Copolymerization of 7-Methylenebicyclo[4.1.0]heptane with Carbon Monoxide Initiated by Optically Active Palladium Complexes

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Dedicated to Professor *Gambattista Consiglio* on the occasion of his 65th birthday

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Seven Pd-complexes with optically active bis[dihydroxazole]-type ligands promote asymmetric alternating copolymerization of 7-methylenebicyclo[4.1.0]heptane with CO, which produces an optically active polyketone, $-[C(=CH_2)-CO-C_6H_{10}]_n-$. The reaction under increased CO pressure (>5 atm) affords a polymer that contains monomer units with the *cis*-cyclohexane-1,2-diyl group almost exclusively. The polyketone exhibits positive or negative optical rotation depending on the Pd-complex. The highest and lowest $[\alpha]_D^{25}$ of the polymer obtained are $+68.9$ and -76.1, respectively. Addition of dibutylcuprate to a solution of the polymer in the presence of Me_3SiCl transforms the enone groups of the polymer to silyl enol ether groups, which are ozonized to (silyloxy)oxirane moieties.

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1. Introduction. – Alternating copolymerization of olefins with carbon monoxide catalyzed by Pd-complexes has been known to be a convenient method for the preparation of a polymer whose main chain contains carbonyl groups in high density [1]. Since the copolymerization of α-olefins with carbon monoxide produces polyketones with new chiral C-atoms, optically active Pd-catalysts are able to regulate not only tacticity but also enantioselectivity of the polymerization. *Consiglio*, *Brookhart*, *Nozaki*, *Sen*, and co-workers reported results of their studies on the stereoselective copolymerization catalyzed by palladium complexes with optically bidentate N- or P-ligands [2] [3][1]).

Copolymerization of dienes with carbon monoxide is much less common than that of olefins, while it produces polyketones with an olefinic group in the repeating units. Living copolymerization of arylallene or 1,1-dialkylallene with carbon monoxide was achieved by using π-allylrhodium complexes as the initiator, which afforded the corresponding polyenones [5]. 2-Aryl-1-methylenecyclopropane, an isomer of arylbutadiene, was reported to undergo Pd-catalyzed ring-opening copolymerization with carbon monoxide to yield a new polymer having the enone structure [6] [7]. Recently, we found that Pd-complexes with diamine or diimine ligands promoted the copolymer-

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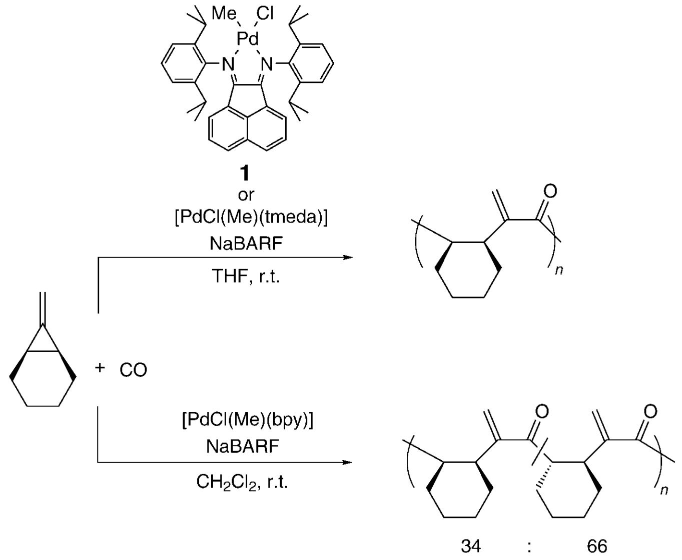
[1]) For reports on other polymerizations producing optically active polymers, see [4].

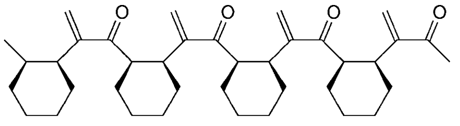
ization of 7-methylenebicyclo[4.1.0]heptane with carbon monoxide to produce a polyketone that contains the cyclohexane-1,2-diyl structure in its repeating unit [8].

Polymerization reactions with [PdCl(Me)(tmeda)]/NaBARF (tmeda = *N*,*N*,*N*′,*N*′-tetramethylethane-1,2-diamine; BARF = tetrakis[3,5-bis(trifluoromethyl)phenyl]borate(1−) = $[B\{3,5-(CF_3)_2C_6H_3\}_4]^-$) and **1**/NaBARF catalysts afford the polymer composed of repeating units with the *cis*-cyclohexane-1,2-diyl group (*cis* selectivity = 98%), while the polymer formed by the reaction promoted by [PdCl(Me)(bpy)]/NaBARF (bpy = 2,2′-bipyridine) contains *cis*- and *trans*-substituted six-membered rings in a 34 : 66 ratio (*Scheme 1*). The thermodynamically stable *trans*-cyclohexane-1,2-diyl group was probably formed *via* *β*-H elimination of the *cis*-cyclohexyl group bonded to Pd of the growing polymer and reinsertion of a C=C bond of the formed cyclohexenyl group into the Pd−H bond. The $^{13}C\{^1H\}$-NMR spectrum of the former polymer with high *cis* content shows a single signal for each C-atom, suggesting a regulated structure, although it does not provide sufficient information to determine the actual tacticity of the polymer. For the polyketone formed from 7-methylenebicyclo[4.1.0]heptane and carbon monoxide, the diads **A**–**C** are possible. Two regulated tacticities are possible for the monomer units with the *cis*-cyclohexan-1,2-diyl group. The *cis*-isotactic polymer (see **A**) has molecular chirality and can be optically active, while a molecule of *cis*-syndiotactic polymer (see **B**) is not chiral. Therefore, we investigated the copolymerization of 7-methylenebicyclo[4.1.0]heptane with carbon monoxide using optically active Pd-complexes, aiming at the determination of the tacticity of the produced polyketone.

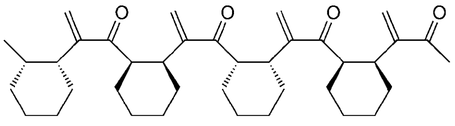
Scheme 1



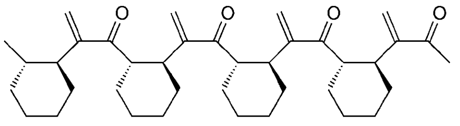
In this paper, we report the results of the copolymerization catalyzed by the seven Pd-complexes **2**–**8** with optically active bis[dihydroxazole] ligands and by complex **9** with an optically active binaphthalenyl ligand, and the chemical properties of the produced polyketones.



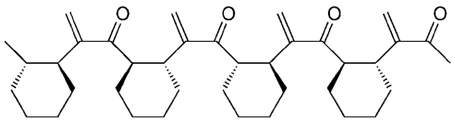
cis-isotactic type (**A**)



cis-syndiotactic type (**B**)



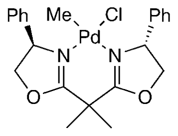
trans-isotactic type (**C**)



trans-syndiotactic type (**D**)

2. Results and Discussion. – *Ring-Opening Copolymerization Catalyzed by Chiral Pd-Complexes.* Typically, the catalyst was prepared by adding NaBARF to a THF solution of Pd-complex **1** followed by the introduction of carbon monoxide. The solution probably contained a mixture of cationic Pd-complexes [PdR(X)L]$^+$BARF$^-$ (R = Me or COMe; X = THF or CO) that were in equilibrium under a carbon monoxide atmosphere. Addition of 7-methylenebicyclo[4.1.0]heptane to the solution initiated ring-opening copolymerization of the substrate with carbon monoxide to produce polyketone $-[C(=CH_2)-CO-C_6H_{10}]_n-$ (**I**).

Table 1 summarizes the results of the copolymerization catalyzed by optically active Pd-complexes **2**–**8**. Pd-complex **2** with the (+)-2,2′-isopropylidenebis[(4*R*)-4,5-dihydro-4-phenyloxazole] ligand, promoted the copolymerization at ambient CO pressure to afford the polyketone containing *cis* and *trans* repeating units in a ratio of 58 : 42 (*Run 1*). The obtained polymer was optically active with a specific optical rotation $[\alpha]_D^{25}$ of +12.1 (c = 0.51, CHCl$_3$). The Pd-complex **3** having the same ligand with the opposite absolute configuration also promoted the copolymerization to give the copolymer with a *cis*/*trans* ratio 56 : 44 and $[\alpha]_D^{25} = -23.7$ (*Run 2*). Increasing the CO pressure in the copolymerization catalyzed by **2** caused an increase of the *cis*/*trans*



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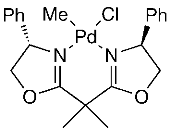

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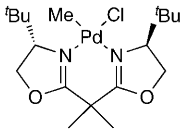

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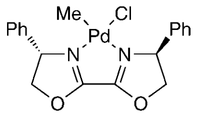

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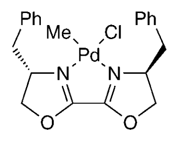

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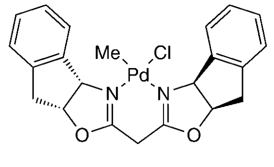

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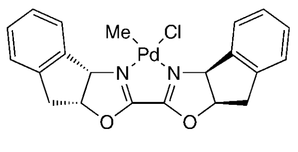

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Table 1. *Asymmetric Copolymerization of 7-Methylenebicyclo[4.1.0]heptane with CO by Pd-Complexes with Optically Active Bis[dihydrooxazole] Ligands*[a])

Run	Pd-Complex	CO [atm]	Time [h]	Conversion[b]) [%]	M_n[c])	M_w/M_n[c])	*cis*/*trans*[b])	$[\alpha]_D^{25}$
1	**2**	1	3	–	4600	1.75	58:42	+12.1
2	**3**	1	3	98	4900	1.60	56:44	−23.7
3	**2**	0.5	6	95	4200	4.02	50:50	+29.2
4	**2**	5	3	97	6500	1.46	60:40	+33.8
5	**2**	10	24	96	11700	1.32	90:10	+59.3
6	**2**	20	48	99	14400	1.14	>99:<1	+68.9
7	**2**	50	48	96	20000	1.21	>99:<1	+67.1
8	**4**	0.5	6	97	3500	1.34	46:54	+1.0
9	**4**	1	3	97	5900	1.59	76:24	0.1
10	**4**	5	24	82	4800	1.78	94:6	−1.7
11	**5**	0.5	18	93	6800	2.11	59:41	−4.0
12	**5**	1	3	86	15700	1.23	97:3	+19.3
13	**5**	5	24	77	11300	1.58	97:3	+36.8
14	**6**	0.5	3	93	5800[d])	2.99	44:56	−14.7
15	**6**	1	3	94	7800[d])	3.18	67:33	−38.0
16	**6**	5	24	93	17300[d])	3.37	>99:<1	−69.7
17	**6**	10	24	69	10800	2.29	>99:<1	−64.5
18	**7**	0.5	3	94	7000	2.18	51:49	−35.9
19	**7**	1	3	95	5100	2.65	62:38	−38.4
20	**7**	5	24	95	12500	1.36	73:27	−46.9
21	**7**	10	24	98	10900	1.66	>99:<1	−64.3
22	**7**	20	48	93	12400	2.06	>99:<1	−70.7
23	**7**	50	48	96	9400	2.38	>99:<1	−75.5
24	**8**	0.5	3	97	3600	2.71	46:54	−26.0
25	**8**	1	3	96	5100	2.57	57:43	−34.6
26	**8**	5	24	92	21100	1.81	>99:<1	−76.1
27	**8**	10	24	64	13100	2.04	>99:<1	−69.2
28	**8**	20	48	45	6500	2.23	>99:<1	−70.8

[a]) Reaction conditions: [7-methylenebicyclo[4.1.0]heptane]/[Pd]/[NaBARF] 100:1:1.2, solvent THF, [Pd] = 25 mM. [b]) Determined by ^{1}H-NMR. [c]) Determined by gel permeation chromatography (GPC) calibrated with polystyrene standards; M_w/M_n = polydispersity. [d]) Bimodal molecular-mass distribution.

ratio and $[\alpha]_D^{25}$ of the polymer (*Runs 1* and *3–7*). The polyketone formed by the reaction under 10 atm CO showed a *cis*/*trans* ratio of the repeating units of 90:10 (*Run 5*). Copolymerizations at 20 and 50 atm of CO pressure afforded the polymer composed exclusively of the monomer units with *cis*-cyclohexane-1,2-diyl groups (>99%). Specific optical rotation values of the polyketones formed by the two reactions described above are high and are similar to each other (+68.9 and +67.1) (*Runs 6* and *7*).

Fig. 1,a and *b*, show ^{1}H-NMR spectra of the polymers obtained from the reactions promoted by **2**/NaBARF under 50 and 0.5 atm of CO pressure, respectively. The polymer obtained under 50 atm CO pressure shows a similar spectrum to that of the polymer obtained from the reaction catalyzed by **1**/NaBARF under atmospheric-pressure CO (*Fig. 1,c*). Two CH signals of the six-membered ring are observed at δ 2.66 and

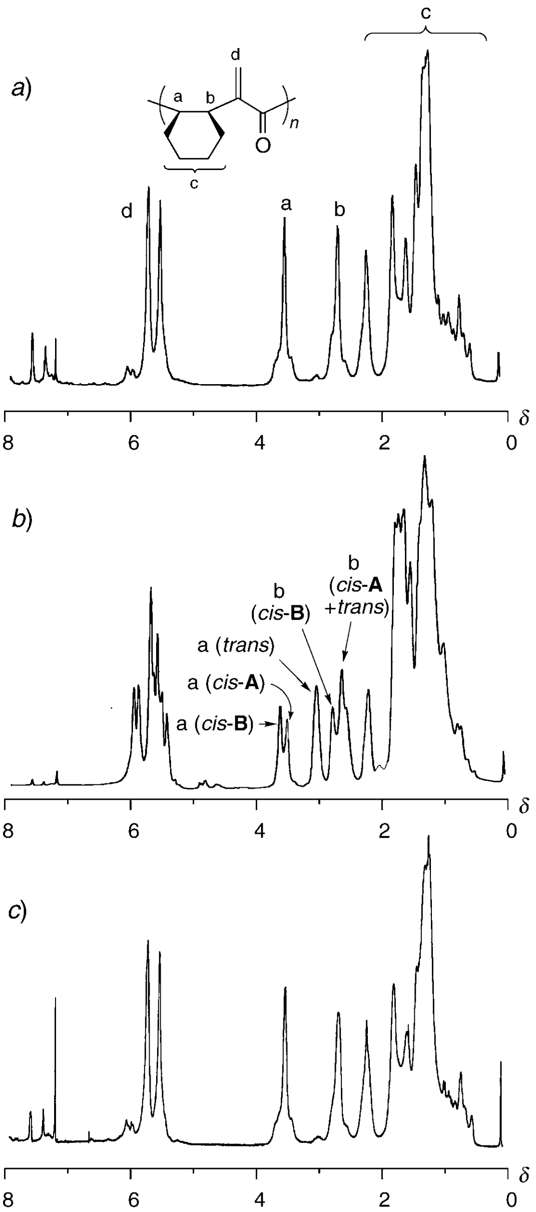

Fig. 1. *^{1}H-NMR Spectra of* **I** *obtained by* **2**/*NaBARF under* a) *50 atm and* b) *0.5 atm of CO pressure, and* c) *that of* **I** *obtained by* **1**/*NaBARF under 1 atm of CO pressure*

3.52 in both spectra. Both polymers should have the same tacticity in the arrangement of the monomer units with the *cis*-cyclohexane-1,2-diyl group. The polyketone showing the spectrum of *Fig. 1,c*, was assigned as being either of the *cis*-isotactic type **A** or the *cis*-syndiotactic type **B** on the basis of the results of detailed NMR studies of stereoisomers of the polymer and model compounds [8]. The polyketones obtained in *Runs 6* and *7* (*Table 1*) are optically active and are assigned to *cis*-isotactic polymers (see **A**) rather than *cis*-syndiotactic ones (see **B**).

The polymer obtained from the reaction catalyzed by **2** at 0.5 atm CO shows two sets of signals that are not observed in *Fig. 1,a* or *c*. Signals at δ 2.81 and 3.68 are assigned to the CH groups of the *cis*-syndiotactic structure of type **B**, which is another regulated tacticity of the polymer composed of the monomer units with the *cis*-cyclohexane-1,2-diyl group. The positions of the signals are similar to those for the polyketone formed from the reaction with [PdCl(Me)(bpy)] as the catalyst in THF [8]. The signal at δ 3.10 can be assigned to the structure composed of *trans*-cyclohexane-1,2-diyl groups.

Polymerization by using the **4**/NaBARF catalyst under 5 atm CO affords a polymer with a high *cis* content, although its optical rotation is much lower ($[\alpha]_D^{25} = -1.7$) than that of the polymer obtained from **2**/NaBARF at 20 and 50 atm CO (*Table 1*, *Runs 8–10*). The reactions catalyzed by **5**/NaBARF and **6**/NaBARF yield a polymer that shows both a high *cis* content of the monomer units and a large optical rotation (up to −69.7) at the CO pressure of 5 atm (*Runs 11–17*). The polymer obtained through the reactions catalyzed by **7** and **8** at CO pressures above 10 atm exhibits large optical rotation and a high content of the *cis*-isotactic structure of type **A** (*Runs 18–28*).

The specific optical rotation of the polymer obtained by using the Pd-complexes **6**–**8** with a bis[(*S*)-dihydrooxazole] ligand is negative, whereas the reaction catalyzed by **5** having also a bis[(*S*)-dihydrooxazole] ligand in the presence of NaBARF leads to a polymer with a positive specific optical rotation, the reason of which is not clear. CD Spectra of the polymer obtained by using **7**/NaBARF under various CO pres-

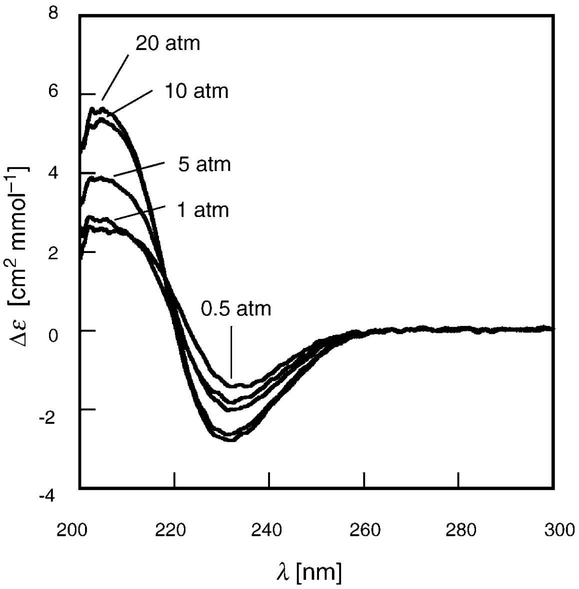

Fig. 2. *CD Spectra of polyketone obtained by copolymerization catalyzed by* **7**/*NaBARF under varied CO pressure*

sures are shown in *Fig. 2*; they indicate an increase of CD intensity caused by the increase of CO pressure during polymerization.

The copolymerization in the presence of [PdCl(Me)(tmeda)]/NaBARF and [PdCl(Me)(bpy)]/NaBARF as catalysts is also affected by the CO pressure, as shown in *Table 2*. Under atmospheric-pressure CO, polymerization catalyzed by [PdCl(Me)(bpy)]/NaBARF yielded a polymer having both *cis* and *trans* repeating units in a 46 : 54 ratio (*Run 1*)[2]. The proportion of the *trans* repeating units increased to 76 and 83% of the total repeating units upon decreasing the CO pressure to 0.5 and 0.25 atm, respectively (*Runs 2* and *3*). Polymerization at the CO pressure of 5 atm produced a polymer with a high content of *cis*-cyclohexane-1,2-diyl groups (92%) (*Run 4*). Polydispersity (M_w/M_n) of the polyketone changed from 2.19 (0.2 atm CO) to 1.12 (5 atm CO) depending on the CO pressure. The decrease of CO pressure in the polymerization led to an increase of polydispersity probably due to the more frequent occurrence of chain transfer during the polymerization. Polymerization catalyzed by [PdCl(Me)(tmeda)]/NaBARF also showed an increase in the content of *cis* repeating units upon increasing the CO pressure (*Runs 5* and *6*). The polymer with 94% *cis* content was obtained by using **1**/NaBARF at 5 atm of CO pressure (*Run 8*). These results indicate that decreasing the CO pressure in the polymerization causes an increase in both the content of monomer units having *trans*-cyclohexane-1,2-diyl groups and the polydispersity of the polymer produced.

Table 2. *Copolymerization of 7-Methylenebicyclo[4.1.0]heptane with CO by Pd-Complexes under Various CO Pressure*[a])

Run	Pd-Complex	CO [atm]	Time [h]	Conversion[b]) [%]	M_n[c])	M_w/M_n[c])	*cis/trans*[b])
1	[PdCl(Me)(bpy)]	1	3	99	6500	2.11	46 : 54
2	[PdCl(Me)(bpy)]	0.5	3	97	7800	1.77	24 : 76
3	[PdCl(Me)(bpy)]	0.2	24	87	4300	2.19	17 : 83
4	[PdCl(Me)(bpy)]	5	3	95	5800	1.12	92 : 8
5	[PdCl(Me)(tmeda)]	1	3	95	10700	1.11	93 : 7
6	[PdCl(Me)(tmeda)]	0.5	3	95	13100	1.19	70 : 30
7	**1**	1	3	93	13600	1.20	91 : 9
8	**1**	5	3	76	12500	1.66	94 : 6

[a]) Reaction conditions: [7-methylenebicyclo[4.1.0]heptane]/[Pd]/[NaBARF] 100 : 1 : 1.2, solvent THF, [Pd] = 25 mM. [b]) Determined by ^{1}H-NMR. [c]) Determined by GPC calibrated with polystyrene standards; M_w/M_n = polydispersity.

In our previous report, we attributed the formation of the monomer units with *trans*-cyclohexane-1,2-diyl groups to the reactions shown in *Scheme 2* [8]. Insertion of CO into the Pd−C bond of *cis*-cyclohexylpalladium groups produces the monomeric units with *cis* structure (see *i*)). β-H Elimination, which results in a polymer with a ter-

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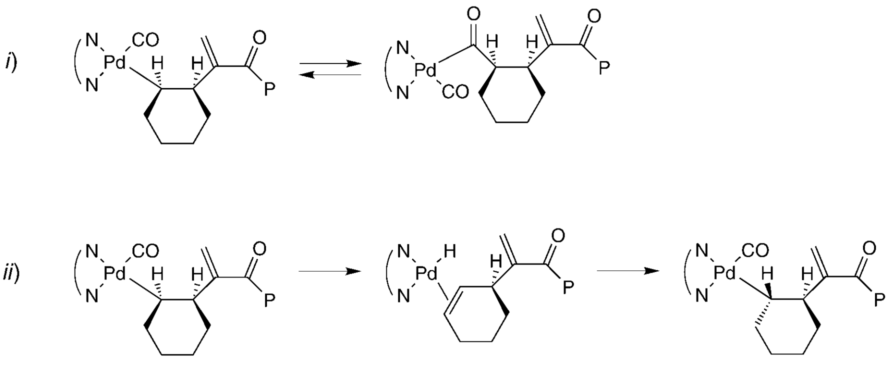
[2]) The cationic Pd-complex, prepared by mixing [PdCl(Me)(bpy)] and NaBARF and subsequent removal of NaCl by filtration produced the polymer with the *cis/trans* ratio of 91 : 9 [8]. On the other hand, when the cationic Pd-complex was used without removing NaCl, the *cis/trans* ratio of the polymer changed to 46 : 54 (*Table 2*, *Run 1*).

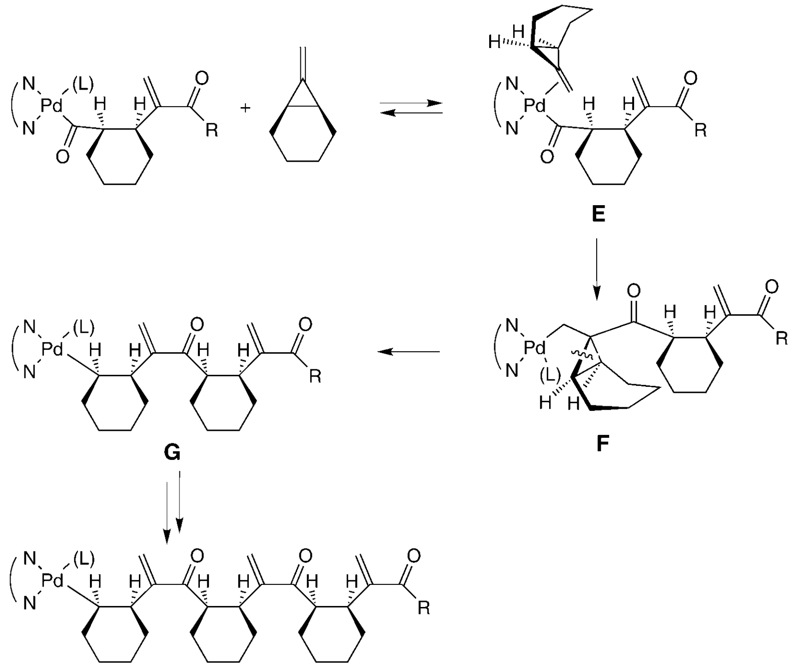
Scheme 2



minal cyclohexene, and the insertion of C=C bonds into the Pd–H bonds lead to thermodynamically stable *trans*-cyclohexane-1,2-diyl groups (see *ii*)). The increase of CO pressure in the polymerization, as shown in *Tables 1* and *2*, renders process *i*) more favorable and results in an increase in the *cis* content in the polymer and a decrease in the polydispersity. Isomerization of the *cis*-cyclohexene-1,2-diyl group at the polymer end into the *trans* form (see *ii*)) involves switching of the coordinating face of the C=C bond of the cyclohexene ring. Polymerization of cyclopentane catalyzed by a zirconocenes derivative was also reported to afford the polymer composed of *trans*-cyclopentane-1,3-diyl repeating units [9]. This isomerization reaction during polymer growth was attributed to β-H elimination of the polymer end followed by dissociation and recoordination of the cyclopentene ring. Polymerization in our study does not accompany chain transfer, and reaction *ii*) in *Scheme 2* may proceed without dissociation of the cyclohexene group from the Pd-center. *Gladysz et al.* studied chemical properties of the coordination face of the alkene ligand without dissociation [10]. A similar reaction can be involved in the polymerization of our study.

Polymerization Mechanism. The polyketone with *cis*-isotactic structure of type **A** is obtained from the reaction catalyzed by **1**/NaBARF, [PdCl(Me)(tmeda)]/NaBARF, [PdCl(Me)(bpy)]/NaBARF, and the complexes with optically active dihydrooxazole-containing ligands **2**–**8**. Since ligands of the two former Pd-complexes are achiral, the *cis*-isotactic structure of the polymer is formed by chain-end control rather than site control during polymerization. *Scheme 3* depicts a stereochemical pathway of polymer growth, which accounts for the formation of the *cis*-isotactic polymer. The *Pd*-acyl group of the growing polymer chain undergoes coordination insertion of the monomer. Coordination of a sterically less hindered side of 7-methylenebicyclo[4.1.0]heptane to the Pd-center produces intermediate **E**, although the coordination of the other side of the olefin may also be possible. Migratory insertion of the C=C bond into the Pd–C bond of **E** forms cyclopropylidenemethyl palladium intermediate **F**. Pd-Promoted C–C bond cleavage of **F** *via* β-alkyl elimination occurs selectively at one side of the three-membered ring of the polymer end to yield intermediate **G** with a cyclohexyl–palladium bond. The selectivity of this process is governed by the geometrical structure of the cyclohexane-1,2-diyl group of **F**. Although the selective formation of the *cis*-isotactic polymer *via* the reactions in *Table 2* (*Runs 4*, *5*, and *8*) is explained

Scheme 3



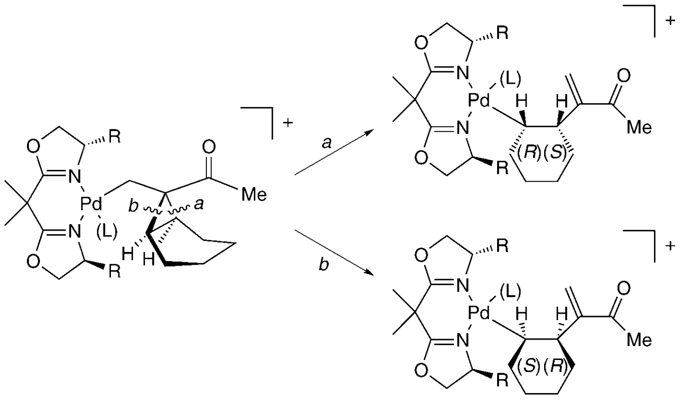
by chain-end control, the isotactic polymerization in *Table 1* may be ascribed to either chain-end control or site control caused by the chiral chelating ligands of the catalyst.

If the chain-end control of the polymerization is effective for regulating the tacticity, the enantioselectivity of the polymerization should be governed by the structure of the auxiliary bis[dihydrooxazole] ligands at the initial stage. *Scheme 4* shows two stereochemical pathways of the initiation of the polymerization. The (cyclopropylidenemethyl)palladium intermediate was formed *via* migratory insertion of 7-methylenebicyclo[4.1.0]heptane into the Pd–COMe bond of the complex having optically active bis[dihydrooxazole] ligands. β-Alkyl elimination of this intermediate *via* cleavage of a C–C bond of the three-membered ring leads to one of the diastereoisomeric cyclohexylpalladium intermediates *via Pathway a* or *b*.

A Pd-complex **9** with an optically active binaphthalenyl ligand and an achiral bidentate N-ligand, 4,7-dimethyl-1,10-phenanthroline (Me_2phen), was used as the catalyst of the copolymerization. Complex **9** was prepared by oxidative addition of optically active (*S*)-2-iodo-2′-methoxy-1,1′-binaphthalene to $[Pd(PPh_3)_4]$ to form the $[PdI(binaphthalenyl)(PPh_3)_2]$ complex according to the method reported by *Ito* [4f], followed by subsequent exchange of the PPh_3 ligands with N-ligands (*Scheme 5*).

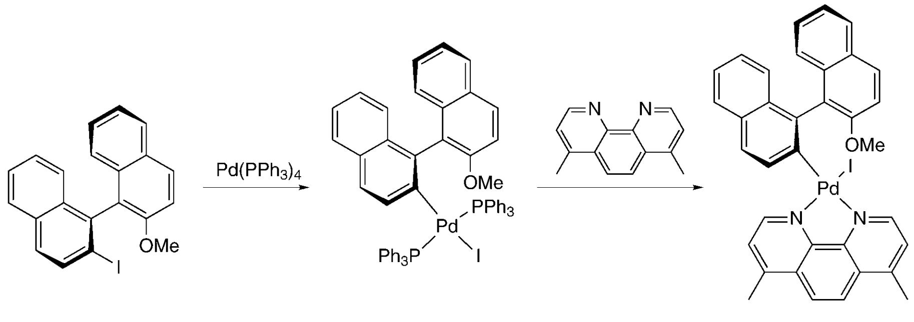
The catalyst **9**/NaBARF promotes copolymerization to give a polymer with high *cis* content and isotacticity (M_n 10400, M_w/M_n 1.42, *cis/trans* $>99:<1$). The $[\alpha]_D^{25}$ of the obtained polymer is -4.79, which is not as high as that obtained by using Pd-complexes with optically active bis[dihydrooxazole] ligands. The apparent lower stereoselectivity for the reaction with **9**/NaBARF than that with **2**–**8**/NaBARF can be attributed to the

Scheme 4



L = CO or solvent

Scheme 5



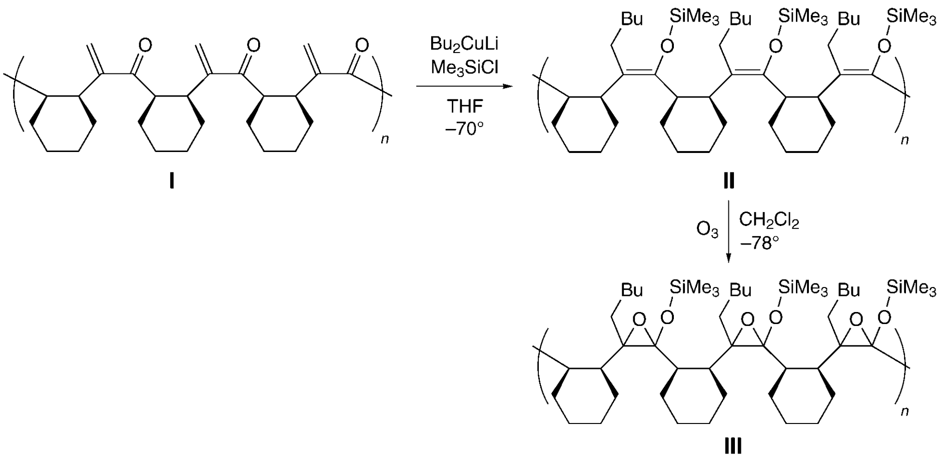
9

low stereoselection efficiency of **9** at the initial stage of polymerization and/or the error of stereoselection during the chain growth. The latter can lead to the formation of isotactic stereoblock copolymers. The higher optical activity of the polymer produced by using a bis[dihydrooxazole]palladium complex than that by using the (binaphthalene)-palladium complex **9** indicates that the effect of the chiral bidentate ligand plays an important role during chain growth.

Polymer Reaction of Copolymers of Methylenecyclopropanes with Carbon Monoxide. The 1,4-addition of organocuprate to the enone group of the polymer **I** and subsequent ozonolysis of the C=C bond were conducted to obtain ketocarboxylic acid, as shown in *Scheme 6*.

Thus Bu_2CuLi/Me_3SiCl efficiently transformed the enone group of **I** (1.47 mmol of repeating units, M_n 24300, M_w/M_n 1.38) to the silyl enol ether structure **II**. The $^{13}C\{^1H\}$-NMR spectrum of the obtained polymer showed no signal of the $CH_2=$ group, whereas the presence of signals assigned to C=C at δ 119.9, 120.6, and 150.7 indicated the quantitative formation of the silyl enol ether structure **II** as a mixture of (*Z*)- and (*E*)-isomers (*Fig. 3,a*). The M_n of **II** was 13400 (M_w/M_n 1.50), which is somewhat lower than

Scheme 6



that of the original polymer (M_n 24300, M_w/M_n 1.38). A similar reaction of the optically active polymer (M_n 9300, M_w/M_n 2.39, $[\alpha]_D^{25} = -65.9$) also afforded the optically active polymer having the silyl enol ether moieties (M_n 7200, M_w/M_n 1.48 $[\alpha]_D^{25} = -66.8$).

The polymer **II** having the silyl enol ether moieties was then subjected to ozonolysis. Thus, **II** (achiral, M_n 7200, M_w/M_n 1.64) was dissolved in CH_2Cl_2, and O_3 was bubbled for 30 min at – 78°. The M_n changed little on ozonolysis, the product **III** exhibiting an M_n of 6300 (M_w/M_n 1.46), indicating that no degradation of **II** took place. The $^{13}C\{^1H\}$-NMR spectrum of **III** showed no signals due to C=C bonds, but the signals assigned to an acetal group at δ 90.6 were observed (*Fig. 3, b*). The trimethylsilyl group also appeared at δ 0–3.5, indicating the formation of the 1-(siloxy)-1,2-epoxyalkane (=1-pentyl-2-(silyloxy)oxirane) moiety. These results indicate that epoxidation of the C=C bonds occurred upon treatment with O_3.

3. Conclusions. – The Pd-complexes with optically active bis[dihydrooxazole] ligands promoted asymmetric alternating copolymerization of 7-methylenebicyclo[4.1.0]heptane with CO to afford the optically active polyketone **I** at high CO pressure (>5 atm). The result and NMR data of the polymer provided sufficient evidence to identify its structure as of the *cis*-isotactic type **A**. Polymerization catalyzed by [PdCl(Me)(bpy)]/NaBARF at 5 atm CO also produces the *cis*-isotactic polyketone. The decrease of CO pressure in the reaction causes increases in the molecular units with *trans*-cyclohexane-1,2-diyl groups and in the polydispersity due to chain-transfer reactions. The polyketone **I** was converted into a polymer **III** with epoxy groups upon treatment with organocuprate followed by O_3.

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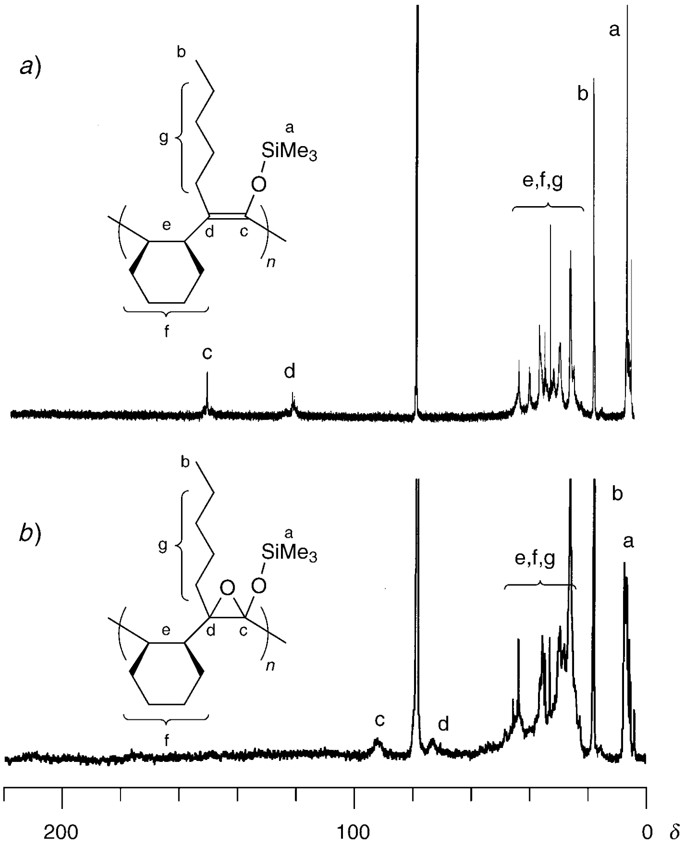

Fig. 3. *$^{13}C\{^1H\}$-NMR Spectra of* a) **II** *and* b) **III**

Experimental Part

General. THF was distilled over 'benzophenone ketyl' (=diphenylmethanone radical ion(1−)) under Ar. The 7-methylenebicyclo[4.1.0]heptane was prepared according to [11]. Bis[dihydrooxazole] ligands were purchased or prepared according to [12]. [PdCl(Me)L] [13] and NaBARF [14] were prepared according to the reported procedures. Specific optical rotation: *Jasco DIP-370*. Gel permeation chromatography (GPC): *Tosoh-HLC-8020* high-speed liquid chromatograph system equipped with a differential refractometer detector and a variable-wavelength UV/VIS detector; at 40° with THF as eluent, flow rate 0.6 ml min^{-1}; *TSKgel SuperHM-L* and *SuperHM-M* columns; the molecular masses were calibrated based on polystyrene standards. Differential scanning calorimetry (DSC): *Seiko-DSC6200R*. CD Spectrum: *Jasco J-820*. ^{1}H- and ^{13}C-NMR Spectra: *Varian-Mercury-300* or *Jeol-JNM-500* spectrometer; δ in ppm rel. to $CHCl_3$ in the $CDCl_3$ solvent (δ 7.26) for ^{1}H and $CDCl_3$ (δ 77.0) for ^{13}C.

*Copolymerization of 7-Methylenebicyclo[4.1.0]heptane with CO at Elevated CO Pressure: Poly[(*cis*-cyclohexane-1,2-diyl)(1-methylene-2-oxoethane-1,2-diyl)]* (**I**). Typically, to a 50-ml stainless-steel vessel containing [PdCl(Me)(bpy)] (0.025 mmol, 7.8 mg) and NaBARF (0.030 mmol, 26.6 mg), THF (1 ml) was added under Ar, and the mixture was stirred for 5–10 min. The vessel was flushed 3 times with CO (*ca.* 5 atm). Then 7-methylenebicyclo[4.1.0]heptane (0.27 g, 2.5 mmol) was added, and CO (5 atm) was charged to the vessel again, and the mixture was stirred for 3 h at r.t. The products were diluted with $CHCl_3$ (2 ml) and poured into a large amount of (*ca.* 200 ml) MeOH. The formed white solid was collected and dried *in vacuo* at 25°: **I** (0.20 g, 58%). ^{1}H-NMR (500 MHz, $CDCl_3$): 0.7–2.2 (*m*, 8 H, CH_2); 2.56, 2.66, 3.52, 3.68 (*m*, 2 H, CH (*cis*-isotactic and *cis*-syndiotactic)); 5.57, 5.63, 5.77 (*s*, 2 H, $C{=}CH_2$). ^{13}C-NMR (125 MHz, $CDCl_3$): 21.1, 25.8, 26.2, 29.1 (CH_2); 38.1, 39.1, 40.7, 42.0 (CH); 124.7 ($=CH_2$); 150.4 (C=); 204.2 (C=O). M_n 5800, M_w/M_n 1.12.

Copolymerization of 7-Methylenebicyclo[4.1.0]heptane with CO at Reduced CO Pressure. Typically, to a 25-ml *Schlenk* flask containing a THF soln. (1 ml) of [PdCl(Me)(bpy)] (0.025 mmol, 7.8 mg), NaBARF (0.030 mmol, 26.6 mg) was added under Ar, and the mixture was stirred for several minutes. The resulting suspension was degassed, flushed with CO (1 atm), and stirred for 10–15 min at r.t. Then 7-methylenebicyclo[4.1.0]heptane (0.27 g, 2.5 mmol) was added with a syringe. The mixture was stirred under Ar/CO 80 : 20 (*v*/*v*) (1 atm) for 24 h at r.t. The products were diluted with $CHCl_3$ (2 ml) and poured into a large amount (*ca.* 200 ml) of MeOH. The formed white solid was collected and dried *in vacuo* at 25°: **I** (0.11 g, 31%). ^{1}H-NMR (500 MHz, $CDCl_3$): 0.7–2.3 (*m*, 8 H, CH_2); 2.64 (*s*, 1 H, C*H*–C(=CH_2)(*trans*)); 2.80 (*s*, 1 H, C*H*–C(=CH_2)(*cis*)); 3.10 (*s*, 1 H, C*H*–C(=O)(*trans*)); 3.65 (*s*, 1 H, C*H*–C(=O)(*cis*)); 5.65, 5.96 (*m*, 2 H, $C{=}CH_2$). ^{13}C-NMR (125 MHz, $CDCl_3$): 25.7, 29.3, 31.6, 34.7 (CH_2); 36.5, 45.1 (CH); 121.6 ($=CH_2$); 152.2 (C=); 205.1 (C=O). M_n 4300. M_w/M_n 2.19.

Enantioselective Copolymerization by Optically Active Pd-Complexes at Elevated CO Pressure. Typically, to a 50-ml stainless steel vessel containing **7** (0.025 mmol, 12.2 mg) and NaBARF (0.030 mmol, 26.6 mg), THF (1 ml) was added under Ar, and the mixture was stirred for several minutes. The vessel was flushed 3 times with CO (*ca.* 5 atm). Then 7-methylenebicyclo[4.1.0]heptane (0.27 g, 2.5 mmol) was added and CO (50 atm) was charged to the vessel again, and the mixture was stirred for 48 h at r.t. The products were diluted with $CHCl_3$ (2 ml) and poured into a large amount (*ca.* 200 ml) of MeOH. The formed white solid was collected and dried *in vacuo* at 25°: **I.** $[\alpha]^{25}_{D} = -75.5$. ^{1}H-NMR (500 MHz, $CDCl_3$): 0.5–2.2 (*m*, 8 H, CH_2); 2.66 (*s*, 1 H, C*H*-C(=CH_2)); 3.52 (*s*, 1 H, C*H*-C(=O)); 5.55 (*s*, 1 H, $C{=}CH_2$); 5.74 (*s*, 1 H, $C{=}CH_2$). ^{13}C-NMR (125 MHz, $CDCl_3$): 21.1, 25.8, 26.0, 28.8 (CH_2); 37.8, 40.8 (CH); 124.8 ($=CH_2$); 150.4 (C=); 204.5 (C=O). M_n 9400, M_w/M_n 2.38.

*(4,7-Dimethyl-1,10-phenanthroline-κN^1,κN^{10})iodo[(1*S*)-2′-methoxy-1,1′-binaphthalen-2-yl)palladium* (**9**). Typically, to a 25-ml *Schlenk* flask containing $[Pd(PPh_3)_4]$ (0.087 mmol, 100 mg) under Ar, (1*S*)-2-iodo-2′-methoxy-1,1′-binaphthalene (0.104 mmol, 43 mg) and THF (3.5 ml) were added and stirred at 50° for 10 h. After THF was evaporated and the residue was washed with Et_2O (3 × 5 ml), [PdI{(*S*)-MeO-$C_{20}H_{12}$}$(PPh_3)_2$], a mixture of *trans* and *cis* isomers, was obtained as yellow powder (45 mg, 50%). To a 25-ml *Schlenk* flask containing [PdI{(*S*)-MeO-$C_{20}H_{12}$}$(PPh_3)_2$] (0.062 mmol, 64 mg) under Ar, 4,7-dimethyl-1,10-phenanthroline (0.068 mmol, 14 mg) and THF (3.0 ml) were added and stirred at r.t. for 3 h. The supernatant phase was washed with THF (3 × 2 ml) at 0° to afford **9** (27 mg, 60%). Yellow powder. $[\alpha]^{25}_{D} = -402$ (CH_2Cl_2, $c = 1.041$). ^{1}H-NMR (300 MHz, C_6D_6): 2.74 (*s*, 3 H, Me–C(4) or Me–C(7) (Me_2phen)); 2.80 (*s*, 3 H, Me–C(7) or Me–C(4) (Me_2phen)); 2.99 (*s*, 3 H, MeO); 6.03 (*d*, *J* = 5.4, 1 H, H–C(3) or H–C(8) (Me_2phen); 6.21 (*d*, *J* = 5.7, 1 H, H–C(3) or H–C(8) (Me_2phen)); 6.83 (*d*, *J* = 9, 1 H (naph)), 7.02 (*d*, *J* = 8.1, 1 H (naph)); 7.08 (*d*, *J* = 10.5, 1 H, H–C(5) or H–C(6) (Me_2phen)); 7.40 (*d*, *J* = 10.5, 1 H, H–C(6) or H–C(5) (Me_2phen)); 7.56 (*d*, *J* = 9.9, 1 H (naph)); 7.63 (*d*, *J* = 7.5, 1 H (naph)); 7.83 (*d*, *J* = 8.1, 1 H (naph)); 7.91 (*d*, *J* = 7.5, 1 H (naph)); 8.04 (*d*, *J* = 4.2, 1 H, H–C(2) or H–(9) (Me_2phen)); 8.25 (*d*, *J* = 9, 1 H (naph)); 8.57 (*d*, *J* = 8.7, 1 H (naph)); 8.99 (*d*, *J* = 4.5, 1 H, H–C(9) or H–C(2) (Me_2phen)); 6.89, 7.22, 7.27, 7.34 (*m*, 4 H (naph)).

Enantioselective Copolymerization in the Presence of Pd-Complex **9**. Typically, to a 25-ml *Schlenk* flask containing **9** (0.0062 mmol, 4.5 mg) and NaBARF (0.07 mmol, 6.6 mg), THF (0.25 ml) was added under Ar, and the mixture was stirred for several minutes. The resulting suspension was degassed, flushed with CO (1 atm), and 7-methylenebicyclo[4.1.0]heptane (0.067 g, 0.62 mmol) was added. The mixture was transferred to a 50-ml stainless-steel autoclave under CO, and the mixture was stirred under CO (10 atm) at r.t. for 24 h (82% conversion). The products were diluted with $CHCl_3$ (1 ml) and poured into a large amount (*ca.* 100 ml) of MeOH. The formed white solid was collected and dried *in vacuo* at 25°: **I** (10.6 mg). $[\alpha]^{25}_{D} = -4.79$. ^{1}H-NMR (500 MHz, $CDCl_3$): 0.5–2.2 (*m*, 8 H, CH_2); 2.68 (*s*, 1 H, C*H*–C(=CH_2)); 3.56 (*s*, 1 H, C*H*–C(=O)); 5.60 (*s*, 1 H, $C{=}CH_2$); 5.78 (*s*, 1 H, $C{=}CH_2$). M_n 10400, M_w/M_n 1.42.

Transformation of **I** *to Poly[(*cis*-cyclohexane-1,2-diyl){1-pentyl-2-[(trimethylsilyl)oxy]ethene-1,2-diyl}]* (**II**). Typically, to CuBr·Me_2S (2.7 g, 13.23 mmol) and THF (22 ml) cooled to −70°, 1.6M BuLi in hexane (13.8 ml, 22.05 mmol) was added dropwise (colorless → brown). The mixture was stirred at − 40° for 30 min and cooled again to − 70°. A THF soln. (4 ml) of polymer **I** (0.4 g, 2.94 mmol) and Me_3SiCl (0.75 ml, 5.9 mmol) was added dropwise and stirred at − 70° for 6 h and at − 40° for 12 h. Ac_2O was added to terminate the reaction, and the produced polymer was extracted with CH_2Cl_2. After evaporation and reprecipitation from MeOH, **II** was obtained. ^1H-NMR (500 MHz, $CDCl_3$): − 0.1 – 0.5 (*m*, 9 H, Me_3Si); 0.85 (*s*, 3 H, Me); 0.5 – 2.0 (br. *m*, 16 H, CH_2); 2.10 (br., 1 H, CH); 2.72 (br., 1 H, CH). ^{13}C-NMR (125 MHz, $CDCl_3$): 1.2 – 2.6 (Me_3Si); 14.5 (Me); 21.4, 22.6, 22.9, 26.4, 28.5, 29.7, 31.6, 33.5 (CH_2), 36.9, 40.6 (CH); 119.9, 120.6, 150.7 (C=C). M_n 7200, M_w/M_n 1.64.

Reaction of **II** *with* O_3*: Poly{{2-pentyl-3-[(trimethylsilyl)oxy]oxirane-2,3-diyl}(*cis*-cyclohexane-1,2-diyl)}* (**III**). Typically, through a soln. of CH_2Cl_2 (5 ml), MeOH (1 ml), and **II** (0.05 g, M_n 7200, M_w/M_n 1.64), O_3 was bubbled at − 78° for 1 h. The mixture was treated with Me_2S and evaporated: **III**. ^{13}C-NMR (125 MHz, $CDCl_3$): 0.0 – 3.5 (Me_3Si); 14.1 (Me); 17 – 34 (CH_2); 37 – 47 (CH); 71.4 (OC); 90.6 (OCOSi). M_n 6300, M_w/M_n 1.46.

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