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Alternating Copolymerization of Arylallenes with Carbon Monoxide Catalyzed by a π-Allylrhodium Complex. Synthesis of New Polyketones with Regulated Structure and Molecular Weight

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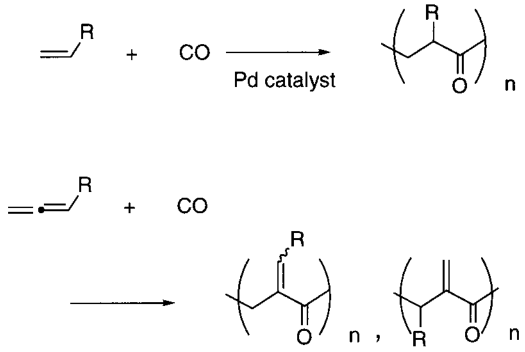
ABSTRACT: A π-allylrhodium complex, $Rh[\eta^3\text{-}CH(Ar)C\{C({=}CHAr)CH_2C({=}CHAr)CH_2CH_2CH{=}CHAr\}CH_2](PPh_3)_2$ ($Ar = C_6H_4OMe\text{-}p$) (**1**), catalyzes alternating copolymerization of arylallenes (phenylallene, (4-methylphenyl)allene, (4-methoxyphenyl)allene, (4-chlorophenyl)allene, (4-fluorophenyl)allene, (4-butylphenyl)allene, and (4-*tert*-butylphenyl)allene) with carbon monoxide (1 atm) at room temperature to give the corresponding polyketones, $I{-}[{-}CO{-}C({=}CHAr)CH_2{-}]_n$ ($I = CH_2C({=}CHAr)C({=}CHAr)CH_2C({=}CHAr)CH_2CH_2CH{=}CHAr$, where $Ar = C_6H_4OMe\text{-}p$). The polymers contain the 2,3-polymerized arylallene unit rather than the 1,2-polymerized unit. The C=C double bond in the repeating unit has a *Z* configuration, which is confirmed by the ^1H NMR spectrum using ROESY technique. The living polymerization is demonstrated by (1) the ^1H NMR spectrum of the polymers showing signals of the terminal group I originally contained in **1**, (2) an increase in molecular weight (M_n) of the polymer with narrow polydispersity throughout the polymerization, and (3) a linear relationship between the molecular weight and the monomer-to-catalyst ratio. Copolymerization of phenylallene with carbon monoxide catalyzed by **1** and subsequent addition of (4-methoxyphenyl)allene to the reaction mixture afford the block copolyketone $I{-}[\{{-}CO{-}C({=}CHPh){-}CH_2{-}\}_m{-}\{CO{-}C({=}CH{-}C_6H_4OMe\text{-}p){-}CH_2{-}\}_n]$, while copolymerization of an equimolar mixture of phenylallene and (4-methoxyphenyl)allene with carbon monoxide gives the random copolyketone $I{-}\{{-}CO{-}C({=}CHPh){-}CH_2{-}/{-}CO{-}C({=}CHC_6H_4OMe\text{-}p){-}CH_2{-}\}_n$. These two copolyketones are characterized by comparison of the $^{13}C\{^1H\}$ NMR spectra.

Introduction

Polyketones prepared from alternating copolymerization of alkene with carbon monoxide catalyzed by Pd complexes are expected to serve as potentially photodegradable plastics and as a precursor of further functionallized polymers.[1,2] Recent remarkable progress in this polymerization has enabled synthesis of living polyketones[3] and of optically active and stereoblock polyketones[4] and elucidation of a detailed mechanism of the reaction that involves alternating insertion of alkene and carbon monoxide into the Pd−C bond of the growing polymer.[5] Similar copolymerization of the 1,2-dienes with carbon monoxide would provide a new class of polyketones that have a unique enone structure in the repeating unit as shown in Scheme 1 and will be functionalized by their reaction with nucleophilic reagents. Only a few studies, however, have been reported on the copolymerization of diene with carbon monoxide.[6] The research group at Shell Co. took out a patent for the copolymerization of allene and CO catalyzed by Pd complexes.[7] Sen and his co-worker reported a Pd complex catalyzed copolymerization of sterically demanding 3,3-dimethylallene with CO and also synthesis of a ternary polymer containing *alt*-ethene−carbon monoxide and *alt*-3,3-dimethylallene−carbon monoxide blocks.[8] Recent studies on reactions of organopalladium complexes disclosed that both CO insertion into a π-allyl−Pd bond and insertion of allene into an alkyl−Pd or an acyl−Pd bond take place by choosing the reaction conditions.[9] Although π-allyl complexes of group 10 transition metals, Ni and Pd, serve as an efficient initiator of homopolymerization of 1,2-dienes,[10] the above copolymerization of 1,2-diene with CO occurs more readily than the homopolymerization under carbon monoxide atmosphere in the presence of the Pd catalyst. Rh complexes catalyze carbonylation of various organic molecules involving insertion of CO into the Rh−C bond[11] and homopolymerization of allene and arylallenes.[12] These chemical properties of organorhodium complexes suggesting possible insertion of CO and of a double bond of 1,2-diene into the Rh−C bond prompted us to investigate copolymerization of 1,2-dienes with carbon monoxide catalyzed by Rh complexes. In this paper, we present the use of a π-allylrhodium complex for the living copolymerization of arylallene with carbon monoxide to give new polyketones with a highly regulated structure. Part of this study has been reported in a preliminary form.[13]

Scheme 1



Results and Discussion

The π-allylrhodium complex $Rh[\eta^3\text{-}CH(Ar)C\{C({=}CHAr)CH_2C({=}CHAr)CH_2CH_2CH{=}CHAr\}CH_2](PPh_3)_2$ ($Ar = C_6H_4OMe\text{-}p$) (**1**) was prepared according to the

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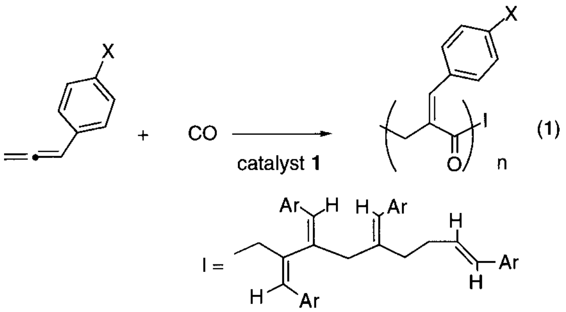
Table 1. Copolymerization of Arylallene with CO Initiated by 1

conditions[a]			product					
					mol wt		analyses	
run	monomer (Ar)	[arylallene]$_0$/[**1**]	polymer	yield (%)[b]	$10^{-3}M_n$[c,d]	M_w/M_n[c]	C (%)[e]	H (%)[e]
1	C_6H_5	50	**2**	91	7.9 (7.2)	1.08		
2	C_6H_5	100	**2**	95	17.1 (14.6)	1.09	82.63 (83.30)	5.54(5.61)
3	C_6H_5	150	**2**	97	25.6 (23.0)	1.14	83.67 (83.32)	5.73 (5.59)
4	C_6H_5	200	**2**	93	35.0	1.10	82.54 (83.32)	5.56 (5.58)
5	C_6H_4Me-*p*	50	**3**	92	11.4	1.09		
6	C_6H_4Me-*p*	100	**3**	96	25.6	1.08	82.16 (83.52)	6.46 (6.34)
7	C_6H_4Me-*p*	150	**3**	58	21.6	1.14		
8	C_6H_4OMe-*p*	50	**4**	93	8.0	1.11		
9	C_6H_4OMe-*p*	100	**4**	94	15.9	1.14	74.89 (75.87)	5.75 (5.81)
10	C_6H_4OMe-*p*	150	**4**	95	19.9	1.06		
11	C_6H_4Cl-*p*	50	**5**	92	7.0 (7.8)	1.10		
12	C_6H_4Cl-*p*	100	**5**	95	13.7 (14.8)	1.09		
13	C_6H_4Cl-*p*	150	**5**	96	21.7 (22.0)	1.16	66.79 (67.58)	4.00 (3.99)
14	C_6H_4F-*p*	50	**6**	91	7.0 (8.1)	1.10		
15	C_6H_4F-*p*	100	**6**	95	14.4 (16.5)	1.09		
16	C_6H_4F-*p*	150	**6**	94	29.0 (24.4)	1.08	73.73 (74.28)	4.54 (4.38)
17	C_6H_4Bu-*p*	50	**7**	92	9.3	1.10		
18	C_6H_4Bu-*p*	100	**7**	70	21.0	1.08	82.29 (83.97)	7.84 (7.98)
19	C_6H_4Bu-*p*	150	**7**	71	30.3	1.10		
20	C_6H_4-*t*-Bu-*p*	50	**8**	92	13.3	1.09		
21	C_6H_4-*t*-Bu-*p*	100	**8**	89	26.0	1.10	82.76 (83.97)	7.70 (7.98)
22	C_6H_4-*t*-Bu-*p*	150	**8**	96	49.5	1.11		

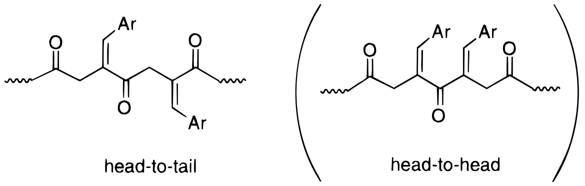
[a] Polymerization was carried out under CO (1 atm) in THF using 0.050 mmol of **1** at room temperature. [b] Isolated yield. [c] Determined by GPC using polystyrene standards. [d] In parentheses are the molecular weights determined from ^1H NMR peak area ratio between the OCH_3 and CH_2 hydrogens based on the molecular formula $H{-}[(CH_2C({=}CHPh)){-}CO]_nCH_2C\{{=}CH(Ar)\}C({=}CHAr)CH_2C({=}CHAr){-}CH_2CH_2CH{=}CHAr$ (Ar = C_6H_4OMe-*p*, *n* = monomer/initiator ratio). [e] Calculated values based on the above formula are shown in parentheses.

previously reported procedure.[14] The copolymerization of phenylallene with carbon monoxide using **1** as the initiator afforded $I{-}[{-}CO{-}CH_2{-}C({=}CHPh){-}]_n$ (**2**; I = $CH_2C({=}CHAr)C({=}CHAr)CH_2C({=}CHAr)CH_2CH_2CH{=}CHAr$, where Ar=$C_6H_4OMe$-*p*). Similar copolymerization of arylallenes with carbon monoxide gave the polyketones $I{-}[{-}CO{-}C({=}CHAr){-}CH_2{-}]_n$ (C_6H_4Me-*p* (**3**), C_6H_4OMe-*p* (**4**), C_6H_4Cl-*p* (**5**), C_6H_4F-*p* (**6**), C_6H_4Bu-*p* (**7**), C_6H_4-*t*-Bu-*p* (**8**)) as summarized in eq 1 and Table 1.



2: X = H; **3**: X = Me; **4**: X = OMe;
5: X = Cl; **6**: X = F; **7**: X = Bu; **8**: X = *t*-Bu

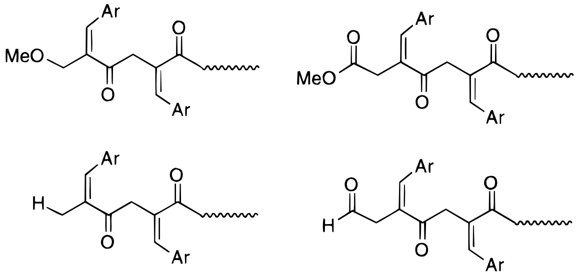
Chart 1



The polymers were characterized by means of NMR spectroscopy as described below. The ^1H NMR spectrum of **2** contains the signals due to CH= and CH_2 hydrogens at δ 7.84 and 4.16, respectively, in addition to the phenyl hydrogen signals. The peak positions and relative peak area ratio indicate the structure shown in eq 1 and the absence of structural units caused by homopolymerization of phenylallene and by copolymerization of 1,2-double bond of phenylallene with carbon monoxide, $[{-}CO{-}CH({=}CH_2){-}CHPh{-}]_n$. To determine configuration around the C=C double bond of the polymer, the ^1H NMR measurement using the ROESY (rotating frame nuclear Overhauser effect spectroscopy) technique was conducted. The ROESY spectrum of **2** on irradiation at the position of the CH_2 hydrogen signals exhibits a residual positive CH= hydrogen peak. The results indicate that the CH= and CH_2 hydrogens showing a positive NOE are at a closer distance than the distance between the CH_2 and phenyl hydrogens and that the C=C double bond of the polymer has the *Z* configuration rather than *E*. Appearance of the CH= hydrogen signal as a single sharp peak indicates strict regulation of the above orientation of the phenyl substituent. The $^{13}C\{^1H\}$ NMR spectrum exhibits signals at δ 198.7, 141.6, 135.0, and 36.8 which are assigned to CO, CH=, C=, and CH_2 carbons, respectively, based on comparison with the gated decoupled spectrum. The simple $^{13}C\{^1H\}$ NMR spectrum and the sharp ^1H NMR signals despite a significant molecular weight (M_n = 35 000 by GPC) suggest the absence of error in the linkage between repeating units such as the head-to-head linkage shown in Chart 1.

The ^1H NMR spectrum exhibits small peaks at δ 3.78−3.64 which are assigned to OMe hydrogens of the polymer end derived from the π-allyl ligand of **1**. Small signals due to other hydrogens of a tetramer structure of 4-methoxyphenylallene originally contained in **1** are observed at δ 2.55, 2.64, 3.48. 5.72, 5.95, and 6.20 in the ^1H NMR spectrum of **2** with lower molecular weight (M_n = 7900 by GPC). Since area ratios between the signals of the repeating unit and of the OMe hydrogens are consistent with the molecular weight of the polymer

Chart 2



and with ratio of the monomer to **1** (vide infra), every polymer molecule should have I as one terminal group. Characterization of another end group of the polyketone formed by quenching of the Rh−C bond of the polymer with MeOH under air was not feasible. The ^{1}H NMR spectra did not show any signals which can be assigned to Me or OMe hydrogens in possible end groups depicted in Chart 2. Efforts to identify the terminal group or to functionalize the polymer end by quenching the polyketone with diethylamine resulted in the partial degradation of the polymer chain. As summarized in Table 2, polyketones **3**−**8** gave the ^{1}H and ^{13}C NMR data similar to **2** and are considered to have similarly regulated structure.

Molecular weights of **2** both from GPC (polystyrene standards) and from ^{1}H NMR peak intensity of the repeating unit and the OMe hydrogens increase linearly with increase in the monomer-to-initiator ratio as plotted in Figure 1. The polydispersity is in the range 1.08−1.14. The molecular weights obtained from ^{1}H NMR peak area ratio between the signals of the end group and those of the repeating unit are almost equal to those calculated from the monomer-to-initiator ratio, while the molecular weights by GPC (polystyrene standards) are somewhat larger than those. All these results suggest living copolymerization of phenylallene with carbon monoxide which occurs quantitatively from the initiator and proceeds without any chain transfer process. As summarized in Table 1, polyketones **3**−**8** obtained from similar copolymerization of arylallene with carbon monoxide have narrow polydispersities and changes in the molecular weights depending on the monomer-to-initiator ratio. Insufficient yield and molecular weight of polyketone **3** obtained from the reaction with a high monomer-to-initiator ratio are ascribed to precipitation of the resulting polymer during the reaction. The substituent on the aryl group of the monomer seems to influence the reactivity of copolymerization to a small degree.

The copolymerization in the present study is believed to proceed via alternating insertion of 2,3-double bond of arylallene and CO into the Rh−C bond of the growing polymer. Additional experiments described below were conducted in order to obtain more detailed mechanistic insights. Introduction of CO (1 atm) to an NMR tube containing a THF-d_8 solution of **1** did not cause change in the ^{1}H NMR signals, whereas further addition of phenylallene (5 times the molar amount of **1**) led to growth of the signals due to {$CH_2-C(=CHPh)-CO$} structural units. A plausible pathway for the coordination and insertion of the monomers is depicted in Scheme 2. The above NMR tube experiment indicates that the equilibrium lies on the side of intermediate **A**, but that **B** can be trapped out by phenylallene addition and conversion to **C**. Plotting of time dependent change of the molecular weight (M_n) of the polymer during the reaction showed polymer growth with narrow molecular weight distribution ($M_w/M_n < 1.11$) until consumption of the phenylallene monomer.[13] The linear time-dependent increase of the molecular weight until consumption of ca. 70% of the monomer also indicates that the rate-determining step of the copolymerization resides not in the insertion of arylallene into the acyl−Rh bond but in that of CO into the π-allyl−Rh bond. Structure of the polyketone with a *Z* configuration of the C=C double bond can be accounted for by taking the above observation and the structure of the intermediate complex into account. The growing polymer end coordinated to Rh in a η^3-allyl fashion prefers the structure containing the aryl substituent at a syn position of the π-allyl ligand (**A** in Scheme 2) rather than an alternative structure with an anti aryl substituent (**A′** in Scheme 2) due to a steric reason. Insertion of CO into the Rh−C bond without syn−anti migration of the aryl group and hydrogen attached to the π-allyl carbon led to formation of the repeating unit that contains aryl and carbonyl groups at cis position of the C=C double bond. Thus, the *Z* configuration around the C=C double bond of the polyketone originates in the orientation of the aryl substituent in the η^3-coordinated growing polymer end. The mechanistic study of alternating copolymerization of ethene and carbon monoxide catalyzed by Pd complexes elucidated the total thermodynamic and kinetic relationship of all the possible intermediates and concluded that the acyl−palladium complex is the most stable species in the catalytic cycle and plays an important role as the resting state of the living copolymerization.[5a] Thermodynamically stable η^3-coordination of the growing polymer end to the Rh center seems to retard insertion of CO into the polymer−Rh bond and to make it the rate-determining step of the present copolymerization.

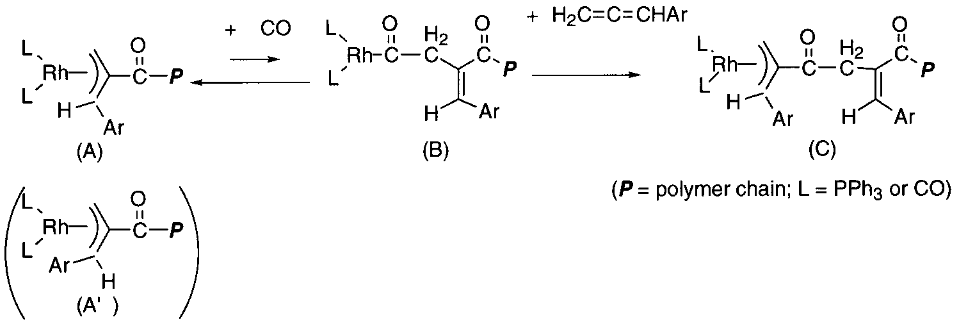
Synthesis of a block copolymer is one of the merits of living polymerization. Copolymerization of phenylallene with carbon monoxide catalyzed by **1** and ensuing addition of (4-methoxyphenyl)allene to the resulting living polymer led to formation of block copolyketone **9** whose structure is shown in Chart 3. Figure 2 shows GPC traces of the living polyketone before and after addition of the second monomer. The elution pattern is shifted completely on addition of the second monomer to the relatively higher molecular weight region, keeping the narrow molecular weight distribution. On the other hand, an equimolar mixture of phenylallene and (4-methoxyphenyl)allene reacts with carbon monoxide in the presence of catalytic amount of **1** to give **10** containing two structural units {$CO-CH_2-C(=Ph)$} and {$CO-CH_2-C(=C_6H_4OMe$-*p*)} randomly. The ^{13}C{^{1}H} NMR spectra demonstrate difference in the structures of **9** and **10** as compared in parts a and b of Figure 3. The block copolyketone **9** exhibits a single resonance of the CH_2 carbon (δ 36.8) and C= carbon (δ 135.1) and two close signals for the carbonyl carbon (δ 198.74 and 198.69) and for the *C*HAr carbon (δ 141.59 and 141.45). Similar structures of the two blocks seem to result in the appearance of the corresponding signals at almost the same positions. The random copolyketone **10** shows the ^{13}C{^{1}H} NMR signals of the carbonyl carbons as a broad signal. The most striking difference in the spectra between the block and random copolyketones is in the signals of the *ipso* carbons of the C_6H_5 and C_6H_4OMe-*p* groups. Polyketone **9** exhibits simple peaks for each of

Table 2. NMR Data of the Polyketones

	$^1H^a$				$^{13}C\{^1H\}^b$
	=CH	aromatic	CH_2	other	
2	7.84 (s, 1H)	7.41−7.24 (m, 5H)	4.16 (s, 2H)		198.7(*C*O), 141.6(=*C*H), 136.1(*ipso*), 135.0(*C*=), 129.2(*ortho*), 128.9(*para*), 128.6 (*meta*), 36.8 (*C*H_2)
3	7.84 (s, 1H)	7.26 and 7.19 (d, 4H, $J = 8$ Hz)	4.18 (s, 2H)	2.28 (s, 3H, CH_3)	198.8 (*C*O), 141.6 (=*C*H), 139.0(*para*), 135.5(*C*=), 132.3(*ortho*), 129.4 (*meta*), 36.8 (*C*H_2), 21.3 (*C*H_3)^c
4	7.82 (s, 1H)	7.31 and 6.94 (d, 4H, $J = 8$ Hz)	4.18 (s, 2H)	3.72 (s, 3H, CH_3)	198.7 (*C*O), 160.2(*para*), 141.4 (=*C*H), 134.4(*C*=), 131.2 (*ortho*), 127.5(*ipso*), 113.8 (*meta*), 55.2 (O*C*H_3), 36.8 (*C*H_2)
5	7.77 (s, 1H)	7.36 and7.26 (d, 4H, $J = 8$ Hz)	4.11 (s, 2H)		198.4 (*C*O), 140.6 (=*C*H), 136.3(*ipso*), 135.1(*C*=), 133.3, 130.6, 129.0 (*meta*), 36.9 (*C*H_2)
6	7.84 (s, 1H)	7.32 and 7.09 (d, 4H, $J = 8$ Hz)	4.13 (s, 2H)		198.6(*C*O), 163.1(*para*, d, $J = 250$ Hz), 140.8 (=*C*H), 135.8(*C*=) 131.3(*ortho*, d, $J = 9$ Hz), 131.0 (*ipso*), 115.8 (*meta*, d, $J = 20$ Hz), 36.8 (*C*H_2)
7	7.85 (s, 1H)	7.27 and 7.19 (d, 4H, $J = 8$ Hz)	4.21 (s, 2H)	*d*	198.8(*C*O), 144.1(*para*), 141.7 (=*C*H), 135.5(*ipso*), 132.5(*C*=), 129.5 (*ortho*), 128.7 (*meta*), 36.8 (*C*H_2), 35.4, 33.3, 22.3, 13.9
8	7.83 (s, 1H)	7.37 and 7.28 (d, 4H, $J = 8$ Hz)	4.21 (s, 2H)	1.22 (s, 9H, CH_3)	198.7(*C*O), 152.2(*para*), 141.6 (=*C*H), 135.5(*ipso*), 132.2(*C*=), 129.4 (*ortho*), 125.7 (*meta*), 36.8 (*C*H_2), 34.7 (*C*(CH_3)$_3$), 31.2 (C(*C*H_3)$_3$).

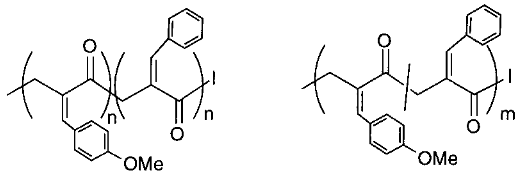
[a] 400 MHz in $CDCl_3$. Signals due to the end group are omitted. [b] 100 MHz in $CDCl_3$. [c] A signal due to the *ipso* carbon was not observed, probably due to its low intensity. [d] 2.55 (t, 2H, $J = 7$ Hz), 1.56 (q, 2H, $J = 7$ Hz), 1.27 (q, 2H, $J = 7$ Hz), 0.85 (t, 3H, $J = 7$ Hz).

Scheme 2



(***P*** = polymer chain; L = PPh$_3$ or CO)

Chart 3



9 **10**

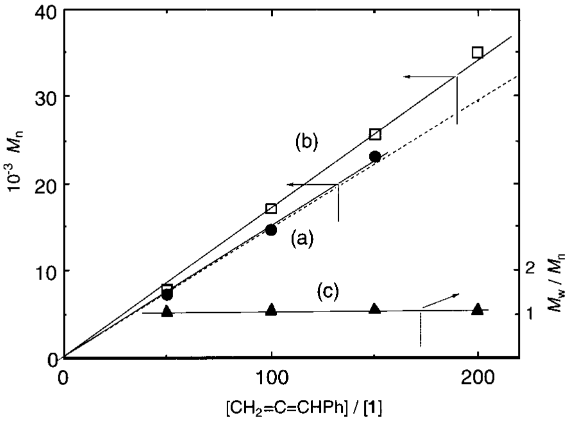


Figure 1. Plots of M_n and M_w/M_n of **2** as a function of the monomer/initiator molar ratio: (a) M_n obtained from ^1H NMR, (b) M_n obtained from GPC, and (c) M_w/M_n. M_n calculated from the monomer/initiator ratio is shown as a dotted line.

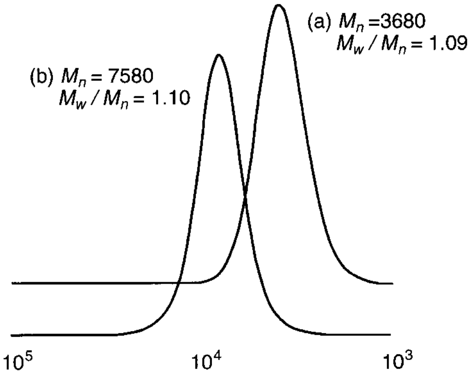


Figure 2. GPC traces during synthesis of block copolymer **9**: (a) after consumption of the first monomer (phenylallene) and (b) after addition of the second monomer ((4-methoxyphenyl)allene) and further reaction with CO.

the carbons of the two blocks (δ 136.2 (C_6H_5) and δ 134.2 (C_6H_4OMe-*p*)), whereas the corresponding signals of **10** are observed as four signals in equal intensity (δ 136.4−136.1 (C_6H_5) and δ 134.4−134.1 (C_6H_4OMe-*p*)). The four signals at 136.4−136.1 are assigned to four possible sequences of the monomer units around the CH_2−C(=CHPh)−CO structural unit shown in Chart 4. Appearance of four signals due to the *ipso* carbon of the C_6H_4OMe-*p* group is also ascribed to the presence of similar triads which are randomly contained in the polymer chain.

In summary, the π-allylrhodium complex promotes living copolymerization of arylallenes with carbon monoxide to give a new class of polyketones. The polymer has a unique enone structure with highly regulated orientation of the aryl substituents. Synthesis of the block and random copolyketones is enabled by the use of the living copolymerization.

Experimental Section

General, Measurement, and Materials. Manipulations of the Rh complexes were carried out under nitrogen or argon using standard Schlenk techniques. Phenylallene, (4-methylphenyl)allene, (4-methoxyphenyl)allene, (4-chlorophenyl)-

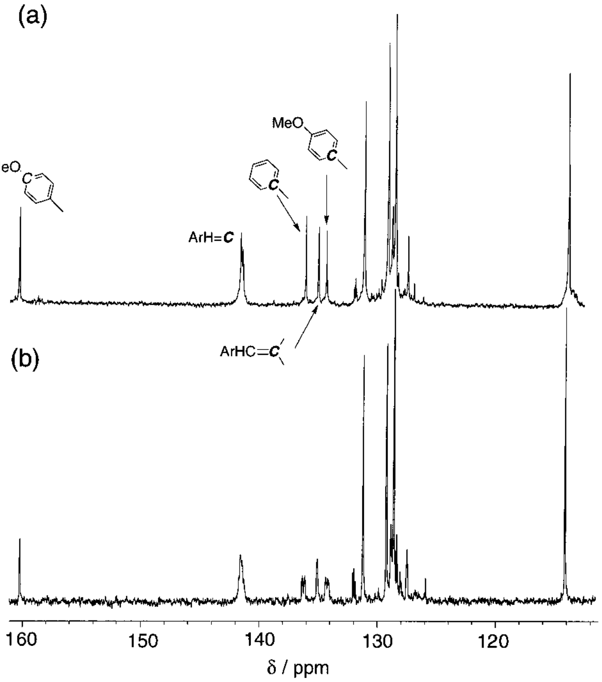
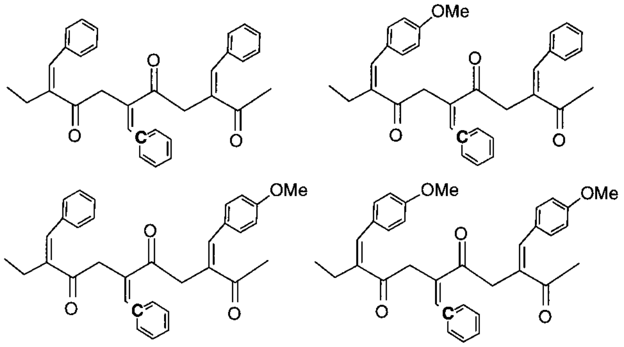


Figure 3. $^{13}C\{^1H\}$ NMR spectra of (a) block copolyketone **9** and (b) random copolyketone **10** at 100 MHz in $CDCl_3$.

Chart 4



allene, (4-fluorophenyl)allene, (4-butylphenyl)allene, and (4-*tert*-butylphenyl)allene were prepared according to the literature.[15] NMR spectra (^1H and ^{13}C) were recorded on a JEOL EX-400 spectrometer. Elemental analyses were carried out by a Yanagimoto Type MT-2 CHN autocorder.

Copolymerization of Arylallene and Carbon Monoxide Initiated by 1. A typical experimental procedure is as follows. A THF (1 mL) solution of phenylallene (150 mg, 1.29 mmol) was prepared in a Schlenk flask (ca. 50 mL volume) equipped with a glassware stopcock that is connected to a rubber balloon (ca. 2 L) filled with carbon monoxide (ca. 1.05 atm). Complex **1** (31 mg, 0.03 mmol) was added to the solution with cooling the flask below −100 °C with liquid N_2. After evacuation of the solution by three freeze−pump−thaw cycles, CO was introduced to the flask by opening the stopcock. When the temperature was raised, the solution changed its color from orange to pale yellow. The reaction mixture was stirred for 21 h at 25 °C. The resulting somewhat viscous soultion was slowly poured into MeOH (ca. 150 mL) to cause precipitation of an off-white solid which was collected by filtration and washed with MeOH repeatedly and dried in vacuo to give $\mathrm{I{-}[(CO){-}C({=}CHPh){-}CH_2{-}]_{\mathit{n}}}$ (**2**) (186 mg, 91%).

Copolymerization of phenylallene with CO under the other conditions as well as copolymerization of other arylallenes with CO was carried out analogously.

Preparation of Block Copolyketone 9. A THF (1 mL) solution of phenylallene (57 mg, 0.49 mmol) was prepared in a Schlenk flask (ca. 50 mL volume) equipped with a glassware stopcock that is connected to a rubber balloon (ca. 2 L) filled with carbon monoxide (ca. 1.05 atm) and equipped with a sidearm containing a THF solution of (4-methoxy)phenylallene (72 mg, 0.49 mmol). Complex **1** (24 mg, 0.02 mmol) was added to the solution with cooling of the flask below −100 °C with liquid N_2. After the solution was degassed by three freeze−pump−thaw cycles, CO was introduced to the flask through the stopcock. When the temperature was raised, the solution changed its color from orange to pale yellow. The reaction mixture was stirred for 1 h at 25 °C, and then the THF solution of (4-methoxyphenyl)allene was added to the reaction mixture by turning the sidearm. After the mixture was stirred for a further 4 h at room temperature, the reaction product was slowly poured into MeOH (ca. 150 mL) to cause precipitation of an off-white solid which was collected by filtration and washed with MeOH several times and dried in vacuo to give $\mathrm{I{-}[\{{-}CO{-}C({=}CHPh){-}CH_2{-}\}_{25}\{CO{-}C({=}CHC_6H_4OMe\text{-}\mathit{p}){-}CH_2{-}\}_{25}]}$ (**9**) (145 mg, 94%). Anal. Calcd for $(C_{10}H_8O)_{25}(C_{11}H_{10}O_2)_{25}(C_{40}H_{41}O_4)$: C, 79.45; H, 5.75. Found: C, 78.62; H, 5.73. ^1H NMR (400 MHz, in $CDCl_3$ at 25 °C): δ 7.82, 7.80 (s, 2H, C=CHPh and $C{=}CHC_6H_4OMe$-*p*), 7.38−7.26 (m, 7H, C_6H_5 and C_6H_4 (*ortho*)), 6.90 (d, 2H, C_6H_4 (*meta*), J = 8 Hz), 4.17 and 4.14 (s, 4H, CH_2), 3.71 (s, 3H, OCH_3). $^{13}C\{^1H\}$ NMR (100 MHz, in $CDCl_3$ at 25 °C): δ 198.74 and 198.69 (*C*O), 160.3 (*para*, C_6H_4OMe), 141.59 and 141.45 (=*C*H), 136.2 (*ipso*, C_6H_5), 135.1 (=*C*), 134.2 (*ipso*, C_6H_4OMe), 131.2 (*ortho*, C_6H_4OMe), 129.2 (*ortho*, C_6H_5), 128.9 (*para*, C_6H_5), 128.6 (*meta*, C_6H_5), 114.2 (*meta*, C_6H_4OMe), 55.3 (OCH_3), 36.8 (CH_2). GPC (polystyrene standards, eluent; $CHCl_3$): $M_n = 8.95 \times 10^3$, $M_w = 9.55 \times 10^3$, and $M_w/M_n = 1.07$.

Preparation of Random Copolyketone 10. Reaction of a mixture of phenylallene (60 mg, 0.52 mmol) and (4-methoxyphenyl)allene (76 mg, 0.52 mmol) with carbon monoxide was carried out in a manner similar to the above copolymerization of phenylallene with carbon monoxide to give $\mathrm{I{-}\{CO{-}C({=}CHPh){-}CH_2{-}/{-}CO{-}C({=}CHC_6H_4OMe\text{-}\mathit{p}){-}CH_2{-}\}}$ (**10**) (162 mg, 99%). Anal. Calcd for $(C_{10}H_8O)_{25}(C_{11}H_{10}O_2)_{25}(C_{40}H_{41}O_4)$: C, 79.45; H, 5.75. Found: C, 78.19; H, 5.67. ^1H NMR (400 MHz, in $CDCl_3$ at 25 °C): δ 7.86, 7.82, and 7.78 (s, 2H, C=CH), 7.31 (broad, 7H, C_6H_5 and C_6H_4, *ortho*), 6.90 (d, 2H, C_6H_4, *meta*, J = 8 Hz), 4.16 (bs, 4H, CH_2), 3.71 (bs, 3H, OCH_3). $^{13}C\{^1H\}$ NMR (100 MHz, in $CDCl_3$ at 25 °C): δ 198.6 (*C*O, broad), 160.3 (*para*, C_6H_4OMe), 141.7−141.3 (=*C*H), 136.4−136.1 (*ipso*, C_6H_5, four signals), 135.1 (=*C*), 134.4−134.1 (*ipso*, C_6H_4OMe, four signals), 131.2 (*ortho*, C_6H_4OMe), 129.2 (*ortho*, C_6H_5), 128.9 (*para*, C_6H_5), 128.6 (*meta*, C_6H_5), 114.2 (*meta*, C_6H_4OMe), 55.3 (OCH_3), 36.8 (CH_2). GPC (polystyrene standards, eluent; $CHCl_3$): $M_n = 8.49 \times 10^3$, $M_w = 9.66 \times 10^3$, and $M_w/M_n = 1.14$.

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References and Notes

(1) Reviews and recent references: (a) Sen, A. *Adv. Polym. Sci.* **1986**, *73/74*, 125. (b) Sen, A. *Acc. Chem. Res.* **1993**, *26*, 303. (c) Drent, E.; Budzelaar, P. H. M. *Chem. Rev.* **1996**, *96*, 663. (d) Drent, E.; van Broekhoven, J. A. M.; Budzelaar, P. H. M. *Recl. Trav. Chim. Pays-Bas.* **1996**, *115*, 263. (e) Abu-Surrah, A. S.; Rieger, B. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2475. (f) Xu, F. Y.; Zhao, A. X.; Chien, J. C. W. *Makromol. Chem.* **1993**, *194*, 2579. (g) Liaw, D.-J. *J. Polym. Sci., Part A: Polym. Chem.* **1993**, *31*, 309. (h) Bronco, S.; Consiglio, G.; Hutter, R.; Batistini, A.; Suter, U. W. *Macromolecules* **1994**, *27*, 4436. (i) Bronco, S.; Consiglio, G.; Di Benedetto, S.; Fehr, M.; Spindler, F.; Togni, A. *Helv. Chim. Acta* **1995**, *78*, 883. (j) Jiang, Z.; Sen, A. *J. Am. Chem. Soc.* **1995**, *117*, 4455. (k) Feng, Y.; Sun, J.; Zhu, Y.; Chen, W. *J. Polym. Sci., Part A: Polym. Chem.* **1997**, *35*, 1283. (l) Abu-Surrah, A. S.; Wursche, R.; Rieger, B.; Eckert, G.; Pechhold, W. *Macromolecules* **1996**, *29*, 4806.

(2) Properties of the polyketones from alkenes and carbon monoxide, see: (a) Kawai, W.; Ichihashi, T. *J. Polym. Sci., Polym. Chem. Ed.* **1974**, *12*, 1041. (b) Kawai, W. *J. Polym. Sci., Polym. Chem. Ed.* **1977**, *15*, 1479. (c) Gooden R.; Hellman, M. Y.; Hutton, R. S.; Winslow, F. H. *Macromolecules* **1983**, *17*, 2830. (d) Frank, Y. X.; James, C. W. *Macromolecules* **1993**, *26*, 3485. (e) Forbes, M. D. E.; Barborak, J. C.; Dukes, K. E.; Ruberu, S. R. *Macromolecules* **1994**, *27*, 1020. (f) Brückner, S.; De Rosa, C.; Corradini, P.; Porzio, W.; Musco, A. *Macromolecules* **1996**, *29*, 1535. (g) De Rosa, C.; *Macromolecules* **1997**, *30*, 5495. (h) Chiantore, O.; Lazzari, M.; Ciardelli, F.; De Vito, S. *Macromolecules* **1997**, *30*, 2589.

(3) Brookhart, M.; Rix, F. C.; DeSimone, J. M.; Borborak, J. C. *J. Am. Chem. Soc.* **1992**, *114*, 5894.

(4) (a) Brookhart, M.; Wagner, M. I.; Balavoine, G. G. A.; Haddou, H. A. *J. Am. Chem. Soc.* **1994**, *116*, 3641. (b) Brookhart, M.; Wagner, M. I. *J. Am. Chem. Soc.* **1996**, *118*, 7219. (c) Jiang, Z.; Adams, S. E.; Sen, A. *Macromolecules* **1994**, *27*, 2694. (d) Nozaki, K.; Sato, N.; Takaya, H. *J. Am. Chem. Soc.* **1995**, *117*, 9911.

(5) (a) Rix, F. C.; Brookhart, M.; White, P. S. *J. Am. Chem. Soc.* **1996**, *118*, 4746. (b) Margel, P.; Ziegler, T. *J. Am. Chem. Soc.* **1996**, *118*, 7337. (c) Carfagna, C.; Formica, M.; Gatti, G.; Musco, A.; Pierleoni, A. *Chem. Commun.* **1998**, 1113.

(6) Copolymerization of 1,4- and 1,5-dienes with carbon monoxide gives polyketones with cyclic structural units. See: Drent, E. Eur. Pat. Appl. 504,985, 1992; *Chem. Abstr.* **1993**, *118*, 103, 023. Borkowsky, S. L.; Waymouth, R. M. *Macromolecules* **1996**, *29*, 6377. Nozaki, K.; Sato, N.; Nakamoto, K.; Takaya, H. *Bull. Chem. Soc. Jpn.* **1997**, *70*, 659.

(7) Maatschappij, B. V. Neth. Appl. 88 01168, 1988; *Chem. Abstr.* **1990**, *113*, 24686f.

(8) Kacker, S.; Sen, A. *J. Am. Chem. Soc.* **1997**, *119*, 10028.

(9) As for insertion of CO into the π-allyl−palladium bond and for insertion of allene into the Pd−C bond, see: Yamamoto, A. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 433 and references therein. Rülke, R. E.; Kliphuis, D.; Elsevier: C. J.; Fraanje, J.; Goubitz, K.; van Leeuwen, P. W. N. M.; Vrieze, K. *J. Chem. Soc., Chem. Commun.* **1994**, 1817. Groen, J. H.; Elsevier: C. J.; Vrieze, K.; Smeets, W. J. J.; Spek, A. L. *Organometallics* **1996**, *15*, 3445. Delis, J. G. P.; Groen, J. H.; Vrieze, K.; van Leeuwen, P. W. N. M.; Veldman, N.; Spek, A. L. *Organometallics* **1997**, *16*, 551.

(10) (a) Otsuka, S.; Mori, K.; Suminoe, T.; Imaizumi, F. *Eur. Polym. J.* **1967**, *3*, 73. (b) Ghalamkar-Moazzam, M.; Jacobs, T. L. *J. Polym. Sci., Polym. Chem. Ed.* **1978**, *16*, 615. (c) Tomita, I.; Kondo, Y.; Takagi, K.; Endo, T. *Macromolecules* **1994**, *27*, 4413. (c) Tomita, I.;. Kondo, Y.; Takagi, K. Endo, T. *Acta Polym.* **1995**, *46*, 432. (d) Tomita, I.; Abe, T.; Takagi, K.; Endo, T. *J. Polym. Sci., Part A: Polym. Chem.* **1995**, *33*, 2487. (e) Takagi, K.; Tomita, I.; Nakamura, Y.; Endo, T. *Macromolecules* **1998**, *31*, 2779. (f) Deming, T. J.; Novak, B. M.; Ziller, J. W. *J. Am. Chem. Soc.* **1994**, *116*, 2366. (g) Nakano, M.; Novak, B. M. *Polym. Prepr. Jpn.* **1996**, *37*, 200. (h) Novak, B. M.; Nakano, M. *Proc. ACS. Div. PMSE* **1997**, *76*, 102.

(11) (a) Pino, P.; Piacenti, F.; Bianchi, M. In *Organic Syntheses via Metal Carbonyls II*; Pino, P., Ed.; Wiley-Interscience Publ.: New York, 1977; pp 43 and 233. (b) Falbe, J. *Carbon Monoxide in Organic Synthesis*; Springer-Verlag: Berlin, 1980. (c) Sanger, A. R. In *Homogeneous Catalysis with Metal Phosphine Complexes*; Pignolet, L. H., Ed.; Plenum Press: New York, 1983; p 216. (d) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry,* 2nd ed.; University Science: Mill Valley, CA, 1987. (e) Parshall G. W.; Ittel, S. D. *Homogeneous Catalysis*; Wiley-Interscience: New York, 1992.

(12) (a) Otsuka, S.; Nakamura, A. *J. Polym. Sci., Part B: Polym. Lett. Ed.* **1967**, *5*, 973. (b) Scholten, J. P.; van der Ploeg, H. J. *J. Polym. Sci., Polym. Chem. Ed.* **1972**, *10*, 3067. (c) Scholten, J. P.; van der Ploeg, H. J. *J. Polym. Sci., Polym. Chem. Ed.* **1973**, *11*, 3205. (d) Leland, J.; Boucher, J.; Anderson, K. *J. Polym. Sci., Polym. Chem. Ed.* **1977**, *15*, 2785. (e) Sóvágó, J.; Newton, M. G.; Mushina, E. A.; Ungváry, F. *J. Am. Chem. Soc.* **1996**, *118*, 9589. (f) Choi, J.-C.; Osakada, K.; Yamaguchi, I.; Yamamoto, T. *Appl. Organomet. Chem.* **1997**, *11*, 957.

(13) Osakada, K.; Choi, J.-C.; Yamamoto, T. *J. Am. Chem. Soc.* **1997**, *119*, 12390.

(14) Choi, J.-C.; Osakada, K.; Yamamoto, T. *Organometallics* **1998**, *17*, 3044.

(15) Moore, W. R.; Ward, H. R. *J. Org. Chem.* **1962**, *27*, 4179.

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