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Controlled Polymer-Chain Growth

Pd-Catalyzed Polymerization of Dienes that Involves Chain-Walking Isomerization of the Growing Polymer End: Synthesis of Polymers Composed of Polymethylene and Five-Membered-Ring Units**

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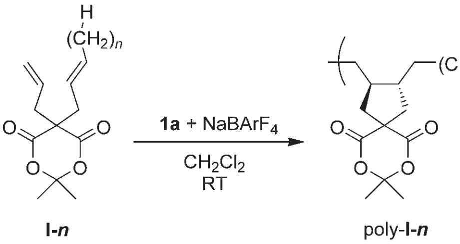
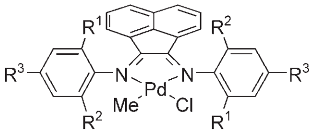
Co-polymerization reactions of ethylene with cyclic olefins, such as norbornene and cyclopentene as well as with 1,5- or 1,6-dienes that undergo cyclization during the polymer growth, produce hydrocarbon polymers with five- or six-membered cyclic units that are located randomly.[1] These reactions that use a co-monomer with a functional group and are catalyzed by late-transition-metal complexes provide a steady route to functionalized polyethylenes. The reaction using ethyl 5-norbornene-2-carboxylate catalyzed by a Ni complex affords polyethylene with the CO_2Et groups located randomly,[2] whereas an alternating co-polymerization of ethylene with 2-(4-methoxyphenyl)-1-methylenecyclopropane catalyzed by a cobalt complex yields a polymer with C_6H_4OMe groups.[3] Recently, we have succeeded in the random co-polymerization of ethylene with isopropylidene diallylmalonate, and obtained a polymer with five-membered cyclic units with ester groups.[4] Although the above random co-polymerization could regulate the averaged densities of the functional group along the polymer chain by changing the molar ratio of the two monomers used, it is not suited for the precise design of the polymer structure. Herein, we report that 1,6-dienes with both terminal and internal C=C bonds undergo a Pd-complex-promoted cyclopolymerization accompanied by the chain walking of the growing polymer,[5,6] and afford polymers with $(CH_2)_n$ spacers of the desired length between the functionalized five-membered rings.

The four Pd complexes **1a**–**1d** were used as the precursors of the catalysts used in this study (Figure 1). A catalyst prepared from **1a** and sodium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate) ($NaBArF_4$) initiates the cyclopolymerization of isopropylidene allyl(crotyl)malonate (**I-1**) at room temperature to produce the polymer -$(CH_2\text{-}C_5H_6(C_5H_6O_4)\text{-}CH_2CH_2)_m$- (poly-**I-1**), as shown in Equation (1) and Table 1 (entry 1).



(1)

Figure 2a shows the $^{13}C\{^1H\}$ NMR spectrum of the polymer. Signals of the CH and CH_2 carbon atoms in the five-membered ring appear at $\delta = 46.9$ and 45.8 ppm, respectively,



1a: $R^1 = R^2 = R^3 = Me$
1b: $R^1 = 2\text{-}Me\text{-}C_6H_4$, $R^2 = R^3 = Me$
1c: $R^1 = R^2 = i Pr$, $R^3 = H$
1d: $R^1 = R^2 = Cl$, $R^3 = H$

Figure 1. Four Pd-catalyst precursors.

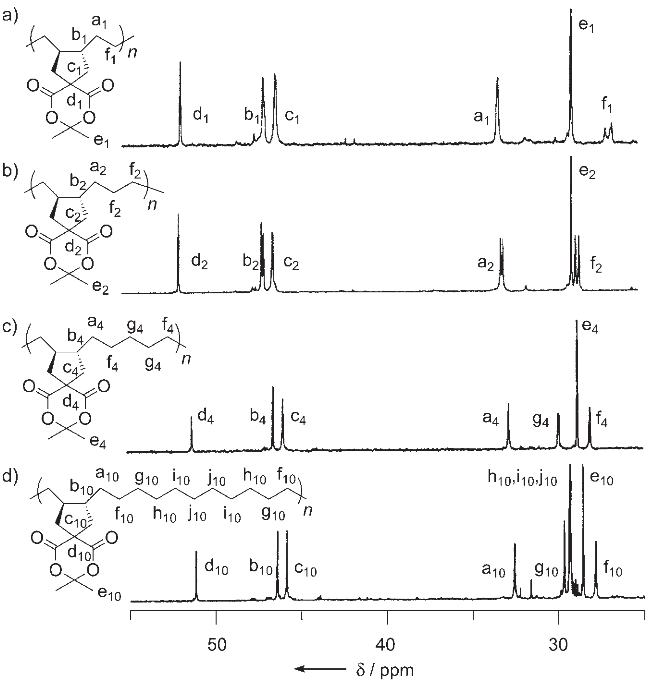


Figure 2. $^{13}C\{^1H\}$ NMR spectra ($CDCl_3$ at 25 °C) of: a) poly-**I-1** (entry 1, Table 1); b) poly-**I-2** (entry 2); c) poly-**I-4** (entry 4); and d) poly-**I-10** (entry 7).

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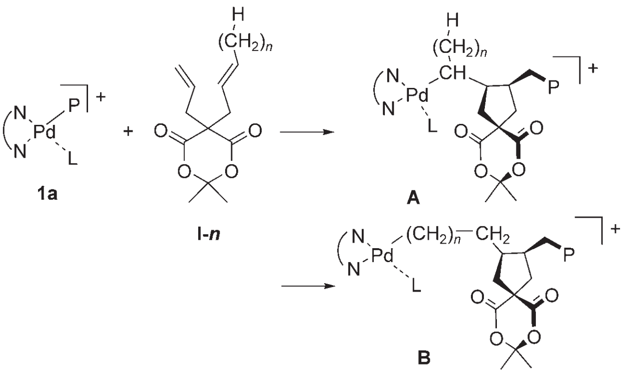
Table 1: Polymerization of 1,6-dienes by Pd complexes.[a]

Entry	Monomer[b]	Cat.	t [h]	Conv. [%][c]	M_n[d]	M_w/M_n[d]
1	**I-1**	**1a**	24	quant.	7900	1.68
2	**I-2**	**1a**	24	quant.	13600	1.75
3	**I-3**	**1a**	24	quant.	12200	1.91
4	**I-4**	**1a**	48	47	10400	1.97
5	**I-5**	**1a**	48	20	10100	2.31
6	**I-6**	**1a**	48	27	11500	1.90
7	**I-10**	**1a**	48	35	6900	1.71
8	**I-2**	**1b**	48	67	1900	1.36
9	**II-1**	**1c**	24	34	18900	1.25
10	**III-1**	**1a**	48	38	10600	1.60
11	**IV-1**	**1d**	24	80	5500	2.23
12[e]	**V-1**	**1c**	40	quant.	19000	1.21

[a] Reaction conditions: Pd complex = 0.01 mmol, NaBARF = 0.012 mmol, [monomer]/[Pd] = 70, solvent = CH_2Cl_2 (0.5 mL), at RT. [b] Roman numeral refers to lower framework; Arabic numeral refers to number of CH_2 groups in upper chain (n). [c] Determined by ^1H NMR spectroscopy. [d] Determined by GC using $CHCl_3$ (entries 1–8, 10–12) or DMF (entry 9) as an eluent. [e] Reaction at −20 °C.

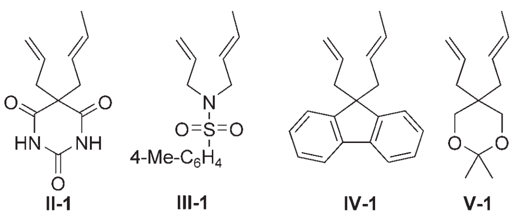


Scheme 1. Plausible mechanism for the polymerization of **I-*n***. P = polymer chain, L = solvent.

which indicates that the rings have an exclusive *trans*-1,2-disubstituted structure.[4,7]

Table 1 shows a summary of the results of the polymerization of the dienes that contain a longer alkyl group, $(CH_2)_nH$ ($n = 2$–6, 10), at one of the vinyl carbon atoms. The polymerization of **I-2** and **I-3** proceeded smoothly to give a polymer with molecular weights (M_n) of 13600 and 12200, respectively (Table 1, entries 2 and 3). The polymerization of **I-4**, **I-5**, **I-6**, and **I-10** for 48 h produces the corresponding polymers in 20–47 % yield (Table 1, entries 4–7), thus suggesting lower reactivities of the above dienes than **I-1**, **I-2**, and **I-3**. The ^{13}C NMR spectra of poly-**I-2**, poly-**I-4**, and poly-**I-10** are shown in Figure 2b–d. The signals from olefinic carbon atoms ($\delta = 115$–140 ppm) and methyl carbon atoms attached to a polymer chain ($\delta = 11$–20 ppm) are not observed. The ^1H NMR spectra of the polymers poly-**I-1** to poly-**I-10**, however, exhibit two small signals at $\delta = 5.2$–5.4 ppm and $\delta = 5.5$–5.7 ppm.[7] These signals may be assigned to the internal olefinic end group, and the relative intensities of the signals of the polymer-chain hydrogen atoms are consistent with the degree of polymerization estimated by GPC. The $^{13}C\{^1H\}$ NMR spectra of poly-**I-1** and poly-**I-2** exhibit two peaks for CH_2 (f_1, f_2) carbon atoms at almost equal intensities, which correspond to the racemo and meso diads of the neighboring five-membered rings. The use of **1b** with a C2-symmetric structure[4] increases the amount of racemo diad (isotactic) to 60 % (Table 1, entry 8).

Scheme 1 shows the polymer growth mechanism proposed on the basis of the polymerization of olefins catalyzed by Brookhart-type Ni and Pd complexes.[6] The insertion of the vinyl (-CH=CH$_2$) group of the monomer into the Pd–polymer bond, followed by the intramolecular insertion of the vinylene (-CH=CH-) group, yields a five-membered ring, similar to the cycloisomerization and cyclopolymerization of diallylmalonates.[4,8] The secondary alkyl–Pd intermediate **A** that is formed is isomerized into **B** with the primary alkyl ligand by chain walking.[6] The coordination/insertion reaction of another monomer molecule occurs after the isomerization. The Pd-catalyzed polymerization of 2-butene was reported to proceed by insertion and chain-straightening reactions to yield a polymer with a regulated structure.[9]



1,6-Octadienes with a barbituric acid group **II-1** and a sulfonamide group **III-1** at the respective 3-positions undergo polymerization catalyzed by **1c** or **1a** to afford a polymer with highly polar groups (Table 1, entries 9 and 10). A diene with a fluorenylidene group **IV-1** also polymerizes to form a polymer without polar substituents (Table 1, entry 11). The diene 5-allyl-5-crotyl-2,2-dimethyl-1,3-dioxane (**V-1**) undergoes living polymerization in the presence of **1c**/NaBArF$_4$ (Table 1, entry 12). Figure 3 shows linear plots of M_n values of the polymer against the conversion of the monomer. The re-addition of **V-1** after the first-stage polymerization ($M_n = 10800$, $M_w/M_n = 1.20$) brings about second-stage polymerization to afford a polymer with an increased molecular weight ($M_n = 22400$, $M_w/M_n = 1.24$).[10]

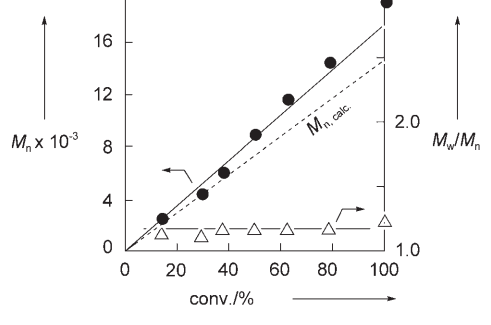


Figure 3. Relationship between the molecular weight of poly-**V-1** and the conversion of **V-1**.

Differential scanning calorimetry (DSC) measurements on the series of poly-**I** and poly-**V** polymers shows a change of the glass transition of these polymers that depends on the structures. The relationship between the glass transition temperature and the alkyl chain length are summarized in Figure 4. Increase of the alkyl chain length of the monomer lowers the glass transition temperature of both of the resulting polymers.

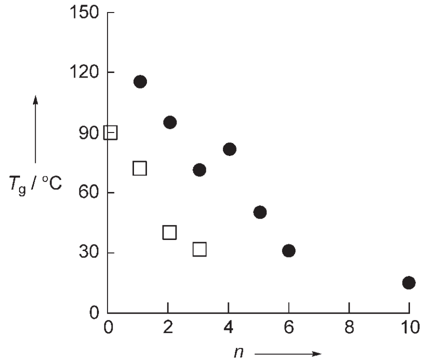


Figure 4. Relationship between the alkyl chain length (n) and glass transition temperature of poly-**I** (●) and poly-**V** (□).

In summary, the polymerization of 1,6-dienes catalyzed by Pd complexes affords polymers with *trans*-1,2-disubstituted five-membered rings. This provides a route for the introduction of the cyclic units and functional groups at regular intervals along a polymer chain.

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