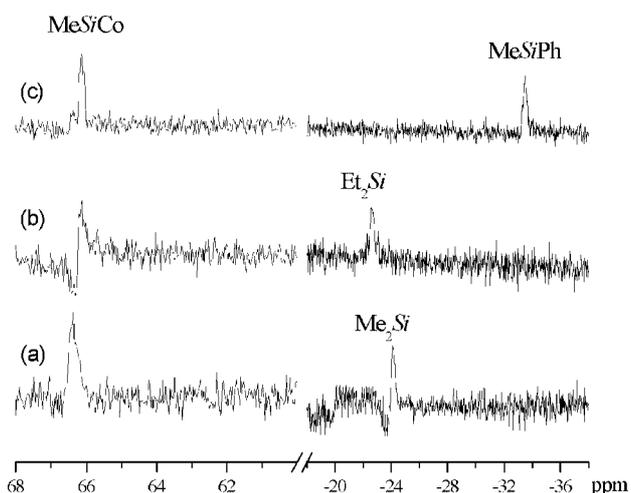


Figure 1. ^{29}Si NMR spectra of copolymers **2(a)**, **3(b)** and **4(c)** in CDCl_3 .

the electron withdrawing ability of the cobalt carbonyl group in an adjacent silane unit. For copolymer **4**, the degree of upfield shift was less pronounced because the phenyl group also possessed electron-withdrawing properties.²² Representative results, such as feeding ratio, composition, conversion, molecular weight, for the preparation of copolymers are shown in Table 1. Molecular weights, measured by gel-permeation chromatography (GPC), ranged from M_w (weight-average molecular weight) = 43 000 to 65 000 g mol^{-1} and conversion yields of the high molecular weight portion were between 9.4 and 28.7 %. The polymerization was a common Wurtz coupling procedure where the co-monomers were introduced simultaneously into a sodium dispersion in refluxing toluene.

As can be seen in Fig 2, copolymer **4b**, with $\text{R}_1 = \text{Me}$ and $\text{R}_2 = \text{Ph}$, exhibited higher molecular weight than copolymers **2b** and **3b**. In the case of the homopolymer, long-length side-chain dialkyldichlorosilanes, such as dihexyldichlorosilane, did not react with the sodium dispersion below 60°C in toluene.²³ In contrast, short-length side-chain

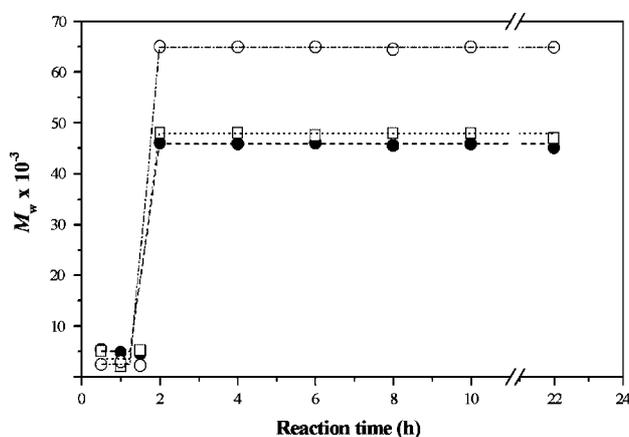


Figure 2. Dependence of copolymer molecular weight on the reaction time; ●: copolymer **2**, □: copolymer **3**, ○: copolymer **4**.

Table 1. Representative results of copolymers with MeSiCo (M_1) and SiR₁R₂ (M_2)^a

Polymers	x^b	y^c	G^d	H^e	η^f	ξ^g	Conversion ^h	$M_w (\times 10^{-3})^i$	$M_n (\times 10^{-3})^i$	M_w/M_n^i	T_d^j (°C)
2a	4	1.3256	0.9825	12.0702	0.0771	0.9470	12.2	43	20	2.14	99, 509
2b	1	1.1277	0.1132	0.8868	0.0725	0.5676	9.5	46	22	2.09	139, 521
2c	0.25	1.2222	0.0455	0.0511	0.0626	0.0703	13.4	45	18	2.47	288, 504, 599
2d	0.2	0.3954	-0.3059	0.1012	-0.3939	0.1303	9.5	43	18	2.41	no ^k
2e	0.1	0.2644	-0.2783	0.0378	-0.3902	0.0530	9.4	49	22	2.24	no ^k
3a	4	0.8868	-0.5107	18.0426	-0.0270	0.9510	12.2	48	28	1.72	103, 486
3b	1	0.6667	-0.5000	1.5000	-0.2058	0.6174	14.5	48	35	1.37	135, 512
3c	0.25	0.0870	-2.6250	0.7188	-1.5925	0.4361	17.3	55	26	2.11	161, 500
3d	0.2	0.1538	-1.1000	0.2600	-0.9247	0.2186	16.3	52	26	2.05	no ^k
3e	0.1	0.2088	-0.3789	0.0479	-0.3876	0.0490	14.7	50	21	2.35	no ^k
4a	4	0.8182	-0.8888	19.5551	-0.0366	0.8041	15.7	60	32	1.88	102, 524
4b	1	0.2048	-3.8824	4.8824	-0.4025	0.5062	26.5	65	33	1.97	96, 298, 540
4c	0.25	0.0417	-5.7452	1.4988	-0.9175	0.2394	28.7	59	29	2.03	107, 305, 567
4d	0.2	0.0345	-5.6000	1.1600	-0.9455	0.1959	26.6	60	29	2.07	no ^k
4e	0.1	0.0046	-21.8000	2.1900	-3.1354	0.3150	26.5	62	29	2.13	no ^k

^a **2:** R₁ = R₂ = Me, **3:** R₁ = R₂ = Et, **4:** R₁ = Me, R₂ = Ph.

^b Denotes the feed ratio of M_1/M_2 .

^c Denotes the copolymer ratio from integration of ¹H NMR.

^d Variable of F-R method, $G = Hr_1 - r_2$, $G = x(y - 1)/y$.

^e Variable of F-R method, $H = x^2/y$.

^f Variable of K-T method, $\eta = (r_1 + r_2/\alpha) \xi - r_2/\alpha$, $\eta = G/\alpha + H$, $\alpha = \sqrt{(H_l \cdot H_h)}$, $\alpha = 0.6755$ for **2**, $\alpha = 0.9296$ for **3** and $\alpha = 4.7628$ for **4**.

^g Variable of K-T method, $\xi = H/\alpha + H$.

^h Conversion (%).

ⁱ Molecular weight and molecular weight distribution calculated by GPC.

^j Decomposition temperatures given by the peaks of the derivative curve of the TGA trace.

^k no = not observed.

dimethyl- and diethyldichlorosilanes reacted easily with the sodium particles at ambient temperature. The variations in molecular weight of copolymers **2**, **3** and **4** were similar to that of the homopolymer published earlier.²⁴ In the case of copolymers **2b**, **3b** and **4b**, the molecular weight increased to $M_w = 46\,000$, $48\,000$ and $65\,000\text{ g mol}^{-1}$ up to 2 h and then did not change very much up to 24 h. This might indicate that the degradation rate did not increase and that these polymers were stable as the reaction proceeded.

Monomer reactivity ratios

With changes in the feed ratio of co-monomer (n/m) from 4 to 0.1, the statistical compositions of copolymers were determined by the relative integration of proton peaks in different alkyl or aromatic side-groups using ¹H NMR (see Table 1). For copolymers **2a–c**, it can be seen that the composition of co-monomer in the polymerization product was almost the same irrespective of the changes in feed ratio. However, when the feed ratio was higher than 1:5 (where an excess Me₂Si was used in the cases of **2d** and **2e**), although the composition of co-monomer in the product was dependent on the feed ratio, the product became insoluble. It has been reported previously that silane polymers with short alkyl chains, such as Me₂Si units, have poor or no solubility in toluene.²⁵ However, the presence of the MeSiCo unit prevented the formation of insoluble product and made the product more soluble as the relative amount of MeSiCo unit was increased. In the case of copolymers **3a–c** and **4a–c**, the composition ratio

of Si–Co versus SiR₁R₂ was increased with increasing feed ratio.

To understand further the copolymerizability of Si–Co and SiR₁R₂, the reactivity ratios were determined. Monomer reactivity ratios were evaluated by a graphical procedure following the Fineman-Ross (F-R) method which uses a linearized version of the copolymer equation:¹⁸

$$G = Hr_1 - r_2 \quad (1)$$

where the transformed variables are

$$G = x(y - 1)/y \quad \text{and} \quad H = x^2/y \quad (2)$$

x and y are defined as

$$x = [M_1]/[M_2] \quad \text{and} \quad y = d[M_1]/d[M_2] \quad (3)$$

where $[M_1]$ and $[M_2]$ are the concentration of monomers and $d[M_1]/d[M_2]$ corresponds to the concentration ratio of the copolymer components. Furthermore,

$$\eta = \left(r_1 + \frac{r_2}{\alpha} \right) \xi - \frac{r_2}{\alpha} \quad (4)$$

according to the Kelen-Tudos (K-T) method with $\eta = G/\alpha + H$ and $\xi = H/\alpha + H$ where η and ξ are mathematical functions of the mole ratios monomers in the feed and in the copolymer, $\alpha = \sqrt{(H_l \cdot H_h)}$ where H_l and H_h are the lowest and highest value of the calculated H from the series of measurements.¹⁹

Details of the copolymerization of MeSiCo with SiR₁R₂ are listed in Table 1. The resulting straight-line plot of G versus H and η versus ξ allowed for the determination of r_1 and r_2 from the slope and the intercept, respectively. The reactivity ratios of MeSiCo and SiR₁R₂ determined by the F-R and K-T methods are given in Table 2 along with the product of the reactivity ratios. The nature of the copolymer sequences for copolymers 2 and 3 appears to be alternating since the product of the reactivity ratios ($r_1 r_2$) is closer to zero than to unity. As shown in Fig 3, the plot between the copolymer and feed composition was sigmoidal and crossed the azeotropic line at the point where $f_1 = F_1 = 0.52$ for copolymer 2. Copolymer 3 showed weak sigmoidal nature and crossed the ideal line at the point where $f_1 = F_1 = 0.11$, indicating an azeotropic copolymer, whereas copolymer 4 appeared to be blocky, because r_2 is higher than r_1 , and $r_1 r_2$ is largely higher than unity. With increasing numbers of carbon atoms in SiR₁R₂, the composition of the copolymers became more block-like due to the greater tendency of gathering same functional units over different ones.

Thermal behavior

The thermal stability of copolymers 2, 3 and 4 under a nitrogen atmosphere was evaluated by thermal gravimetric analysis (TGA) at a heating rate of 10 °C min⁻¹. Decomposition temperatures are given

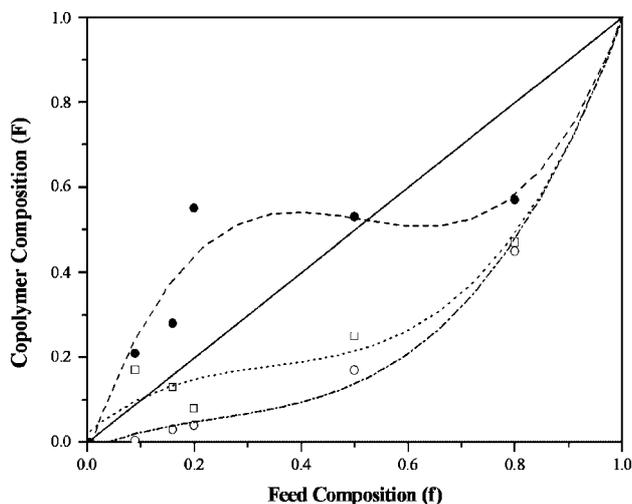


Figure 3. Plot of copolymer composition versus feed composition for copolymers 2 (●), 3 (□) and 4 (○).

Table 2. Reactivity ratios of MeSiCo (M_1) and SiR₁R₂ (M_2) copolymers calculated by F-R and K-T methods

Polymers	Method	r_1	r_2	$r_1 r_2$
2	F-R	0.093	0.134	0.013
	K-T	0.146	0.173	0.025
3	F-R	0.036	1.173	0.043
	K-T	-0.232	0.889	-0.207
4	F-R	0.506	10.545	5.331
	K-T	0.368	10.038	3.690

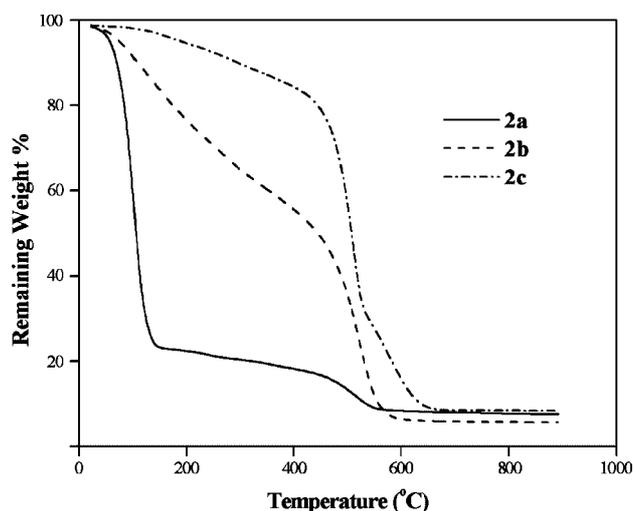


Figure 4. TGA traces for copolymers 2a, 2b and 2c (heating rate 10 °C min⁻¹).

in Table 1. Representative curves are shown in Fig 4 for the copolymer 2 series.

The initial decomposition of MeSiCo units in copolymer 2a was observed at 99 °C, while those of copolymers 2b and 2c were observed at 139 and 288 °C, respectively. It can be concluded that the increase in the relative amount of SiR₁R₂ in the co-monomer composition produced copolymers with higher portion of SiR₁R₂ units, which increased the copolymer thermal stability. However, as the SiR₁R₂ units in the copolymer composition was increased, the weight loss of SiR₁R₂ unit increased abruptly above 400 °C. From this fact, we assumed that a large proportion of alkyl-substituted copolymers would lead to block-like structures.

As can be seen in Fig 5, the decomposition of homopolymer²⁴ occurs at 93 °C, while copolymers 2a, 3a and 4a exhibited a broader decomposition temperature range due to the two-step process involved. The two-step decomposition process was even clearer for block-like copolymers and the

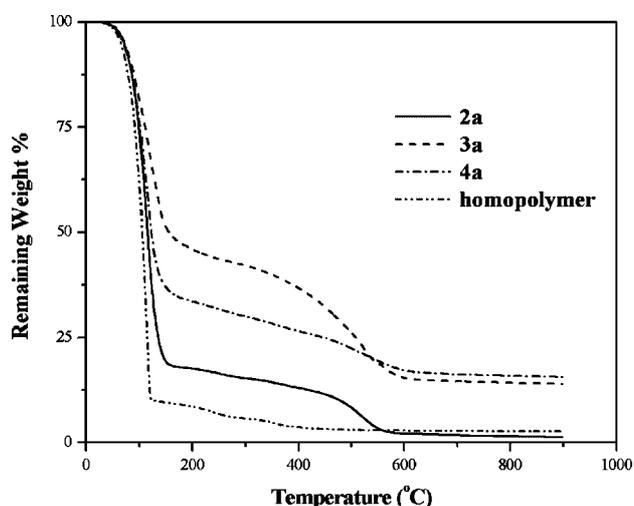


Figure 5. Selected TGA traces for copolymers 2a, 3a and 4a and homopolymer (heating rate of 10 °C min⁻¹).

relative importance of the second step increased with increasing content of SiR_1R_2 units. As the first decomposition of homopolymer is mainly due to the scission of the carbonyl groups in cobaltsilyl units, the same decomposition mechanism is believed to be occurring in copolymers **2a**, **3a** and **4a**, although the separation between first and second decompositions became less apparent for the random copolymers due to the simultaneous decomposition of MeSiCo and SiR_1R_2 units. The process responsible for the second decomposition is related to SiR_1R_2 main-chain scissions, which could not be seen in the homopolymer. For the copolymer **2**, **3** and **4** series, the second decomposition temperature and ceramic conversion yield (residue at 800 °C) were increased with the increase in the relative amount of alkyl or aromatic silanes. As can be seen in the case of copolymer **3** and **4**, the increase in the length of alkyl or aromatic groups also increased the second decomposition temperature.

CONCLUSION

Organosilicon–cobalt complexes were synthesized using direct synthesis, and characterized by IR, NMR, GC/MS, and elemental analysis. The yellow crystalline material showed limited stability in the solid state toward atmospheric oxidation when held at low temperature in the absence of light. The molecular weight of copolymers **2**, **3** and **4**, which were prepared by Wurtz coupling, increased to $M_w = 46\,000$, $48\,000$ and $65\,000\text{ g mol}^{-1}$ after 2 h, then did not greatly changed up to 24 h. Copolymerization was strongly dependent on the substituents at the silicon atoms and on the copolymer composition. The composition of the copolymer could be controlled approximately by adjusting the feed ratio. When the number of carbons in SiR_1R_2 was increased, the composition of copolymer became block-like due to steric hindrance

of their copolymers, which also increased thermal stability. The two-step thermal decomposition of the copolymers is also proof of their block-like structure.

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