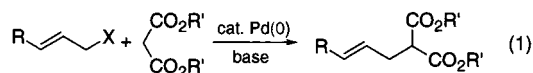# Palladium-Catalyzed Allylic Substitution Polymerization: Polycondensation of Carbon−Carbon Bond Formation by Linkage between Csp³ and Csp³ of Monomers
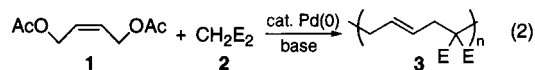
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The palladium-catalyzed allylic substitution reaction is a versatile carbon−carbon bond-forming process that proceeds under mild conditions (eq 1). Under the appropriate conditions,

$$R \diagup \diagdown X + \begin{matrix} CO_2R' \\ CO_2R' \end{matrix} \xrightarrow[\text{base}]{\text{cat. Pd(0)}} R \diagup \diagdown \diagup \begin{matrix} CO_2R' \\ CO_2R' \end{matrix} \quad (1)$$

very high regio- and stereoselectivities can also been achieved.[1] Nonetheless, no application of this reaction for polymer formation has been reported yet. In general, polymerization reactions that proceed via π-allylpalladium intermediates are rare.[2−5] Thus, the importance of developing a new polymerization reaction using this chemistry to form Csp³−Csp³ bonds is highlighted by the fact that most well-established C−C bond-forming polymerizations take advantage of the high reactivity of unsaturated carbons (Scheme 1).[6,7] In this Communication, we describe applications of the palladium-catalyzed allylic substitution reaction for a general polymerization reaction via polycondensation between bis-allylic monomers and malonate-type carbanions (eq 2).

$$AcO \diagup \diagdown \diagup OAc + CH_2E_2 \xrightarrow[\text{base}]{\text{cat. Pd(0)}} \left(\diagup \diagdown \diagup \diagdown \begin{matrix} \\ E \ E \end{matrix} \right)_n \quad (2)$$
$$\mathbf{1} \qquad \mathbf{2} \qquad\qquad \mathbf{3}$$

We examined polymerization between (*Z*)-1,4-diacetoxybut-2-ene (**1**) and diethyl malonate (**2a**, E = CO₂Et) in the presence of 1 mol % of Pd₂(dba)₃ (eq 2). After extensive scouting of reaction conditions, we found that the condensation polymerization was successful when 1,4-bis(diphenylphosphino)butane (dppb) was used as a ligand and *N,O*-bis(trimethylsilyl)acetamide

(1) Reviews: (a) Tsuji, T. *Palladium Reagents and Catalysts, Innovations in Organic Synthesis*; John Wiley: New York, 1995; p 290. (b) Godleski, S. A. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Semmel-hack, M. F., Eds.; Pergamon Press: Oxford, 1991; Vol 4, p 585. (c) Trost, B. M.; Van Vranken, D. L. *Chem. Rev.* **1996**, *96*, 395. (d) Frost, C. G.; Howarth, J.; Williams, J. M. J. *Tetrahedron: Asymmetry* **1992**, *3*, 1089. (e) Consiglio, G.; Waymouth, R. G. *Chem. Rev.* **1989**, *89*, 275.

(2) (a) Suzuki, M.; Sawada, S.; Saegusa, T. *Macromolecules* **1989**, *22*, 1505. (b) Suzuki, M.; Ii, A.; Saegusa, T. *Macromolecules* **1992**, *25*, 7071. (c) Suzuki, M.; Sawada, S.; Yoshida, S.; Eberhardt, A.; Saegusa, T. *Macromolecules* **1993**, *26*, 4748.

(3) (a) Bochmann, M.; Kelly, K. *J. Chem. Soc., Chem. Commun.* **1989**, 532. (b) Bochmann, M.; Kelly, K.; Lu, J. *J. Polym. Sci., Part A: Polym. Chem.* **1992**, *30*, 2511.

(4) (a) Miyaki, N.; Tomita, I.; Endo, T. *Macromolecules* **1996**, *29*, 6685. (b) Miyaki, N.; Tomita, I.; Endo, T. *J. Polym. Sci., Part A: Polym. Chem.* **1997**, *35*, 2097.

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

(6) (a) Parshall, G. W.; Ittel, S. D. *Homogeneous Catalysis*, 2nd ed.; John Wiley & Sons: New York, 1992. (b) *Catalysis in Precision Polymerization*; Kobayashi, S. Ed.; John Wiley & Sons: Chichester, 1997.

(7) For one of the rare examples of Csp³−Csp³ bond formation for polymerization, see: Boardman, F. H.; Grice, A. W.; Rüther, M. G.; Sheldon, T. J.; Bradley, D. D. C.; Burn, P. L. *Macromolecules* **1999**, *32*, 111. In organic synthesis, cross-couplings between Csp³ centers are also rare: Giovannini, R.; Stüdemann, T.; Devasagayaraj, A.; Dussin, G.; Knochel, P. *J. Org. Chem.* **1999**, *64*, 3544 and references cited therein.

Scheme 1. Representative Patterns of C−C Bond-Forming Polymerization
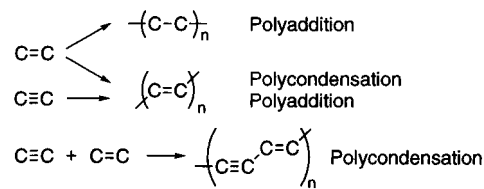
Scheme 2
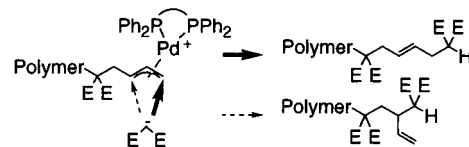
(BSA) as a base in CH₂Cl₂.[8] Polymerization at 25 °C was followed by ¹H NMR and SEC[9] analysis of the crude reaction mixture. This bis-acetate **1** was completely consumed after 7 h by ¹H NMR analysis, and M_n reached 19 000 after 96 h.[10] The regioselectivity of this reaction was exclusive, and no vinyl groups which could be formed via the internal attack of the allylpalladium complex by the malonate anion (Scheme 2) were detected by ¹H NMR. At the elevated temperature (40 °C), polymerization proceeded more effectively. The exclusive regioselectivity was retained, and M_n reached 21 800 after 11 h.[10] The ¹H NMR spectrum of the polymer suggested polymerization was terminated by a trace difference of molar ratio between **1** and **2a**, because the only acetyl group was detected as termini of the polymer chain. Although the stereochemistry of **3** was not confirmed, ¹³C NMR indicated high stereoregularity, and on mechanistic grounds an *E*-config-uration could be proposed for the double bonds of the polymer backbone.[3]

Table 1 illustrates the scope of the polymerization using various combinations of monomers. Each polymer was isolated in a good to excellent yield, and the polydispersity index (M_w/M_n) was generally around 1.5, except for entry 9. The substituted malonate **4** was not problematic for polymerization and afforded **5** with alternating unsaturated and saturated segments (entry 2). Sharing a double bond in two allylic moieties was not necessary (entries 3−8 and 10). Although the low regioselectivity of the cinnamyl-type substrate has been reported,[11] in our case high regioselectivity was observed in all cases (entries 3−6). Several nucleophiles were examined using **6**, and the present system of polymerization appeared to be general. The substrate **8**, which is a regioisomer of **6**, was also polymerized under the same conditions (entries 7 and 8). As we expected for this substrate, the α/γ-regioselectivity completely reversed to form the polymer with the same structure pattern as **7**. The stereochemistry of **7a**−**d** was unambiguously confirmed as *E*-configuration by the coupling constant of the olefin ($J = 15.8$ Hz) by ¹H NMR, and within the limits of detection ¹³C NMR also suggested that the selectivity was exclusive. In one of the most intriguing applications of this
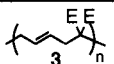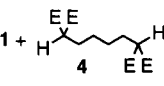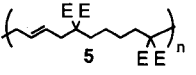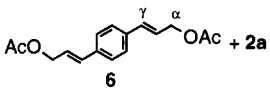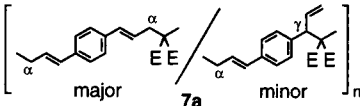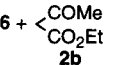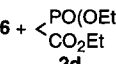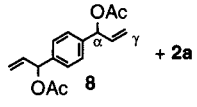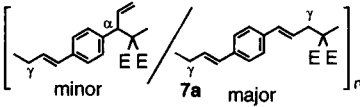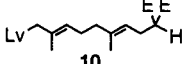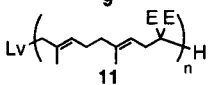
(8) We examined the following conditions: PPh₃, P(*o*-tolyl)₃, dppm (1,1-bis(diphenylphosphino)methane), dppe (1,2-bis(diphenylphosphino)ethane), dppp (1,3-bis(diphenylphosphino)propane), dppb, 2,2′-bipyridine, and dppf (1,1-bis(diphenylphosphino)ferrocene) as ligands, and CH₂Cl₂, C₆H₆, CH₂-ClCH₂Cl, CH₃CN, Et₂O, and THF as solvents. Although we examined other bases, such as CsCO₃, Et₃N, ᶦPr₂NEt, and EtO⁻ from the leaving group of EtOCO₂−, no or little polymerization occurred.

(9) Size exclusion chromatography (SEC) was performed in CHCl₃ at 40 °C (polystyrene standard).
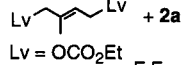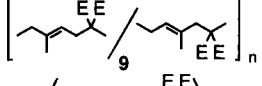
(10) See Supporting Information for experimental details.

(11) The palladium-catalyzed reaction of cinnamyl acetate with the sodium salt of methylmalononitrile gave a mixture of regioisomers ($\alpha/\gamma = 69/31$): Kadota, I.; Shibuya, A.; Gyoung, Y. S.; Yamamoto, Y. *J. Am. Chem. Soc.* **1998**, *120*, 10262.

Table 1. Palladium-Catalyzed Regioselective Allylic Substitution Polymerization[a]

Entry	Monomer(s)	Polymer	Yield,[b] %	Ratio,[c] α/γ	M_n,[d] x 10³	M_w/M_n[d]
1	1 + 2a (E = CO₂Et)	3	91	> 99/1[e]	21.8	1.51
2	1 + 4	5	82	> 99/1[e]	9.6	1.44
3[f]	6 + 2a	7a (major / minor)	93	94/6	9.9	1.41
4[f]	6 + 2b	7b	93	95/5	10.3	1.44
5[f]	6 + CH₂(COMe)₂ 2c	7c	99	94/6	9.9	1.45
6[f]	6 + 2d	7d	87	96/4	7.1	1.41
7[f]	8 + 2a	7a (minor / major)	97	8/92	10.3	1.42
8[f]	8 + 2b	7b	86	3/97	15.7	1.56
9[g]	10 (Lv = OCO₂Et) + 2a	9	83	> 99/1[e]	4.5	1.84
10[g]	10 (Lv = OCO₂Et, E = CO₂Et)	11	98	> 99/1[e]	7.6	1.46

[a] The reactions were carried out using each monomer (0.50 mmol) and BSA (3 mmol) in the presence of Pd₂(dba)₃ (0.005 mmol) and dppb (0.01 mmol) at 40 °C for 11 h in CH₂Cl₂ unless otherwise noted. [b] Isolated yield. [c] By ¹H NMR. [d] Estimated by SEC (CHCl₃, polystyrene standard). [e] No vinyl groups of γ-selectivity were detected by ¹H NMR. [f] Reaction conditions: 25 °C for 2 h and then 40 °C for 9 h. [g] Reaction conditions: 40 °C for 24 h.

polymerization, we examined the reaction of some allylic derivatives from natural sources.[12] The polymerization reactions were sluggish under the same conditions, probably because of steric hindrance at trisubstituted olefin in the initial oxidative addition to Pd(0). Changing the leaving group from AcO− to EtOCO₂− enhanced the reactivity on the substrates, and the polymerization proceeded with excellent regioselectivity (entries 9 and 10). Since the terpenes were not symmetrical, head-to-head, head-to-tail, and tail-to-tail couplings occurred at random in the two-component system (entry 9). The diester **10**, with an internal allylic carbonate, derived from geraniol was synthesized and polymerized. Exclusive α-regioselectivity and almost quantitative yield were obtained (entry 10). Very high *E,E*-configuration for the double bonds was suggested by ¹³C NMR.[13]

In conclusion, we have developed a palladium-catalyzed allylic substitution polymerization. The characteristics of the polymerization are as follows: (1) It offers a versatile method of C−C bond-forming polymerization by linkage between Csp³ and Csp³ of monomers, which had rarely been successful. (2) It takes advantage of carbon−carbon double bonds of monomers to form π-allylpalladium intermediates, with all double bonds retained in the polymer chain. (3) The polymerization system tolerates various functional groups, such as carbonyl and ether groups. (4) Readily available allylic alcohols of terpenes could be used as monomers, and this may be important for the development of new type of ecofriendly materials based on renewable natural resources.[12] Further studies directed toward the optimization of reaction conditions and the utilization of terpene-derived compounds for the polymer applications are currently under investigation.

(12) We have recently succeeded in the development of biodegradable polymers based on carbohydrate-derived materials: (a) Okada, M.; Okada, Y.; Aoi, K. *J. Polym. Sci., Part A: Polym. Chem.* **1995**, *33*, 2813. (b) Okada, M.; Okada, Y.; Tao, A.; Aoi, K. *J. Appl. Polym. Sci.* **1996**, *62*, 2257. (c) Okada, M.; Tachikawa, K.; Aoi, K. *J. Polym. Sci., Part A: Polym. Chem.* **1997**, *33*, 2813.

(13) The stereochemistry of methyl group at trisubstituted olefin could be assigned by ¹³C NMR. *cis*-CH₃ of the olefinic proton appears between 23 and 26 ppm, while *trans*-CH₃ does between 15 and 20 ppm: Kusumi, T.; Ohtani, I. In *NMR Chemical Shifts Shu*; Kodan-sha: Tokyo, 1993; p 12.

Supporting Information Available: Experimental details, spectroscopic data (¹H, ¹³C, IR) of each polymer in Table 1, and DSC charts of **3**, **5**, and **7a** for T_g and T_m (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.