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Palladium-Catalyzed Living/Controlled Vinyl Addition Polymerization of Cyclopropenes

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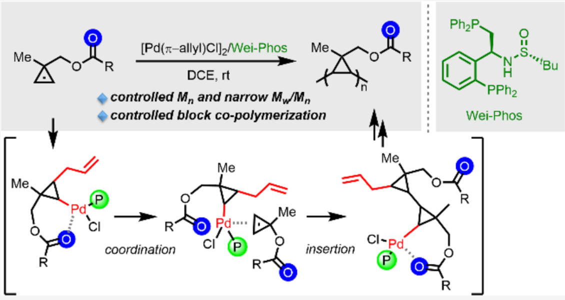

ABSTRACT: Despite the various utilities of cyclopropenes (CPEs) in organic synthesis and ring-opening metathesis polymerization (ROMP), their vinyl addition polymerization has been sporadically explored, and the corresponding living/controlled polymerization remains a formidable challenge. The major obstacle is the intrinsic instability of the intermediate and the kinetic barrier for propagation. Herein a living/controlled vinyl addition polymerization of 3-methyl-3-carboxymethyl CPEs, catalyzed by [Pd(π-allyl)Cl]$_2$ ligated by a sulfinamide bisphosphine ligand, is demonstrated. A plot of the number-average molecular weight (M_n) versus the conversion was found to be linear during the polymerization, with the molecular weight dispersity (M_w/M_n) remaining narrow. The M_n values increased linearly with the increase in the initial feed ratio of monomer to catalyst. Furthermore, controlled block copolymerization via sequential monomer addition was successful. All of these points corroborate the living nature of this polymerization. The synergistic coordination action of the catalyst ligand and the lateral carbonyl group in the cyclopropene moiety plays a key role in achieving the efficient polymerization in a living/controlled manner.

■ INTRODUCTION

Cyclopropenes (CPEs) are the smallest unsaturated hydrocarbon ring compounds. Owing to the extremely high ring strain (54.1 kcal/mol), CPEs exhibit diverse reactivities.[1,2] In particular, transition-metal-catalyzed reactions of CPEs have been extensively studied, and a series of highly efficient transformations have been established as useful tools in synthetic organic chemistry.[3−7] In addition to their applications in organic synthesis, transition-metal-catalyzed polymerization with CPEs has also been explored. As a unique type of monomers, CPEs can be polymerized under transition-metal catalysis through different mechanisms, affording polymers with distinct backbone structures. Most of the studies in this regard are focused on ring-opening metathesis polymerization (ROMP) with Schrock-type or Grubbs-type catalysts, leading to the formation of flexible unsaturated polymers.[8,9]

On the contrary, enduring efforts have been engaged in the vinyl addition polymerization of cyclic olefins, which lead to polymers with a saturated cyclic backbone structure.[10] The structural rigidity imparted by the saturated rings in these polymers affords beneficial physical properties, such as mechanical and thermal stability, a high glass-transition temperature, and a low dielectric constant. However, addition polymerizations of cyclic olefins are almost exclusively limited to norbornene and cyclopentene scaffolds,[11−13] with only a few examples of living polymerization.[14]

Although addition polymerization of CPEs with palladium catalyst was first explored in the 1970s, only cyclodimerized species or oligomeric (pallada)cycles were obtained.[15−17] In 1996, Risse and coworkers reported the polymerization of 3,3-dialkyl substituted CPEs with π-allyl-coordinated cationic Pd(II) catalysts, affording polycyclopropanes with high molecular weight (M_n = 42 000 g mol^{-1}) in an uncontrolled manner (M_w/M_n = 2.35).[18] They later reported a detailed study on this polymerization, in particular the macromolecular structure of the three-membered ring repeating units (Scheme 1a).[19] As far as our knowledge is concerned, this is the only successful example of the palladium-catalyzed vinyl addition polymerization of CPEs. Noteworthily, a Rh(I)-catalyzed vinyl polymerization of CPEs involving 1,4-Rh(I) migration has recently been reported by Shintani and Nozaki.[20]

On the contrary, polycyclopropanes have attracted attention for their unique structure and the corresponding properties. In particular, their applications in covalent polymer mechanochemistry have attracted considerable attention.[21−23] However, the synthetic methods for achieving main-chain cyclopropane polymers remain rare in the literature. So far, the postfunctionalization of polybutadiene has been the most widely practiced method.[24−26]

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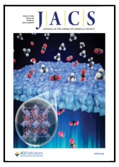
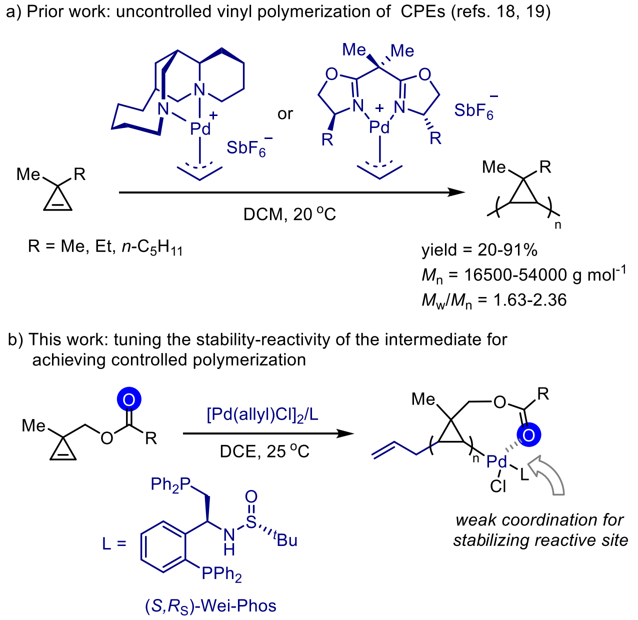


Scheme 1. Palladium(II)-Catalyzed Vinyl Addition Polymerization of CPEs



One of the major obstacles for achieving high molecular weight in the Pd(II)-catalyzed vinyl addition polymerization of CPEs is the stability and the reactivity of the cationic palladium active center, which may undergo protonation or ring-opening reactions, leading to chain transfer or termination. Previous studies by Risse and coworkers indicated that the chelating ligand of the Pd(II) catalyst and the substituents on CPEs could significantly affect the polymerization behavior of CPEs.[18,19] Recently, Xia and coworkers confirmed that the reactivity of CPEs in ROMP can be dramatically altered by tuning the substituents on CPEs.[9] In particular, 3-carboxymethyl CPEs show very interesting modes of reactivity as monomers in ROMP, presumably attributed to the chelation of the oxygen to the metal center that may affect the rate of propagation.[27]

We have conceived that a properly tethered carbonyl oxygen may tune the stability of the Pd(II) intermediate in the Pd(II)-catalyzed vinyl addition of CPEs, so that the polymerization may proceed in a controlled manner (Scheme 1b). Herein we report a vinyl addition polymerization of 3-methyl-3-carboxymethyl CPEs, catalyzed by $[Pd(\pi\text{-allyl})Cl]_2$ ligated by a bidentate sulfinamide bisphosphine ligand. The polymerization proceeds in a living/controlled manner, as demonstrated by the narrow dispersity and the formation of controlled block copolymers through the sequential addition of different monomers.

■ RESULTS AND DISCUSSION

Inspired by Xia and coworkers' work on living-ROMP with CPEs,[9,27] we prepared a series of 3-methyl-3-carboxymethyl CPEs **1**−**8** as the monomers in Pd(II)-catalyzed addition polymerization (Figure 1).

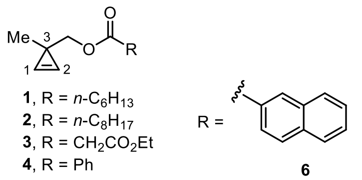


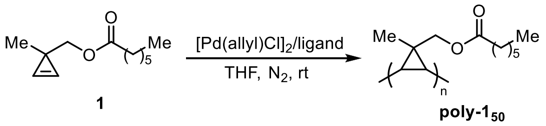
Figure 1. Structures of CPE monomers.

We began the study by using CPE **1** as the monomer. With $[Pd(allyl)Cl]_2$ as the Pd(II) source, we examined a series of phosphine ligands (Table 1). In the polymerization experiment, the phosphine ligand and $[Pd(allyl)Cl]_2$ were first dissolved in tetrahydrofuran (THF). The resultant solution was stirred at room temperature for 30 min, and it was used as the initiator for the polymerization. The polymerization was carried out in THF ($[\mathbf{1}]$ = 0.15 mol/L) at 25 °C. As a control experiment, the polymerization was first conducted using $[Pd(allyl)Cl]_2$ alone, without adding ligand. The monomer conversion was >99% in 12 min. Upon the completion of the reaction, the reaction solution was precipitated in methanol, and a polymer product was obtained in 52% yield with a M_n of 14 000 g mol^{-1} and a M_w/M_n value of 1.49, suggesting that $[Pd(allyl)Cl]_2$ is efficient in initializing the polymerization of **1** but with less controllability (entry 1). Subsequently, monodentate phosphine ligand PPh_3, PCy_3, and P^tBu_3 were introduced to the reaction (entries 2−4). With PPh_3 as the ligand, the reaction became very slow (entry 2). When using PCy_3 or P^tBu_3 as the ligand, a slight decrease in M_w/M_n values could be observed, presumably due to the increase in the steric bulk of the ligand that could prevent termination and chain-transfer events.[19] Reducing the ratio of P^tBu_3 to $[Pd(allyl)Cl]_2$ from 2 to 1 markedly increased the yield and molecular weight, and M_w/M_n was further decreased (compare entries 4 and 5). The M_n (11 600 g mol^{-1}) was close to the theoretical value (9800 g mol^{-1}), indicating the controllable trend of the polymerization (entry 5).

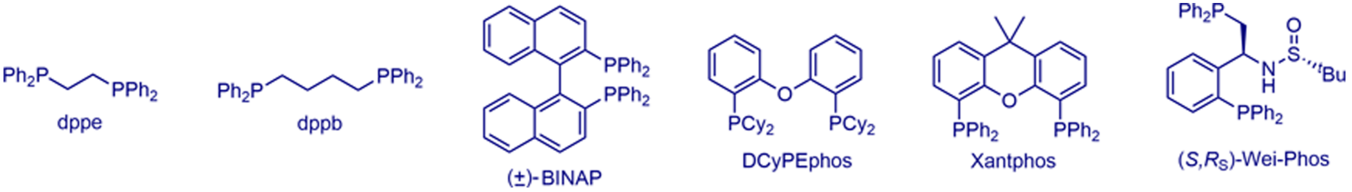
Furthermore, bidentate phosphine ligands dppe, dppb, BINAP, DCyPEphos, and Xantphos were examined (entries 6−10). An interesting comparison is between dppe and dppb (entries 6 and 7). With dppb, the reaction was much slower, suggesting that the polymerization is significantly affected by the bite angle of the ligand. The deference of the reaction rates between DCyPEphos and Xantphos may be attributed to the rigidity of the ligand (entries 9 and 10). A general tendency, in which the M_w/M_n values decreases with the increases in the rigidity and bulk of the bidentate phosphine ligand, could be observed. Thus we further applied (S,R_S)-Wei-Phos,[28] a bulky chiral bidentate phosphine ligand bearing a sulfinamide moiety, in this polymerization. Gratifyingly, the catalyst system of $[Pd(allyl)Cl]_2$/(S,R_S)-Wei-Phos gave **poly-1₅₀** with a M_w/M_n of 1.13. The M_n of 10 600 g mol^{-1} is close to the theoretical value (9800 g mol^{-1}), suggesting that approximately each Pd(II) catalyst initializes a polymer chain, and the initiation should be a highly efficient process (entry 11).

The polymerization of CPE **1** using Pd(II)/(S,R_S)-Wei-Phos ($[\mathbf{1}]_0/[Pd(II)]_0$ 50:1) was also conducted in various organic solvents (Table S1 in the Supporting Information). These results showed that the polymerization could be smoothly performed at room temperature in various solvents, including 1,2-dichloroethane (DCE), toluene, chloroform, dichloromethane, 1,4-dioxane, and chlorobenzene. In these solvents, all of the resultant polymers exhibited M_w/M_n values below 1.20 and M_n values close to the theoretical value, whereas the reaction in DCE afforded the optimal results in terms of the molecular weight and yield. Notably, the reactions in n-hexane and MeCN afforded **poly-1₅₀** with M_n of 16 100 and 27 300 g mol^{-1}, respectively, largely exceeding the theoretical value

Table 1. Pd(II)-Catalyzed Polymerization of 1: Effect of Catalyst Ligands[a]



entry	ligand[b]	t (h)	conversion (%)[c]	M_n (g mol^{-1})[d]	M_w/M_n[d]	yield (%)[e]
1	none	0.2	>99	14000	1.49	52
2	PPh_3	22	38	7100	1.89	20
3	PCy_3	0.3	>99	17400	1.35	72
4	P^tBu_3	0.5	>99	8600	1.32	38
5	P^tBu_3	0.5	>99	11600	1.27	63
6	dppe	0.3	>99	9800	1.44	49
7	dppb	24	75	10100	1.70	54
8	(±)-BINAP	0.3	>99	6900	1.39	46
9	DCyPEphos	8	98	11800	1.55	61
10	Xantphos	0.3	99	13800	1.24	59
11	(S,R_S)-Wei-Phos	0.16	>99	10600	1.13	45



[a] Polymerizations were carried out in THF at 25 °C, $[\mathbf{1}]_0$ = 0.15 mol/L. The initial feed ratio of monomer to catalyst is 50:1 in all cases. [b] For entries 2−4, the feed ratio of phosphine ligand to $[(\pi\text{-allyl})PdCl]_2$ is 2. For entries 5−11, the ratio is 1. [c] Conversion was analyzed by ^1H NMR spectra. [d] M_n and M_w/M_n were determined by size-exclusion chromatography (SEC) against a polystyrene standard. [e] Isolated yield after precipitated in methanol.

(9800 g mol^{-1}). The M_w/M_n values for these two reactions are 1.23 and 2.03, respectively. The results indicate that the differences in the solubility and the coordination behavior of these solvents significantly affect the initiation and chain propagation of the polymerization process. Next, the effect of the reaction temperature was examined with DCE as the solvent. The reaction temperature showed only a marginal effect on the M_n and M_w/M_n, whereas the reaction time was largely prolonged at low temperature (80 °C, <10 min, conv. = >99%, M_n = 9800, M_w/M_n = 1.27, yield = 62%; −20 °C, 960 min, conv. = 99%, M_n = 8400, M_w/M_n = 1.14, yield = 46%). (For details, see Table S2 in the Supporting Information.) Moreover, all of the reactions could be performed without inert gas atmosphere protection, indicating that the living center of Pd(II) is sufficiently robust in promoting the chain growth in the propagation process.

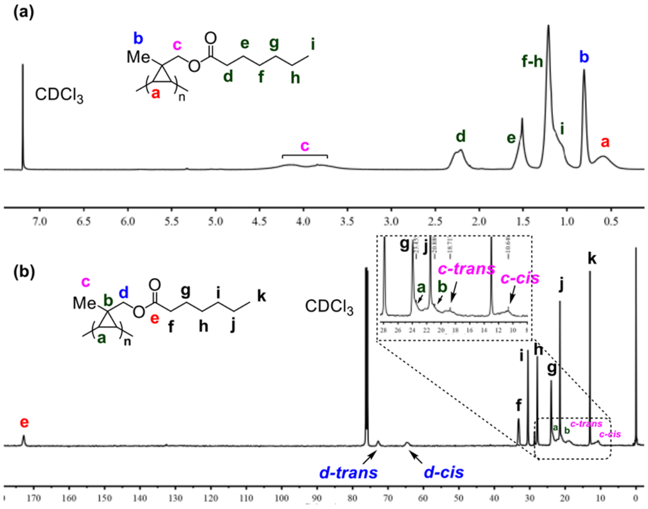


Figure 2. (a) ^1H NMR (500 MHz) and (b) ^{13}C NMR (126 MHz) spectra of **poly-1₅₀**.

The structure of **poly-1₅₀** was characterized by ^1H and ^{13}C NMR spectroscopy (Figure 2). The ^1H NMR spectrum of **poly-1₅₀** exhibits signals of the cyclopropane backbone [δ 0.66 (br, 2H)], whereas the vinyl protons [δ 7.28 (d, 2H)] of CPE **1** have all disappeared. No olefinic proton peaks can be observed in the ^1H NMR spectra of the **poly-1₅₀**, confirming that the polymerization proceeds through vinyl addition with the retention of the three-membered ring in the polymer backbone. The broad peak [δ 1.15 (br, 3H)] and the other sharper peaks in the region below 2.5 ppm represent the methyl substituent and the n-hexyl moiety on the side chain of the cyclopropane. The two broad peaks between 4.6 and 3.4 ppm belong to the methylene connected to the acyloxy group. The difference in the chemical shifts of the methylene protons indicates that the methylene groups are located in different chemical environments. In ^{13}C NMR spectra, the distinguishable broad peaks at 72.8 and 64.6 ppm are assigned to the protons of methylene connected to the acyloxy group. The similar broad peaks near 18.9 and 10.7 ppm are assigned to the methyl group on the cyclopropane unit and the n-hexyl group, respectively. Other signals are assigned to the two carbons of the cyclopropane backbone, n-hexyl carbons, and the ester carbonyl group. Compared with the ^{13}C NMR spectra data reported by Risse,[19] we assume that the polymer structure of **poly-1₅₀** has similar 1,2-cis-linked triangular repeating units. Notably, the substantial chemical shift difference of Δδ >8 for the two methyl carbons (δ 10.6 and δ 18.9) of the cyclopropane units of **poly-1₅₀** indicates the differentiated chemical environment for the methyl groups pointing to

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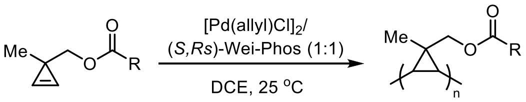
Table 2. Polymerization of CPEs with Pd(II)/(*S*,R_S)-Wei-Phos[a]



1-8 **polys-1-8**

entry	CPE	$[M]_0/[Pd(II)]_0$[b]	*t* (h)	M_n (g mol^{-1})[c]	M_w/M_n[c]	yield (%)[d]
1	**1**	200	9	38000	1.27	68
2	**1**	250	9	45000	1.28	80
3	**1**	300	9	51000	1.34	88
4	**1**	500	16	67000	1.39	83
5	**1**	1000	16	103000	1.62	81
6	**2**	50	2	12100	1.17	60
7	**2**	100	2	19300	1.19	64
8	**2**	150	2	29600	1.23	74
9	**3**	50	9	7700	1.23	53
10	**3**	100	9	14100	1.16	73
11	**3**	150	9	21800	1.14	78
12	**4**	50	12	9300	1.25	78
13	**4**	100	12	15400	1.26	74
14	**4**	150	12	22600	1.30	80
15	**4**	200	9	28000	1.37	84
16	**4**	250	9	30000	1.33	89
17	**4**	300	9	35000	1.26	90
18	**5**	50	9	12500	1.15	82
19	**5**	100	9	16600	1.33	70
20	**5**	150	9	24800	1.33	80
21	**6**	50	12	8100	1.24	89
22	**6**	100	12	13500	1.25	78
23	**6**	150	12	20600	1.26	88
24	**7**	50	9	7500	1.25	70
25	**7**	100	9	13900	1.22	89
26	**7**	150	9	21000	1.23	84
27	**8**	50	9	7100	1.25	80
28	**8**	100	9	12900	1.22	85
29	**8**	150	9	20800	1.27	74

[a] Polymerizations were carried out in DCE at 25 °C ([**1**] = 0.15 mol/L). [b] Initial feed ratio of monomer to catalyst. The TLC check showed full conversion of the monomer in all cases. [c] M_n and M_w/M_n were determined by SEC against a polystyrene standard. [d] Isolated yield after precipitated from methanol.

different directions. The assignment of the ^{1}H NMR and ^{13}C NMR spectra was further confirmed by ^{1}H−^{1}H COSY and ^{1}H−^{13}C HSQC NMR spectroscopy and FT-IR analyses (Figures S7−S9 in the Supporting Information).

The polymerization with CPE monomers **1**−**8** shown in Figure 1 was then conducted with the Pd(II)/(*S*,R_S)-Wei-Phos catalyst system in DCE at 25 °C. The polymerization for each of the monomers was conducted with different loadings of the catalyst. All of the reactions were run to full conversion, and the corresponding polymer products could be isolated in reasonably good yields through the precipitation in methanol (Table 2). The M_w/M_n values were in the range of 1.14 to 1.62, whereas the experimental M_n values were, in general, close to the corresponding theoretical values. In most cases, the experimental values were smaller than the theoretical values. This might be attributed to some unidentified side reactions of CPE monomers under the polymerization conditions, which would consume the monomers to some extent. It is noteworthy that for monomer **1**, the polymerization with $[M]_0/[Pd(II)]_0 = 1000$ also proceeded smoothly, affording **poly-1$_{1000}$** with M_n of >1 × 10^5 g mol^{-1}. The structures of **poly-2**−**8** were confirmed by ^{1}H NMR (Figures S10, S13, S16, S21, S24, S27, and S30 in the Supporting Information). In all of the cases, the resultant polymers showed good solubility in common organic solvents (THF, $CHCl_3$, CH_2Cl_2, toluene). The thermal properties of **poly-1**−**8** were characterized by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). TGA data confirmed the excellent thermal stability with decomposition temperatures generally above 220 °C, which is attributed to the rigid main-chain structure. The resultant polymers were all amorphous, and DSC thermograms revealed that their glass-transition temperatures (T_g) ranged from −20 to 124 °C. In addition, the resultant polymer also exhibited a narrow molecular weight distribution when initialized by the catalyst system of $[Pd(allyl)Cl]_2$ with (±)Wei-Phos (Table S4 and Figure S1 in the Supporting Information)

Furthermore, the relationship of the initial feed ratios of the monomer to the catalyst was studied in detail with CPE **1** and **4** (Figure 3 and Table S3 in the Supporting Information). Thus, for the polymerization of **1**, $[\mathbf{1}]_0/[Pd(II)]_0$ was varied from 25 to 150. As shown in Figure 3a, the molecular weight of **poly-1** products shifted to a higher region with the increase in the monomer-to-catalyst ratio, whereas all of the **poly-1**

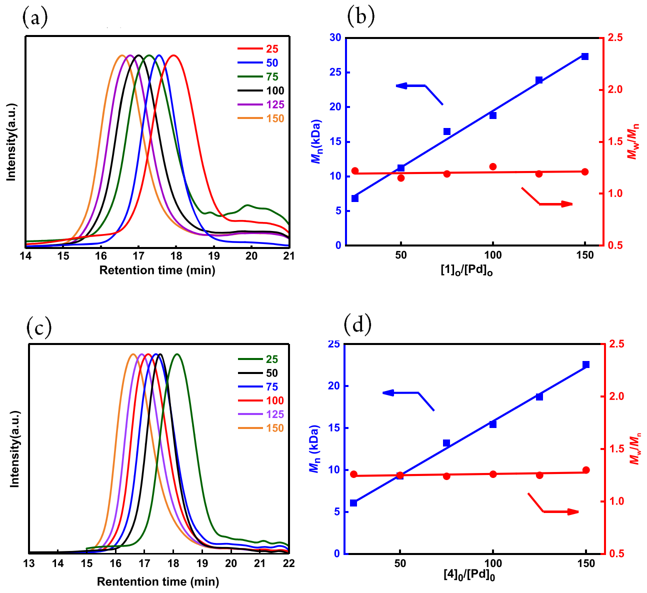


Figure 3. (a) SEC chromatograms of **poly-1** obtained using different initial feed ratios of monomer to catalyst. (b) Plots of the M_n and M_w/M_n values of **poly-1** as a function of the initial feed ratios of **1** to Pd(II)/(S,R_S)-Wei-Phos. (c) SEC chromatograms of **poly-4** obtained using different initial feed ratios of monomer to catalyst. (d) Plots of the M_n and M_w/M_n values of **poly-4** as a function of the initial feed ratios of **4** to the Pd(II)/(S,R_S)-Wei-Phos.

products retained monomodal elution peaks with narrow molecular weight distributions. The controlled nature of the polymerization could be verified by the linear relationship of molecular weight and $[\mathbf{1}]_0/[\mathrm{Pd(II)}]_0$, along with the narrow M_w/M_n values between 1.15 and 1.26 (Figure 3b). Under the same conditions, the polymerization of CPE **4**, which bears methyl benzoate groups, also showed good controllability, as we observed a linear increase in M_n up to 22 600 g mol^{-1} for a $[\mathrm{M}]_0/[\mathrm{Pd(II)}]_0$ of 150 and M_w/M_n 1.30 (Figure 3c,d and Table S3 in the Supporting Information). The structure of **poly-4** was also confirmed by ^{1}H NMR, ^{13}C NMR, ^{1}H−^{1}H COSY NMR, ^{1}H−^{13}C HSQC NMR, and FT-IR (Figures S16−S20 in the Supporting Information).

Next, we proceeded to study the kinetics of the polymerization by using CPE **1** as the monomer. We performed a trace experiment using ^{1}H NMR spectroscopy for the polymerization of CPE **1** with the Pd(II) catalytic system ($[\mathbf{1}]_0$ = 0.15 mol/L, $[\mathbf{1}]_0/[\mathrm{Pd(II)}]_0$ = 50:1) in DCE (Scheme S7 in the Supporting Information). The M_n of the resultant polymer shifted to a higher region with the increased conversion ratio of the monomer (Figure 4a). We observed a linear relationship between M_n and monomer conversion by monitoring the polymerization of CPE **1**, and dispersity values remained ~1.20 (Figure 4b). When the negative logarithm of the $[\mathrm{M}]/[\mathrm{M}]_0$ of the monomer was plotted against time, a linear relationship was obtained, as shown in Figure 4c, which indicated that the propagation followed first-order kinetics (Figure 4d). The slope of this linear plot provided the apparent rate constant of propagation, $k_p^{app} = 8.6 \times 10^{-3}$ s^{-1}, indicating a slow propagation process in the polymerization.

In the kinetic experiment, we observed that >90% of the monomer was consumed within 9 min, suggesting that the Pd(II)/(S,R_S)-Wei-Phos catalyst was highly effective and the polymerization was faster relative to the previously reported polymerization of CPE monomers with other Pd(II) initiators.[18,19] The initiation was too fast to be characterized by the trace experiment using ^{1}H NMR spectra because 17% conversion of the monomer had been reached within 30 s before the first aliquot was measured. The fast initiation rate of this Pd(II) catalyst system suggests that the presence of an appropriate phosphine ligand not only stabilize the Pd(II) species during the propagation but also enhances the activity of the Pd(II) catalyst, thus leading to a controlled/living polymerization process.

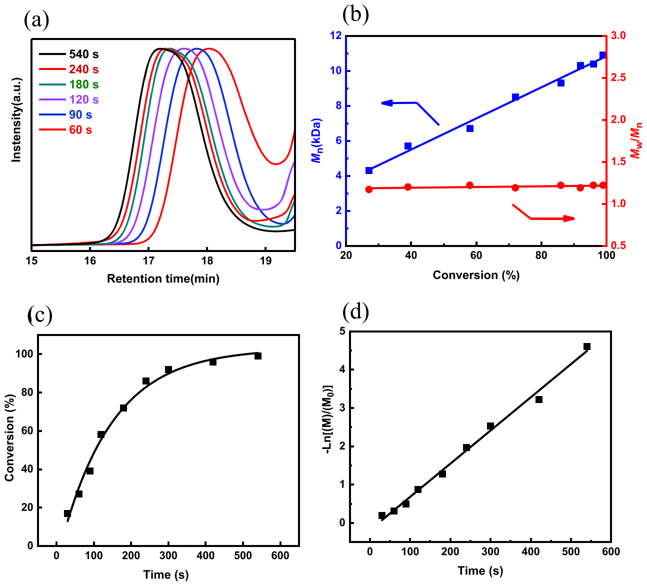
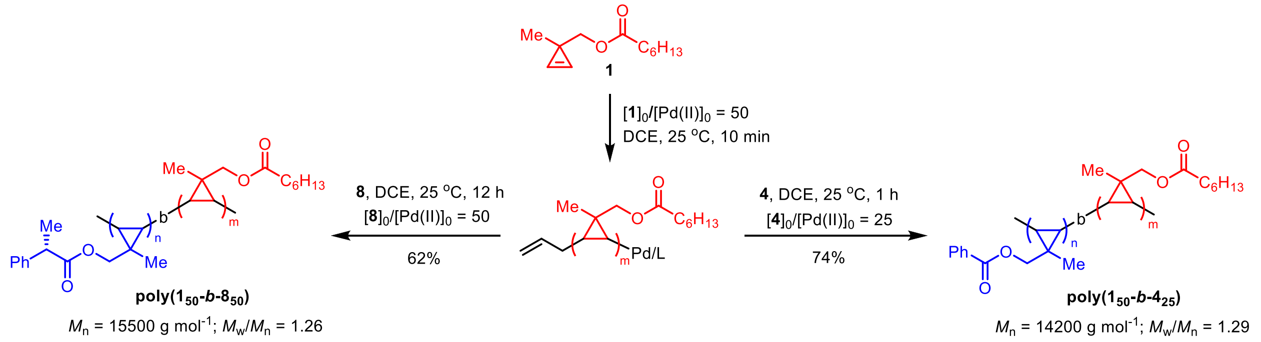


Figure 4. (a) Time-dependent SEC chromatograms for the polymerization of CPE **1** initiated by Pd(II)/(S,R_S)-Wei-Phos. (b) Plots of M_n and M_w/M_n values as a function of the CPE **1** conversion. (c) Plot of the conversion of CPE **1** versus time. (d) Plot of $-\ln[\mathrm{M}]/[\mathrm{M}]_0$ versus time.

Furthermore, diblock copolymerization could be obtained by the sequential addition of CPE monomer **1** and monomer **4** ($[\mathbf{1}]/[\mathbf{4}]/[\mathrm{Pd(II)}]$ 50:25:1) (Scheme 2). Size-exclusion chromatography traces showed the sharp shift from the first block of **poly-1** to a higher M_n while maintaining a narrow M_w/M_n of 1.29, confirming the chain-end fidelity of this polymerization system (Figure 5a). The formation of the expected diblock copolymer **poly(1_{50}-*b*-4_{25})** was also supported by the integrations of their respective ^{1}H NMR spectra (Figure 5b). Furthermore, **poly(1_{50}-*b*-8_{50})** could also be similarly obtained with a narrow M_w/M_n of 1.26. These results further confirm the living/controlled nature of this polymerization system.

To gain insights into the mechanism of this polymerization, in particular, the influence of the monomer structure and the catalyst on the polymerization behavior, we performed a series of control experiments (Scheme 3). First, we conducted the polymerization catalyzed by Pd(II)/(S,R_S)-Wei-Phos using various CPE monomers under identical conditions. When the methyl substituent of the CPE monomer is retained and the carboxymethyl substituent was replaced by an alkyl substituent (**9**), alkoxymethyl substituent (**10**), or carboxylate substituent (**11**), the polymerization also proceeded effectively, affording the corresponding polymers with high M_n but relatively broad M_w/M_n. In the case of **9** and **10**, the lack of coordination between the palladium center and the monomer substituent can be taken into consideration, which may lead to less control in the polymerization. The reaction with CPE monomer **11**

Scheme 2. Block Copolymerization Experiments



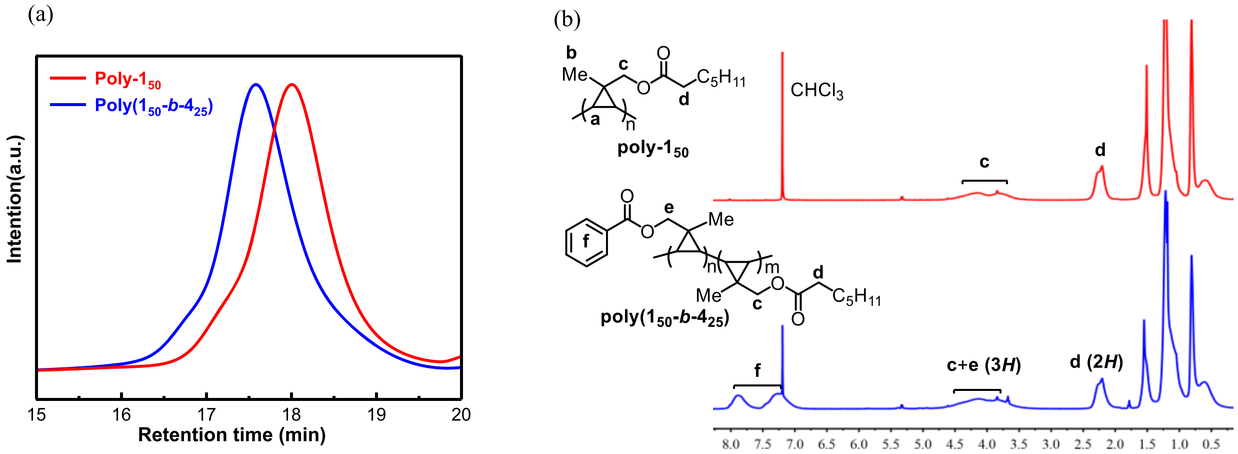
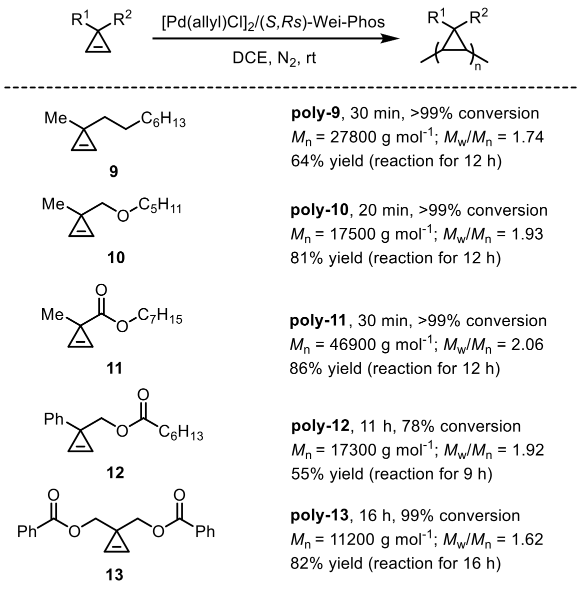


Figure 5. (a) SEC traces of chain extension reactions for **poly-1_{50}** and **poly(1_{50}-*b*-4_{25})**. (b) ^{1}H NMR (500 MHz) spectra of **poly-1_{50}** and **poly(1_{50}-*b*-4_{25})**.

Scheme 3. Effect of CPE Monomer Structure on the Polymerization[a]

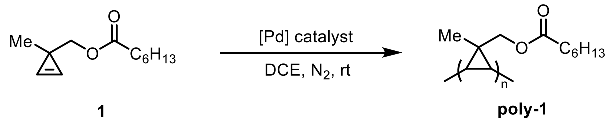


[a] Reaction conditions: $[M]_0$ = 0.15 mol/L; $[M]_0/[Pd(II)]_0$ = 50; $[Pd(allyl)Cl]_2$/(*S*,R_S)-Wei-Phos = 1. The M_n and M_w/M_n values were determined by SEC. The yields refer to the isolated polymers after precipitation in methanol.

gave **poly-11** with M_n of 46 900 and M_w/M_n of 2.06. Notably, Xia and coworkers have previously reported that an electron-withdrawing ester substituent markedly influences the coordination and reactivity of the double bond in the CPE monomer with a ruthenium catalyst, as observed in ROMP.[29] For **11**, the observed different polymerization behaviors may be ascribed to weaker coordination due to steric reasons, resulting in uncontrollable reactivity. For the related vinyl addition polymerization with norbornene derivatives, it has also been shown that the coordination of the carbonyl oxygen of the suitably located ester moiety to the palladium center alters the polymerization activity.[30−33]

On the contrary, replacing the methyl substituent on the CPE monomer with phenyl (**12**) or benzoxy substituents (**13**) also led to a broad molecular weight distribution. In the case of **12**, the electronic effects of the substituent on the C=C bond of CPE are relatively small, whereas the steric hindrance of the substituent may hamper the coordination of **12** with the palladium center, leading to slow initiation and propagation. Circumstantial evidence for this reasoning includes that fact that only a broad peak can be observed at 4.65 ppm in the ^{1}H NMR spectra of **poly-12**, in contrast with **poly-1**, where two broad peaks between 3.4 and 4.6 ppm could be observed (Figure S4a in the Supporting Information). A plausible interpretation is that in the case of **12**, the propagation selectively proceeds through the insertion from the less hindered face. For CPE monomer **13**, the large M_w/M_n value may be attributed to the relatively strong interaction and steric hindrance of the coordinating substituents on the palladium

Table 3. Effect of Pd(II) Catalyst on the Polymerization[a]



entry	[Pd] catalyst[b]	cocatalyst[c]	M_n (g mol^{-1})[d]	M_w/M_n[d]	yield (%)[e]
1	$[Pd(allyl)OAc]_2$	none	16100	1.41	64
2	$[Pd(allyl)OAc]_2$/L	none	29600	1.73	51
3	$[Pd(1\text{-cinnamyl})Cl]_2$/L	none	11600	1.16	75
4	$[Pd(1\text{-methylallyl})Cl]_2$/L	none	13300	1.19	60
5	$[Pd(allyl)Cl]_2$/L	AgOTf	11000	1.82	49
6	$[Pd(allyl)Cl]_2$/L	$NaBPh_4$	7800	1.36	14
7	$[Pd(allyl)Cl]_2$/L	$AgSbF_4$	9800	1.35	79

[a]Reaction conditions: $[M]_0$ = 0.15 mol/L; $[M]_0/[Pd(II)]_0$ = 50. Reaction was carried out for 9 h. [b][Pd(II)]/ligand = 1; L = (*S*,*R*$_S$)-Wei-Phos. [c][Pd]/cocatalyst = 2. [d]M_n and M_w/M_n values were determined by SEC against a polystyrene standard. [e]Yields refer to the isolated polymers after precipitation from methanol.

center, leading to a slow initiation rate and uncontrollable chain propagation. We have noted that coordinating solvents, such as MeCN, similarly affect the polymerization of the Pd(II) system, giving a large M_w/M_n value (Table S1 in the Supporting Information).

The above experiments demonstrate the influence of the steric bulk and the coordinating capacity of the substituents on the vinyl addition polymerization of CPEs. It is reasonable to conclude that the polymerization controllability in the case of CPEs **1**−**8** should be the result of the synergistic interaction of a weak coordinating carboxymethyl group and the methyl group, which has a suitable steric bulk (Figure S4b in the Supporting Information).

Next, we studied the effect of the palladium catalyst on the polymerization, as shown in Table 3. First, we observed that replacing the counteranion Cl^- with AcO^- led to a broader molecular weight distribution, either with or without the ligand (*S*,*R*$_S$)-Wei-Phos (entries 1 and 2). Second, replacing the allyl ligand in the $[Pd(allyl)Cl]_2$ precursor with butenyl ligand ($[Pd(1\text{-methylallyl})Cl]_2$) or cinnamyl ligand ($[Pd(1\text{-cinnamyl})Cl]_2$) was found to not affect the polymerization, affording the corresponding polymer with similar M_w/M_n values and slightly increased molecular weight (entries 3 and 4). We also studied the effect of the cocatalyst (AgOTf, $NaBAr_4$, $AgSbF_6$). These cocatalyst did not improve the polymerization, giving larger M_w/M_n values or low efficiency (entries 5−7). Thus we speculate that the weakly interacting anionic ligand Cl^- remains associated with the palladium(II) center during the coordination−insertion process, whereas the allyl ligand functions as a migratory group in the initiation step.

To substantiate this hypothesis, we analyzed the α-end group of the polymer by ^1H NMR (Figure 6). Thus CPE **4** was taken as the monomer and reacted with three catalyst precursor ($[Pd(allyl)Cl]_2$, $[Pd(1\text{-methylallyl})Cl]_2$, and $[Pd(1\text{-(cinnamyl)})Cl]_2$) using the (*S*,*R*$_S$)-Wei-Phos ligand with an initial monomer to Pd(II) catalyst feed ratio of 10:1. As expected, the ^1H NMR spectra of the resultant polymer products were clearly distinguished by the olefinic hydrogen chemical shifts of the terminal group resonance in the ^1H NMR spectra at 5.76 ppm (H^a) in **poly-4a**, 5.38 ppm (H^b) in **poly-4b**, and 6.2 ppm (H^c) in **poly-4c** (in $CDCl_3$). In addition, the two broad peaks at the chemical shift around 2.0 ppm refer to the H^d of the methylene group of the polymer.[34−36] For the polymerization with CPE **1** or **2** as the monomer, similar results were obtained in the analysis of the starting group of the resultant polymer (Figures S2 and S3 in the Supporting Information). These results are consistent with the previous observations for the cationic (allyl)Pd(II)-catalyzed vinyl addition polymerization of NB.[37,38]

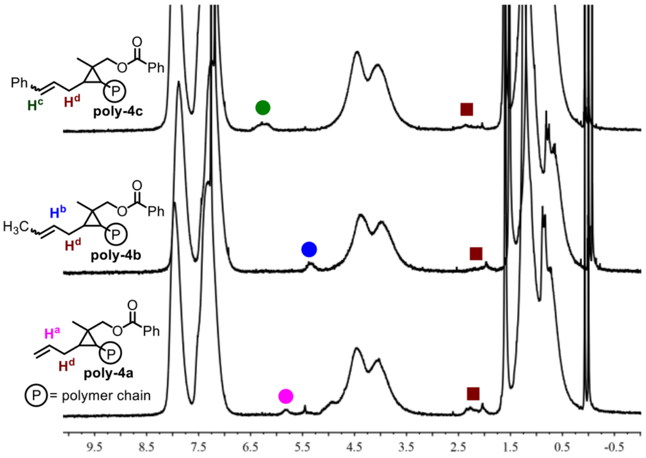
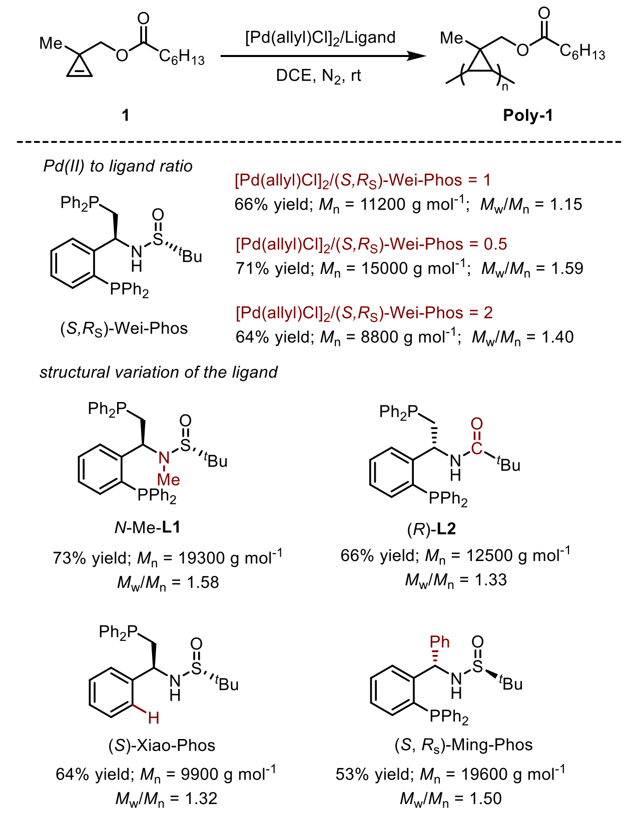


Figure 6. Analysis of the starting group of the **poly-4**$_{10}$ with ^1H NMR (500 MHz).

We then examined the influence of the ligand on the polymerization, as summarized in Scheme 4. First, the ratio of $[Pd(\pi\text{-allyl})Cl]_2$/(*S*,*R*$_S$)-Wei-Phos was found to affect the reaction, with the Pd(II) to ligand ratio of **1** affording the narrowest molecular weight distribution. It was thus assumed that the catalytic center of each active chain is composed of two palladium atoms and one ligand. However, the identity of the Pd catalyst in promoting the polymerization remains unclear. It was observed that the M_n significantly increased with a wider M_w/M_n for the ligand *N*-Me-**L1**, in which N−H was replaced by *N*-Me in the sulfinamide moiety. This suggests that hydrogen bonding may play a role in stabilizing the intermediate. The reaction was less affected when the S═O of the sulfinamide moiety was replaced by C═O, as shown in the ligand of (*R*)-**L2**. With the ligands (*S*)-Xiao-Phos and (*R*)-Ming-Phos, the polymerization led to relatively wider M_w/M_n values for both, but the effect of (*R*)-Ming-Phos was more substantial. These results suggest that the alkyl diarylphosphine moiety in the ligand may play a vital role in stabilizing and tuning the reactive intermediate.

Scheme 4. Effects of the Ligands on the Polymerization[a]



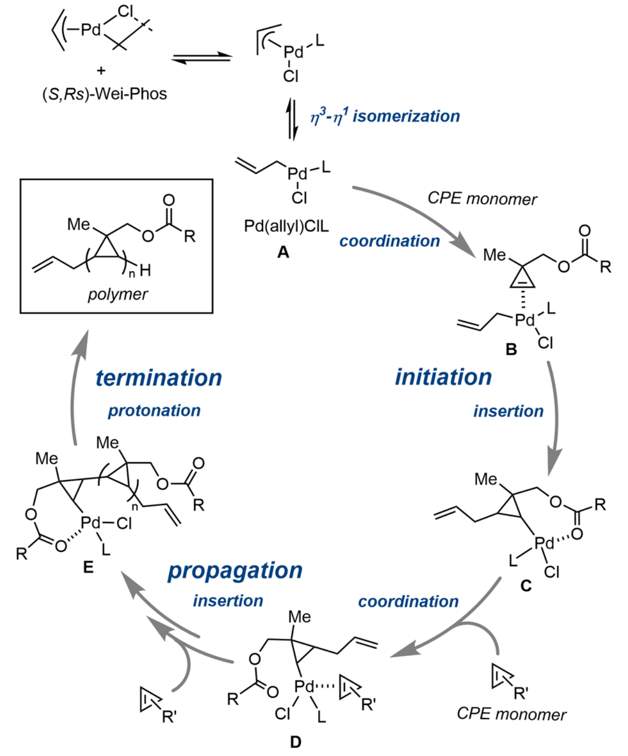
[a]Reaction conditions: $[M]_0$ = 0.15 mol/L; $[M]_0/[Pd(II)]_0$ = 50. If not otherwise noted, [Pd(II)]/ligand = 1. The M_n and M_w/M_n values were determined by SEC against a polystyrene standard. The yields refer to the isolated polymers after precipitation in methanol.

On the basis of the available information, a plausible reaction mechanism is proposed, as shown in Schemes 5. In the initiation step, a highly active species **A** is formed from the precatalyst $[Pd(allyl)Cl]_2$ through coordination with (S,R_S)-Wei-Phos and $\eta^3-\eta^1$ isomerization. In this process, the side arm of the ligand probably facilitates and stabilizes the generation of species **A**. Subsequently, coordination of the C═C bond of the CPE monomer occurs to form palladium complex **B** followed by allyl migratory insertion to form intermediate **C**, which is stabilized by the weakly coordinated carbonyl oxygen group of the CPE monomer. In the propagation, the insertion of CPE monomers into Pd−C bonds is proposed to involve the T-shaped, three-coordinate palladium(II) intermediate bearing a vacant site.[19,20,37,38] We propose that the weakly coordinating carbonyl group plays a crucial role in stabilizing the reactive site, thus avoiding chain transfer or chain termination. Finally, the reactive site is protonated by added methanol or other quenchers, or it may reinitiate the polymerization process with other CPE monomers to generate a block copolymer.

CONCLUSIONS

In summary, we have demonstrated a living/controlled vinyl addition polymerization of CPEs by $[Pd(allyl)Cl]_2$/(S,R_S)-Wei-Phos. The palladium-catalyzed polymerization of CPEs produced the corresponding main-chain polymer bearing completely saturated and rigid three-membered ring moieties in good yields with controlled M_n and narrow M_w/M_n. The controllability of this polymerization system benefits from the synergistic action of the ligand and CPE monomers substituted by a carboxymethyl group, which enables fast initiation and slow propagation.

Scheme 5. Mechanism for the Polymerization



In the propagation, the insertion of Pd-allyl proceeds through a dynamic four-coordinate palladium(II) intermediate, in which the palladium center with a monodentate phosphine ligand is weakly coordinated by the carbonyl group of the ester substituent. The reactive site is thus stabilized, whereas the reactivity is still maintained to permit an efficient and controllable vinyl addition polymerization to proceed.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.1c09071.

Experimental procedures and spectral data for all new compounds (PDF)

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Notes

The authors declare no competing financial interest.

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