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Homogeneous Catalysis

Dipalladium Catalyst for Olefin Polymerization: Introduction of Acrylate Units into the Main Chain of Branched Polyethylene**

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Abstract: *A dipalladium complex with a double-decker structure catalyzes ethylene–acrylate copolymerization to produce the branched polymer containing the acrylate units in the polymer chain, not at the branch terminus. The cooperation of the two palladium centers, which are fixed in a rigid framework of the macrocyclic ligand, is proposed to have a significant dinuclear effect on the copolymerization.*

The discovery of nickel(II) and palladium(II) diimine catalysts for olefin polymerization initiated a new field of reactions using molecular catalysts because it led to the synthesis of polymers which could hardly be obtained using early-transition-metal catalysts.[1] The modification of *N*-aryl groups of a ligand affects the productivity and selectivity of polymerization. Nickel and palladium catalysts with C_2-symmetrical structures promote the isotactic polymerization of propene,[2] the isomerization polymerization of 4-alkylcyclopentenes, and the cyclopolymerization of 1,6-dienes with high selectivity.[3] Another direction in the modification of these catalysts is to block the apical sites of a square-planar metal center and to prevent chain transfer by the associative exchange between a vinyl-terminated polymer and a monomer. Nickel complexes with bulky *N*-aryl diimine ligands catalyze ethylene polymerization even at elevated temperatures or in the presence of dihydrogen.[4] The complexes with a cyclic structure show high thermal stability of the catalyst for the polymerization of ethylene and α-olefins.[5] Recently, we reported a dinuclear nickel catalyst with a rigid macrocyclic bis(phenoxyimine) ligand.[6,7] The olefin polymerization by the dinuclear catalysts is enhanced not only by the steric circumstance of an apical site of the metal center but also by the interaction of the polymer end with the other metal.[8] Cationic palladium diimine catalysts copolymerize ethylene with acrylates and yield a highly branched polymer containing ester groups at the end of the branches.[9] Herein we report a dinuclear palladium complex of a macrocyclic ligand with two diimine coordination groups. It catalyzes the copolymerization of ethylene with acrylic esters to afford polymers having different structures from those obtained by polymerization catalyzed by mononuclear palladium diimine complexes and neutral palladium catalysts with phosphine-sulfonate ligands.[10]

The structures of the mononuclear complex **1**[1] and the dinuclear complexes **2** and **3** are shown in Figures 1 a and b. The X-ray crystallographic structure of the macrocyclic ligand of **2** (Figure 1 c) indicated that the two acenaphthene groups are aligned in a parallel fashion with a distance of 3.49 Å. The ^{1}H NMR spectrum of **2** contains two signals corresponding to the 9-Me groups of xanthene, and also indicates a double-decker structure of the complex with two palladium centers on the same side of the xanthene plane. Major signals resulting from the hydrogen atoms on the Pd−Me groups are observed at $\delta = 0.89$ and 0.84 ppm, and correspond to two possible isomers regarding positions of the Me and Cl ligands on the palladium centers. Although the ^{1}H NMR spectrum of **3** suggests the presence of minor isomers such as **3′** (Figure 1 d), the ESI-MS profile and ^{1}H NMR spectrum of a solution prepared by dissolving **3** and NaBARF (BARF = B{$C_6H_3(CF_3)_2$-3,5}$_4^-$) (NaBARF/Pd = 1.1) show the selective formation of the monocationic complex [**3**-Cl]$^+$ as a single isomer with the two acenaphthene groups stacked in parallel form.[11] A similar reaction of **3** with NaBARF (NaBARF/Pd = 1.2) under an ethylene atmosphere results in the formation of a dicationic complex (*m*/*z* 549.1084, correspond-

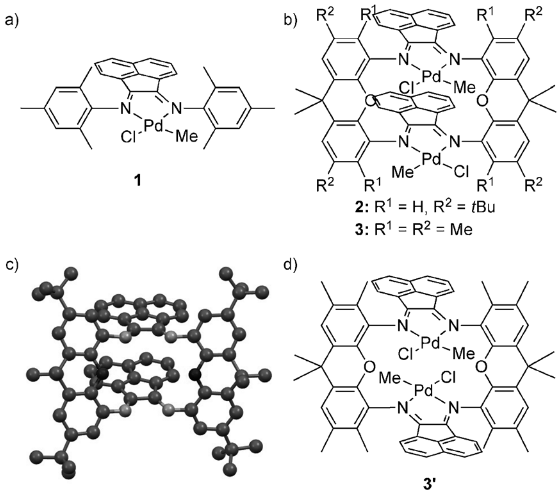

Figure 1. Structures of a) mononuclear and b) dinuclear palladium complexes used in this study, c) the ligand of **2** as determined by X-ray crystallography, and d) a possible isomer of **3**.

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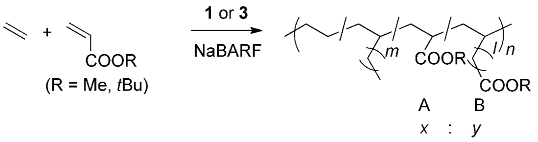
Table 1: Ethylene polymerization and copolymerization catalyzed by di- and mononuclear palladium complexes.[a]

Run	Cat.	Co-monomer (conc. [M])	p_{Ethylene} [MPa]	Yield [g]	TON ethylene	TON acrylate	Co-monomer[b] incorp. [mol%]	x/y[b,d]	Branches[b] /1000 C	M_w[c]	M_w/M_n[c]
1	**1**	–	1	3.70	13200	–	–	–	110	20500	2.27
2	**2**	–	1	2.40	8550	–	–	–	55	1650	1.54
3	**3**	–	1	4.53	16100	–	–	–	72	69400	4.08
4	**1**	MA (1.7)	1	0.109	376	4.2	1.1	21:79	93	3400	1.52
5	**3**	MA (1.7)	1	0.192	586	32	5.2	77:23	43	63700	7.82
6	**3**	MA (1.7)	0.5	0.031	88	8.5	9.3	44:56	37	22800	3.66
7	**3**	MA (1.7)	2	0.490	1580	55	3.4	85:15	47	42800	5.61
8	**3**	MA (2.2)	1	0.079	234	15	6.6	72:28	40	38000	4.7
9	**1**	TBA (1.4)	1	0.438	1460	22	1.6	46:54	92	5280	1.55
10	**3**	TBA (1.4)	1	0.923	2860	94	3.3	92:8	46	118000	6.39
11	**3**	TBA (2.1)	2	1.61	5370	76	1.6	$>99:<1$	48	125000	8.33
12	**1**	*t*Bu butenoate (1.4)	1	0.487	1560	35	2.2	4:96[e]	87	5120	1.56
13	**3**	*t*Bu butenoate (1.4)	1	0.664	1960	80	3.9	12:88[e]	33	10900	6.27
14	**1**	Et pentenoate (1.4)	1	1.06	3420	81	2.3	–	82	5000	1.57
15	**3**	Et pentenoate (1.4)	1	1.05	2740	216	7.3	–	35	23500	12.1

[a] Reaction conditions: [Pd] = 10 μmol, co-cat. = NaBARF (12 μmol), solvent = CH_2Cl_2, total volume of CH_2Cl_2 and co-monomer = 10 mL, at 40 °C, 18 h. [b] Determined by NMR spectroscopy. [c] Determined by GPC based on a polystyrene standard using THF as the eluent. [d] x and y are as in Equation (1). [e] x'/y'. x' and y' as in Equation (2).

ing to [**3**–2Me–2Cl]/2 by ESI-MS).[12] The associative coordination of an ethylene molecule probably enhances the removal of the second Cl ligand. The reaction of the macrocyclic ligand of **3** with an equivalent of [(cod)PdMeCl] leads to the dipalladium complex **3** rather than the monopalladium complex, in addition to unreacted macrocyclic ligand.[11] This result indicates the introduction of the second palladium center is enhanced by the coordination of the first pallaium center to one of the diimines of the macrocyclic ligand.

The complexes **1**–**3** catalyze ethylene polymerization in the presence of NaBARF (Table 1, runs 1–3), although the productivity of **2** is much lower than those of **1** and **3**. The polyethylene formed using the dinuclear catalysts **2** and **3** is less branched than that obtained using a mononuclear one.[13] Both the mononuclear and dinuclear complexes **1** and **3** catalyze the copolymerization of ethylene with acrylates [Eq. (1)], although the resulting polymers have different structures and molecular weights, as summarized in Table 1. The polymerization of ethylene (1 MPa) in the presence of methyl acrylate (MA; [MA] = 1.7 M), catalyzed by **3**/NaBARF, afforded a polymer with $M_w = 63700$ (run 5).



(1)

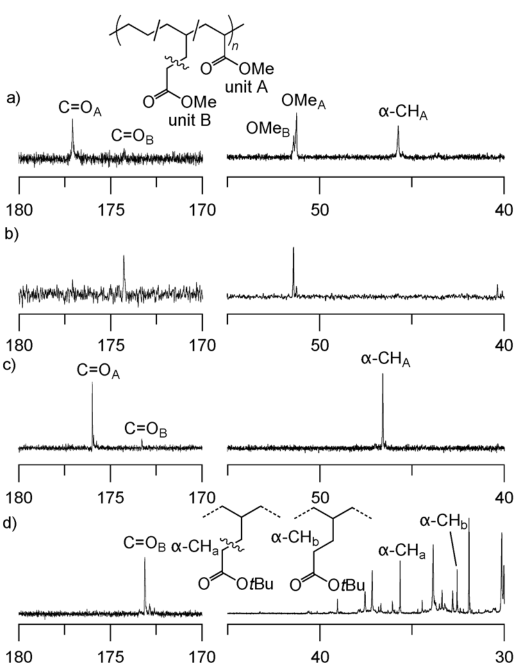


Figure 2. $^{13}C\{^1H\}$ NMR spectra ($CDCl_3$ at RT) of polymers obtained by using **1**/NaBARF or **3**/NaBARF catalysts. Spectra for a) run 5, b) run 4, c) run 10, and d) run 13 as detailed in Table 1.

Figures 2a and b show a comparison of the $^{13}C\{^1H\}$ NMR spectra of the copolymers. The polymer obtained from the reaction, catalyzed by **3**/NaBARF under 1 MPa of ethylene, exhibits signals corresponding to the carbonyl and methoxy carbon atoms of the acrylate units in the polymer chain (unit A, $\delta = 177.1$ and 51.2 ppm) at a much higher intensity than those of the acrylate terminus (unit B; $\delta = 174.3$ and 51.4 ppm) as well as a signal corresponding to the α-CH carbon atom of unit A ($\delta = 45.8$ ppm). The spectrum of the polymer from the reaction using **1**/NaBARF as the catalyst contains the signals corresponding mainly to unit B. On the basis of the ^1H NMR spectra of these polymers, the ratios of unit A to unit B are 77:23 for the former polymer (Table 1, run 5) and 21:79 for the latter (run 4), and the dinuclear catalyst results in a higher acrylate content (5.2 mol%) than that form the mononuclear one (1.1 mol%). Both polymers are hyperbranched as confirmed by the observation of isobutyl branches at $\delta = 19.6$ and 11.8 ppm in the $^{13}C\{^1H\}$ NMR spectra.

The copolymerization using the **3**/NaBARF catalyst under various ethylene pressures (Table 1, runs 6 and 7) indicated that an increase in the ethylene pressure results in a decrease in acrylate content and an increase in the unit A/unit B ratio. The copolymerization under 2 MPa of ethylene yielded a polymer with unit A/unit B ratio of 85:15. The copolymerization at the increased MA concentration (2.2 M) resulted in an increase in the acrylate content of the copolymer up to 6.6 mol %. Ethylene and *tert*-butyl acrylate (TBA) undergo smooth copolymerization catalyzed by **1**/NaBARF and **3**/NaBARF. The reaction catalyzed by **3**/NaBARF at 1 MPa of ethylene yielded a copolymer with a higher acrylate content (3.3 mol %) and a higher unit A/unit B ratio (92:8; Figure 2c) than that from the mononuclear catalyst (1.6 mol % and 46:54; Table 1, runs 9 and 10). An increase in ethylene pressure to 2 MPa afforded a copolymer whose acrylate unit was present in the main chain exclusively (run 11). The copolymerization of ethylene with *tert*-butyl butenoate also proceeds in the presence of catalytic amounts of **1**/NaBARF and **3**/NaBARF to give polymers containing the co-monomer unit in 2.2 and 3.9 mol %, respectively (runs 12 and 13) [Eq. (2)].

(2)

The $^{13}C\{^1H\}$ NMR spectrum of the latter copolymer shows α-CH_2 signals ($\delta = 35.7$ and 32.6 ppm) and a carbonyl carbon signal ($\delta = 173.1$ ppm) for the terminus of the branches (Figure 2d). The signals corresponding to the co-monomer unit in the polymer chain (unit A′) have not been clearly observed. The ^1H NMR spectrum showed α-CH_2 signals of the butenoate unit in the main chain (unit A′) and terminus (unit B′) at $\delta = 2.15$ and 2.20 ppm, respectively, and the peak area ratio suggested that the butenoate unit is incorporated mainly in the terminal groups ($x'/y' = 12:88$). The copolymerization of ethylene with ethyl pentenoate forms a polymer whose acrylate units are present mainly as terminal groups, although the precise ratio of acrylate units in the main chain to those in the terminal group was not determined owing to the severe overlap of ^1H NMR signals.

The ethylene-TBA copolymer (Table 1, run 11) undergoes hydrolysis of its *tert*-butoxycarbonyl group upon addition of Me_3SiI to yield a polymer with COOH side groups.[10g] Although the ethylene-acrylate copolymer obtained using the mononuclear complex shows glass-transition temperatures of only −84 to −87 °C, the ethylene-TBA copolymers and hydrolyzed copolymer have weak melting points between 8–29 °C and 16–35 °C, respectively.[14] Films of the ethylene-TBA copolymer and its hydrolysis product are soft and can be stretched, as shown in Figure 3a, whereas the homopolyethylene obtained by **3** is too soft to form such a film.

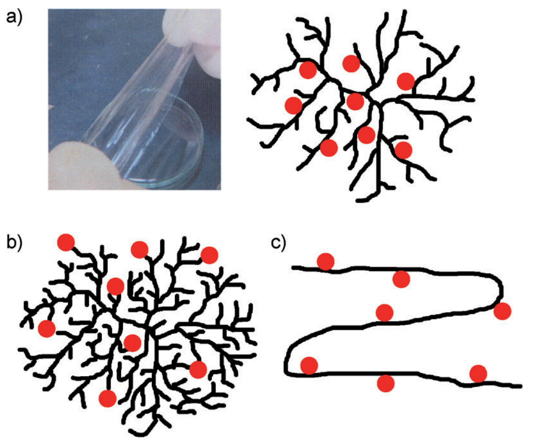


Figure 3. a) Stretched film of ethylene–*tert*-butyl acrylate copolymer obtained using **3**/NaBARF and structure of ethylene-acrylate copolymer obtained a using dinuclear palladium catalyst, diimine palladium catalyst (b), and phosphine-sulfonate palladium catalyst (c). Red circles = the ester group.

Young's modulus of the hydrolyzed ethylene-TBA copolymer is 4.6 MPa, which is larger than the original ethylene-TBA copolymer (1.6 MPa; Figure 4). The polymer structure, having the ester or carboxylic acid groups in the main chain (inner side of the branched polymer), probably influenced the polymer properties. These results are in contrast to the previously reported ethylene-acrylate copolymers obtained using diimine palladium complexes (highly branched copolymers with acrylate units on their terminus, amorphous; Figure 3b) and phosphine-sulfonate complexes (linear copolymers with acrylate units on their main chain, crystalline; Figure 3c).

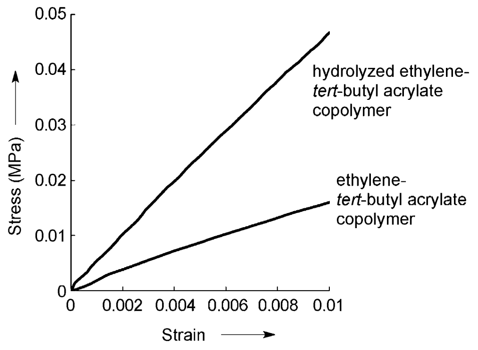
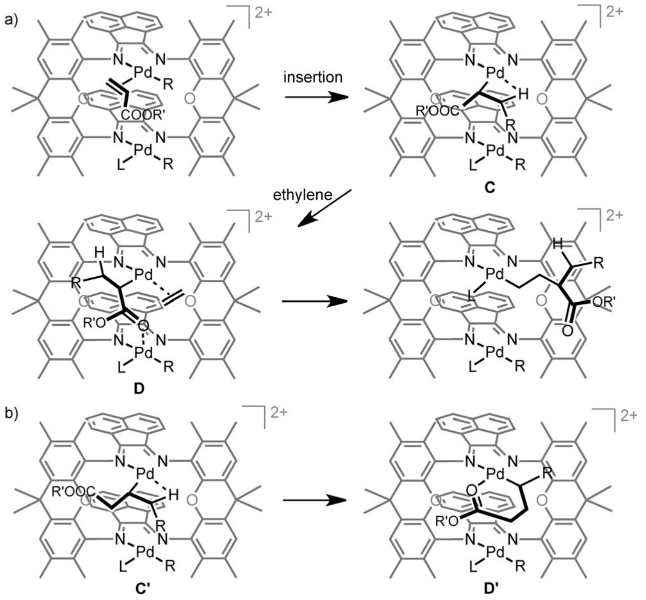


Figure 4. Stress–strain relationships of ethylene–*tert*-butyl acrylate copolymer and hydrolyzed ethylene–*tert*-butyl acrylate copolymer.

Scheme 1a shows the successive insertion of acrylate and ethylene proposed for the copolymerization using **3**/NaBARF. The acrylate undergoes 2,1-insertion into the metal–polymer bond to form a four-membered palladium chelate intermediate (**C**), similar to the reaction using the mononuclear catalyst,[9a,b] and the intermediate undergoes the direct coordination of ethylene to the palladium center. The species formed (**D**) is stabilized by the coordination of carbonyl oxygen atom to the apical site of the other palladium



Scheme 1. Plausible mechanism of the chain growth in the copolymerization of ethylene with acrylate using **3**.

center, thus causing the migratory insertion of an ethylene ligand into the Pd−CH(COOR) bond.[15] The insertion of ethylene occurs before isomerization under sufficiently high ethylene pressure, thus incorporating an acrylate unit into the polymer chain. The larger *x*/*y* ratio and higher TON for ethylene-TBA copolymerization compared to that of the MA reaction are accounted for by the preference of direct ethylene insertion into the Pd−CH(COO*t*Bu) bond, although less bulky MA tends to form C,O-chelating intermediates.[9a,b] As shown in Scheme 1 b, butenoate also undergoes 2,1-insertion into the metal–carbon bond to form the alkylpalladium species **C′**. Rapid isomerization by chain walking and coordination of the carbonyl oxygen atom to the palladium center yields a stable six-membered palladium chelate intermediate (**D′**). It causes the incorporation of the butenoate unit at the terminus of the branches similar to the mononuclear catalysis.[9a,b]

In summary, a dinuclear palladium complex with a double-decker structure promotes the copolymerization of ethylene with acrylate. The acrylate unit is mainly incorporated into the main chain of a branched copolymer. The close proximity of palladium centers, supported by a rigid macrocyclic ligand, make the successive insertion of acrylate and ethylene smooth.

Experimental Section

General procedure for copolymerization by **3**/NaBARF: Dichloromethane (6.0–9.5 mL) was added to a 50 mL autoclave containing **3** (6.00 mg, 0.005 mmol) and NaBARF (10.5 mg, 0.012 mmol) under argon and then stirred at 40 °C for 2 min (600 rpm). Polar monomer (0.5–4.0 mL, sum of volume of dichloromethane and polar monomer: 10 mL) was added and ethylene (0.5–2 MPa) was charged and stirred for 18 h. The reaction mixture was poured into large amount of chloroform and was treated with activated carbon. After filtration, the volatile fractions were removed in vacuo at 60 °C to give oily or elastomeric copolymers.

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Keywords: copolymerization · homogeneous catalysis · palladium · polymers · reaction mechanism

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[11] For detailed analysis of the dinuclear complexes, please see the Supporting Information.

[12] The ESI-MS peak obtained in the presence of ethylene corresponds to the dicationic dihydride complex (see Figure S7 in the Supporting Information). It is formed by insertion of ethylene into the two Pd–Me bonds followed by β-hydrogen elimination of the olefins.

[13] Brookhart and co-workers reported that the propylpalladium complex is in equilibrium between the primary and secondary alkyl ligands and that the π coordination of ethylene to palladium shifts the equilibrium to the primary one. The less branched polyethylene from **3**/NaBARF than **1** can be attributed to the strong coordination of ethylene with the metal center of the dicationic complex. See: a) D. J. Tempel, L. K. Johnson, R. L. Huff, P. S. White, M. Brookhart, *J. Am. Chem. Soc.* **2000**, *122*, 6686–6700; b) L. H. Shultz, D. J. Tempel, M. Brookhart, *J. Am. Chem. Soc.* **2001**, *123*, 11539–11555.

[14] Homopolyethylene obtained by the reaction catalyzed by **3**/NaBARF also shows a weak melting point at 6.5 °C.

[15] Attempt to observe the species **D** by ^{1}H NMR spectroscopy of the mixture of **3**, NaBARF, and MA was unsuccessful. In the absence of ethylene, the rapid isomerization of **D** would be favored. Please see the Supporting Information.