Macromolecules **1996,** *29,* 6685−6690

Three-Component Coupling Polymerization of Bisallene, Aryl Dihalide, and Nucleophiles *via* π-Allylpalladium Complex

Nobuyuki Miyaki, Ikuyoshi Tomita, and Takeshi Endo*

Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226, Japan

Received March 31, 1995; Revised Manuscript Received June 17, 1996[⊗]

ABSTRACT: A novel palladium(0)-catalyzed three-component coupling polymerization of a bisallene (1,2,10,11-dodecatetraene, **1**), aryl dihalides (**2a**−**e**), and a nucleophile (sodium diethyl malonate, **3**) is described. By the reaction of **1**, 4,4′-diiodobiphenyl (**2a**), and **3** in the presence of a palladium catalyst in 1,4-dioxane at 80 °C for 2 days, a polymer (**4a**) was obtained in high yield (97%, $\bar{M}_n = 11\,100$). The structure of the resulting polymer (**4a**) was confirmed by ^{13}C-, ^{1}H-NMR, and IR spectra, from which the double bonds in the polymer backbone were detected quantitatively and were found to be mainly composed of *E*-isomer. The concentration of the palladium catalyst was found to affect the degree of polymerization. By using some aryl dihalides (**2b**−**e**), the corresponding polymers were also obtained in high yield.

Introduction

Allene derivatives are attractive candidates for the construction of reactive polymers bearing unsaturated systems by supplying either one part of the double bonds. However, little has been done concerning the polymerization of allene derivatives. Although polymerizations by means of radical[1] or ionic[2] catalysts are suitable for some allene derivatives bearing appropriate substituents, these methods are susceptible to the polymerization conditions as well as the substituents on the allene monomers.

For the synthesis of structurally well-defined polymers from various kinds of allene derivatives, it is necessary to construct polymerization methods by means of much selective intermediates. Allene derivatives can produce π-allylmetals by the olefin-insertion reaction toward some carbon-metal bonds. Recently, we have described a living coordination polymerization of alkoxyallenes using allylnickel catalysts, where the propagation reaction is composed of the successive insertion of allene moieties toward the allylnickel propagating end. In this coordination polymerization, the produced polymer contained double bonds (i.e., exo-methylenes) quantitatively.[3]

π-Allylmetal complexes play quite important roles in organic synthesis, especially for the coupling reactions with nucleophilic reagents.[4] Ahmar et al. and Tsuji et al. have successfully applied π-allylpalladium complexes generated from allene derivatives for the further coupling reactions with various nucleophilic reagents.[5] By the application of this coupling reaction to the polymer synthesis, a novel polycondensation may be developed in which three different monomer units can be incorporated at the same time. Within the authors' knowledge, such polymerizations have been limited to cases of palladium-catalyzed syntheses of polyesters and polyamides based on the carbonylative cross-coupling reactions.[6]

Herein, we would like to report a novel three-component coupling polymerization of a bifunctional allene (**1**), various aryl dihalides (**2a**−**e**), and a nucleophile (**3**) using a palladium catalyst (Scheme 1).

Experimental Section

Instruments. IR spectra were obtained on a JASCO FT/IR-5300 spectrophotometer. ^{1}H-NMR spectra were recorded in $CDCl_3$ on a JEOL JNM-EX90 (90 MHz) or a JEOL JNM-GX270 (270 MHz) instrument. ^{13}C-NMR spectra were recorded in $CDCl_3$ on a JEOL JNM-GX270 (67.5 MHz) instrument. Gel permeation chromatographic (GPC) analyses were carried out on a Tosoh HLC-8020 (TSK gel G5000HXL, G4000HXL, and G2500HXL; standard polystyrene samples; tetrahydrofuran as an eluent). GPC−low angle laser light scattering (LALLS) analysis was carried out on a Tosoh HLC-8020 (TSK gel G4000HXL, standard polystyrene samples, tetrahydrofuran as an eluent) and a Tosoh LS-8000 instrument. Gas chromatographic analyses were done on a Shimadzu GC-8A instrument. The inherent viscosity was measured by an Ostward viscometer in 1,4-dioxane solution (0.5 g/dL) at 30 °C.

Materials. Sodium diethyl malonate (**3**) was prepared from sodium hydride and diethyl malonate and was purified by washing successively with *n*-hexane. 1,2-Bis(diphenylphosphino)ethane (dppe) was purified by the recrystallization from methanol. 1,4-Dioxane and diethyl ether were dried over sodium metal and distilled under nitrogen. Methyl propargyl ether[7] was dried over calcium hydride and distilled under nitrogen. 4,4′-Dibromobiphenyl and 1,4-diiodobenzene were purified by recrystallization from methanol. 4,4′-Diiodobiphenyl was purified by recrystallization from toluene. Other reagents were used as received.

Synthesis of Monomers. 1,2,10,11-Dodecatetraene (1). **1** was prepared by modification of the reported procedure for the synthesis of *n*-butylallene.[7] To a mixture of 11.9 g (0.17 mol) of methyl propargyl ether, 30 mL of dry ether, and copper(I) bromide (0.25 g, 0.76 mmol) was added dropwise a solution of 1,6-hexyldimagnesium dibromide in 150 mL of ether (prepared from 0.13 mol of 1,6-dibromohexane) with vigorous stirring and efficient cooling, so that the temperature of the reaction mixture could be kept between 0 and −10 °C (the addition took 30 min). The cooling bath was then removed and a small amount of copper(I) bromide was added. After 30 min, the reaction mixture was poured into a mixture of 100 g of finely crushed ice, 10 g of ammonium chloride, and 20 mL of 36% hydrochloric acid. The aqueous layer was extracted with ether and the ethereal layer was dried over magnesium sulfate. After the evaporation of the solvent, the obtained oil was purified by SiO_2 column chromatography (*n*-hexane) followed by distillation (53−56 °C/3 mmHg) to yield 19% (0.24 mol, 3.9 g): ^{1}H-NMR (δ, ppm) 1.00−1.15 ($-CH_2-$, m, 8H), 1.70−2.20 ($C{=}CCH_2$, m, 4H), 4.35−4.71 ($C{=}C{=}CH_2$, m, 4H), 4.90−5.17 ($CH{=}C{=}C$, m, 2H); ^{13}C-NMR (δ, ppm) 28.2, 28.8, 29.1, 74.3, 90.0, 208.0; IR (neat) 2984, 2930, 1956, 1689, 1439, 1311, 841 cm^{-1}.

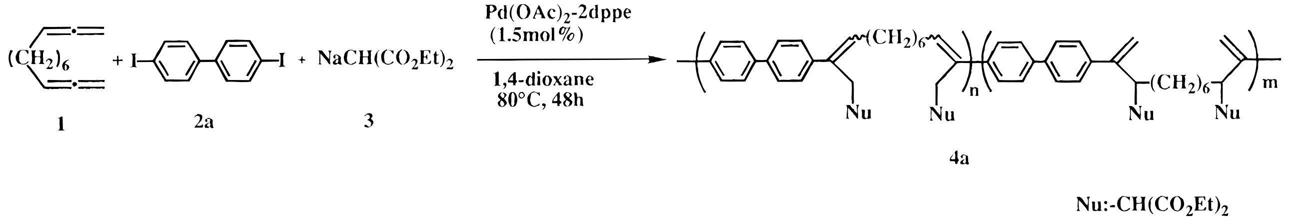
1,6-Bis(4-iodophenoxy)hexane (2d). To a mixture of acetone (100 mL), *p*-iodophenol (5.00 g, 22.7 mmol), and potassium carbonate (15.8 g, 114 mmol) was added 1,6-dibromohexane (2.44 g, 10.0 mmol), and the mixture was refluxed for 2 days. After evaporation of the solvent, water (100 mL) was added and the mixture was extracted with ether

---

[⊗] Abstract published in *Advance ACS Abstracts,* September 15, 1996.

S0024-9297(95)00443-8 CCC: $12.00

Scheme 1



and dried over magnesium sulfate. The crude product was purified by recrystallization from CH_2Cl_2/*n*-hexane to yield 60% (3.10 g, 6.00 mmol): mp 127−132 °C; ^{1}H-NMR (δ, ppm) 1.30−2.00 ($-CH_2-$, m, 8H), 3.92 ($-OCH_2-$, t, $J = 4.1$ Hz, 4H), 6.66 ($-C_6H_4-$, d, $J = 6.0$ Hz, 4H), 7.54 ($-C_6H_4-$, d, $J = 6.0$ Hz, 4H); ^{13}C-NMR (δ, ppm) 25.8, 29.1, 67.9, 82.5, 116.9, 138.2, 158.9; IR (KBr) 2938, 2863, 1583, 1572, 1487, 1474, 1397, 1304, 1285, 1248, 1181, 1119, 1103, 1073, 1022 cm^{-1}.

1,6-Bis((4-iodophenacyl)oxy)hexane (2e). In a one-necked flask equipped with a Stark−Dean apparatus, a mixture of *p*-iodobenzoic acid (5.2 g, 25 mmol), 1,6-hexanediol (1.2 g, 10 mmol), and *p*-tolueneslufonic acid monohydrate (0.38 g, 2.0 mmol) in 30 mL of toluene was refluxed for 2 days. The reaction mixture was precipitated with *n*-hexane and the precipitate was further purified by recrystallization from CH_2Cl_2/*n*-hexane to yield 30% (1.7 g, 3.0 mmol): mp 115−120 °C; ^{1}H-NMR (δ, ppm) 1.30−2.00 ($-CH_2-$, m, 8H), 4.32 ($-OCH_2-$, t, $J = 4.2$ Hz, 4H), 7.75 ($-C_6H_4-$, m, 8H); ^{13}C-NMR (δ, ppm) 25.7, 28.6, 65.1, 101, 130, 131, 138, 166; IR (KBr) 3090, 2948, 1715, 1583, 1462, 1389, 1306, 1267, 1175, 1119, 1003, 968, 756 cm^{-1}.

Model Reactions. Coupling Reaction of *n*-Butylallene, Iodobenzene, and 3.[5] To a test tube equipped with a magnetic stirrer chip were added iodobenzene (0.204 g, 1.00 mmol), **3** (0.398 g, 2.00 mmol), $Pd(OAc)_2$ (11.2 mg, 0.050 mmol, 5 mol %), dppe (40.0 mg, 0.10 mmol), and 1,4-dioxane (3 mL), and the mixture was kept stirring at ambient temperature for several minutes under nitrogen. To the resulting solution was added *n*-butylallene (97.0 mg, 1.00 mmol), and the reaction was carried out at 80 °C for 1 day. After evaporation of the solvent under the reduce pressure, the remaining material was dissolved in CH_2Cl_2 that was washed with water several times and dried over magnesium sulfate. After evaporation of the solvent, the products were purified by SiO_2 column chromatography (*n*-hexane/ethyl acetate = 3/1) to yield 75% of the mixture of *E*, *Z*, and *exo* isomers (0.25 g, 0.75 mmol): ^{1}H-NMR (δ, ppm) 0.9−1.50 (CH_3, $-CH_2-$, 17H), 2.15−2.30 ($C{=}CCH_2$, br, 2H), 3.15 ($-CH_2-$, d, 2H, $J = 6.7$ Hz), 3.33 ($-CH-$, t, 1H, $J = 6.7$ Hz), 4.00−4.17 ($-OCH_2-$, m, 4H), 5.06 ($C{=}CH_2$, s), 5.30 ($C{=}CH_2$, s), 5.55 ($-C{=}CH-$, t, $J = 7.3$ Hz), 5.73 ($-C{=}CH-$, t, $J = 7.3$ Hz), 7.27 (C_6H_5, 5H), *E*:*Z*:*exo* = 87:10:3; ^{13}C-NMR (δ, ppm) 14.0, 14.1, 22.5, 28.3, 28.9, 32.0, 50.7, 61.3, 126.7, 126.9, 128.2, 128.3, 128.7, 132.6, 136.0, 142.0, 169.1; IR (neat) 2959, 2926, 2854, 1736, 1464, 1369, 1228, 1198, 1154, 1036 cm^{-1}.

The controlled experiments for the detection of byproducts were carried out by using *n*-butylallene and 4-iodobenzene under similar conditions in the presence of *n*-decane as an internal standard. The reaction mixture was directly analyzed by GC. In the case of the reaction using iodobenzene, biphenyl was detected in 3% yield. By using 4-iodobiphenyl instead of iodobenzene, biphenyl was also detected as a reduced product in 1% yield.

Polymerizations. Coupling Polymerization of 1, 2a, and 3 (A Typical Procedure). To a test tube equipped with a magnetic stirrer chip were added **2a** (0.305 g, 0.75 mmol), **3** (0.540 g, 3.00 mmol), $Pd(OAc)_2$ (5.05 mg, 0.022 mmol, 1.5 mol %), dppe (0.0179 mg, 0.044 mmol, 3 mol %), and 1,4-dioxane (4.5 mL), and the mixture was kept stirring at ambient temperature for several minutes under nitrogen. To the resulting solution was added **1** (0.122 g, 0.75 mmol) and the test tube was sealed under reduced pressure. After reaction at 80 °C for 2 days, the reaction mixture was precipitated into methanol/water (v/v = 1/1). The obtained polymer was freeze-dried from benzene to give **4a** in 97% yield (0.46 g, 0.73 mmol): ^{1}H-NMR, see Figure 1; ^{13}C-NMR (δ, ppm) 14.3, 28.7, 29.5, 29.8, 50.8, 51.8, 61.3, 126.7, 126.8, 127.1, 132.6, 139.3, 139.4, 140.8; IR (neat) 3630, 3584, 3463, 3029, 2980, 2928, 2855, 1734, 1603, 1497, 1445, 1038 cm^{-1}. Anal. Calcd for $C_{38}H_{46}O_8$: C, 72.13; H, 7.59. Found: C, 70.28; H, 7.63.

The dependence of the molecular weight of the produced polymer on polymerization time was examined as follows: To a two-necked flask were added $Pd(OAc)_2$-2dppe (1.5 mol %), **2a** (0.305 g, 0.75 mmol), **3** (0.540 g, 3.0 mmol), and 1,4-dioxane (4.5 mL), and the mixture was stirred at ambient temperature for several minutes under nitrogen. Then, **1** (0.122 g, 0.75 mmol) was added to the mixture and the polymerization was carried out at 80 °C for 2 days. A small portion of the reaction mixture was sampled and reprecipitated into methanol/water (v/v = 1/1) after the designated reaction times (i.e., 3, 6, 12, 18, 24, 30, 36, 48, 54, and 60 h) and the molecular weight of the precipitated polymer was analyzed by GPC. Dependence of the feed ratio of **1**/**2a** on the molecular weight was also examined under similar conditions by varying the concentrations of **1** and **2a**. Amounts of **1** and **2a** used are summarized in Table 1. The effect of the amount of the palladium catalyst (Table 2) was examined under similar conditions by varying the concentration of the palladium catalyst.

Coupling Polymerizations of 1, Various Aryl Dihalides (2b−e), and 3. Polymerizations were carried out in a manner similar to the case of **2a**, as mentioned above.

4b: from **1** (0.122 g, 0.75 mmol), **2b** (0.247 g, 0.75 mmol), and **3** (0.54 g, 3.00 mmol); yield 93% (0.39 g, 0.70 mmol); ^{1}H-NMR (δ, ppm) 1.10−1.50 (CH_3, $-CH_2-$, 20H), 2.15−2.30 ($C{=}CCH_2$, br, 4H), 3.15 ($-CH_2-$, d, 4H, $J = 7.3$ Hz), 3.33 ($-CH-$, t, 2H, $J = 7.0$ Hz), 4.00−4.20 ($-OCH_2-$, m, 8H), 5.06 ($C{=}CH_2$, s), 5.32 ($C{=}CH_2$, s), 5.52 ($-C{=}CH-$, t, $J = 7.3$ Hz), 5.70 ($-C{=}CH-$, t, $J = 7.3$ Hz), 7.23 ($-C_6H_4-$, 4H), *E*:*Z*:*exo* = 87:10:3; ^{13}C-NMR (δ, ppm) 14.0, 14.1, 28.7, 28.8, 29.5, 29.9, 50.7, 61.3, 61.4, 126.6, 126.7, 128.3, 132.3, 135.5, 140.5, 169.1; IR (neat) 2930, 2857, 1743, 1458, 1370, 1035, 860 cm^{-1}.

4c: from **1** (0.122 g, 0.75 mmol), **2c** (0.392 g, 0.75 mmol), and **3** (0.54 g, 3.00 mmol); yield 92% (0.52 g, 0.69 mmol); ^{1}H-NMR (δ, ppm) 1.13−1.85 (CH_3, $-CH_2-$, 30H), 2.18−2.20 ($C{=}CCH_2$, br, 4H), 3.10 ($-CH_2-$, d, 4H, $J = 7.3$ Hz), 3.32 ($-CH-$, t, 2H, $J = 7.3$ Hz), 3.90−4.20 ($-OCH_2-$, m, 12H), 4.98 ($C{=}CH_2$, s), 5.25 ($C{=}CH_2$, s), 5.48 ($-C{=}CH-$, t, $J = 7.8$ Hz), 5.61 ($-C{=}CH-$, t, $J = 7.3$ Hz), 6.83 ($-C_6H_4-$, d, 4H, $J = 8.8$ Hz), 7.20 ($-C_6H_4-$, d, 4H, $J = 8.8$ Hz), *E*:*Z*:*exo* = 84:12:4; ^{13}C-NMR (δ, ppm) 14.0, 26.0, 28.6, 28.9, 29.3, 29.5, 29.9, 50.7, 61.3, 67.8, 114.2, 127.7, 128.3, 131.2, 134.2, 135.3, 158.2, 169.2; IR (neat) 3056, 2986, 2934, 1730, 1607, 1510, 1265, 737, 706 cm^{-1}.

4d: from **1** (0.122 g, 0.75 mmol), **2d** (0.234 g, 0.75 mmol), and **3** (0.54 g, 3.00 mmol); yield 100% (0.47 g, 0.75 mmol); ^{1}H-NMR (δ, ppm) 1.11−1.56 (CH_3, $-CH_2-$, 20H), 2.15−2.37 ($C{=}CCH_2$, br, 4H), 3.06−3.27 ($-CH_2-$, m, 4H), 3.28−3.41 ($-CH-$, m, 2H), 4.00−4.31 ($-OCH_2-$, m, 8H), 5.11 ($C{=}CH_2$, s), 5.40 ($C{=}CH_2$, s), 5.77 ($-C{=}CH-$ t, $J = 7.3$ Hz), 5.77 ($-C{=}CH-$, t, $J = 7.3$ Hz), 7.35−7.36 ($-C_6H_4-$, 4H), 7.52−7.55 ($-C_6H_4-$, 4H), *E*:*Z*:*exo* = 81:10:9; ^{13}C-NMR (δ, ppm) 14.3, 28.7, 29.5, 29.8, 50.8, 51.8, 61.3, 126.7, 126.8, 127.1, 132.6, 139.3, 139.4, 140.8; IR (neat) 3630, 3584, 3463, 3029, 2980, 2928, 2855, 1734, 1603, 1497, 1445, 1038 cm^{-1}.

4e: from **1** (0.122 g, 0.75 mmol), **2e** (0.423 g, 0.75 mmol), and **3** (0.54 g, 3.00 mmol); yield 88% (0.53 g, 0.66 mmol); ^{1}H-NMR (δ, ppm) 0.99−1.80 (CH_3, $-CH_2-$, 28H), 2.00−2.40 ($C{=}CCH_2$, 4H), 3.00−3.47 ($-CH_2-$, 6H), 3.90−4.49 ($-OCH_2-$, 12H), 4.98 ($C{=}CH_2$, s), 5.40 ($C{=}CH_2$, s), 5.60 ($-C{=}CH-$, m), 5.80 ($-C{=}CH-$, t, $J = 7.3$ Hz), 7.18−7.56 ($-C_6H_4-$, 4H), 7.94−

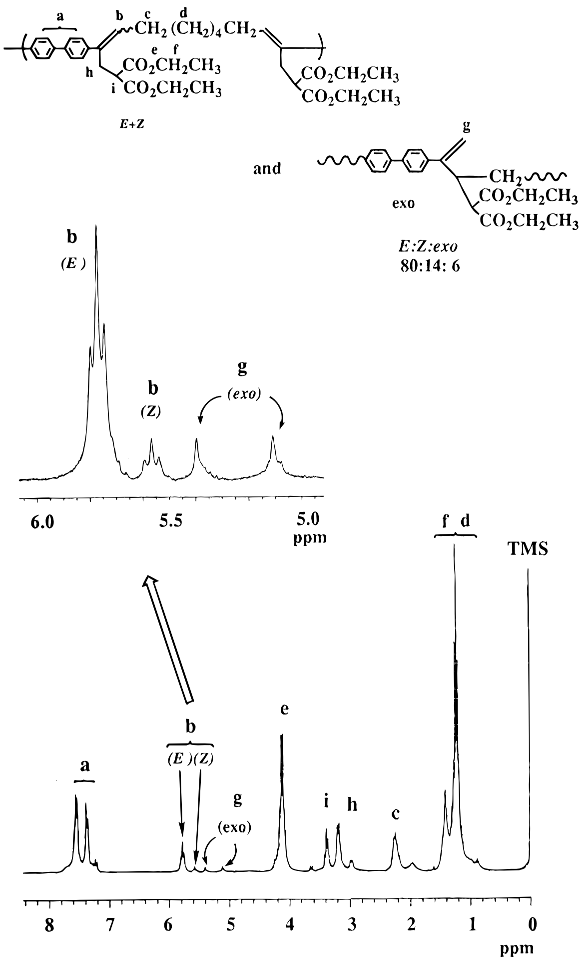


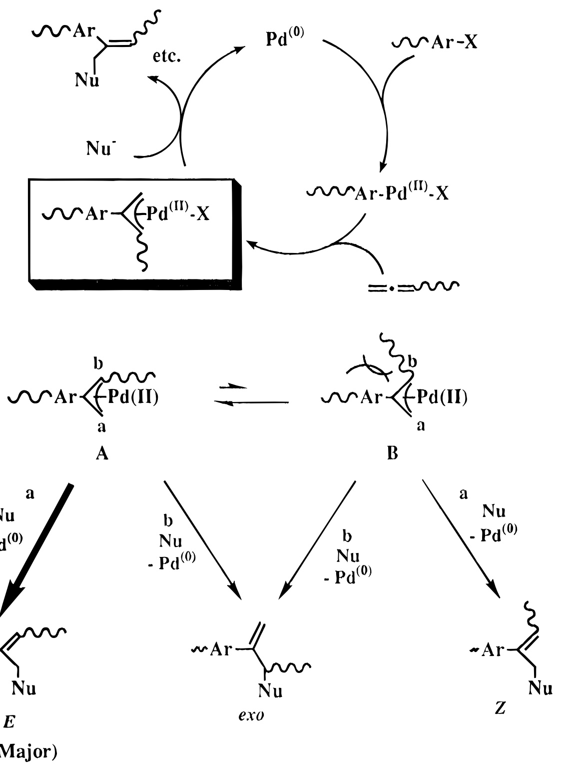
Figure 1. ^{1}H-NMR spectrum of **4a**.

8.07 (−C_6H_4−, 4H); IR (neat) 2980, 2932, 1732, 1464, 1275, 1181, 1105, 1020 cm^{-1}.

Results and Discussion

The polymerization was carried out at 80 °C for 2 days by using 1,2,10,11-dodecatetraene (**1**), 4,4′-diiodobiphenyl (**2a**), and sodium diethyl malonate (**3**) (1:1:4 molar ratio) in 1,4-dioxane in the presence of Pd(OAc)$_2$ (1.5 mol %) and 1,2-bis(diphenylphosphino)ethane (3 mol %, 2 equiv to Pd). After the reaction, a polymer (**4a**) was isolated by the precipitation with methanol/water (v/v = 1/1) as a yellow gum in almost quantitative yield (97%). The obtained polymer (**4a**) was soluble in common organic solvents such as CH_2Cl_2, THF, benzene, *N*,*N*-dimethylformamide, and dimethyl sulfoxide. The number average molecular weight ($\bar{M}_n$) of the polymer was estimated to be 11 100 from the GPC measurement. The inherent viscosity of a polymer fractionated by HPLC ($\bar{M}_n = 23\,000$ in GPC) was determined to be 0.97 dL/g. Low angle laser light scattering (LALLS) measurement of the sample ($\bar{M}_w = 53\,600$ in GPC) estimated the $\bar{M}_w$ to be 106 100. For the structural elucidation of **4a**, a model reaction was carried out with *n*-butylallene, iodobenzene, and **3** (in the molar ratio of 1:1:2) as described by Ahmer et al.[5a] In this case, products were isolated in 75% yield as a mixture of *E*-, *Z*-, and *exo*-isomers. From the ^{1}H-NMR spectrum of these isomeric mixtures, specific peaks for *E*- (5.73), *Z*- (5.55), and *exo*-isomers (5.30, 5.06 ppm) were observed[8] (Figure 1). On the basis of the integral ratios of these peaks, the isomeric ratios were determined as *E*:*Z*:*exo* = 82:11:7. From the ^{1}H-NMR spectrum of the obtained polymer (**4a**), the protons of the double bonds in the polymer were observed at 5.10−5.85 ppm, from which three units (*E*-, *Z*-, and *exo*-units) could be attributed, similar to the model compounds. The *E*:*Z*:*exo* ratio in the polymer was estimated as 80:14:6, in good agreement with that obtained from the model experiment. Clearly, the double bonds in the obtained polymer were detected quantitatively by the comparison of the intensities of these peaks and all the other peaks.[9]

Scheme 2



On the basis of the reported mechanism for palladium-catalyzed coupling reactions,[5] the present polymerization can be supposed to proceed as shown in Scheme 2. The arylpalladium(II) halide generated by the oxidative addition of aryl halide with Pd(0)[10] undertakes allene insertion. The resulting π-allylpalladium(II) complex is attacked by the nucleophile at the three different positions to give three different components accompanied by the regeneration of the palladium(0) species. The π-allylpalladium intermediate may have a conformational equilibrium between **A** and **B**. The equilibrium should favor comformer **A** rather than **B** because of the steric repulsion of substituents on α- and β-positions (i.e., the main chain of the polymer). The attack of the nucleophile at terminal carbon (**a**), may give rise to *E*- and *Z*-units from comformers **A** and **B**, respectively. The predominant formation of *E*-unit can be explained by the above mentioned equilibrium. Similarly, the attack at the substituted carbon (**b**) may produce *exo*-units both from **A** and **B**, although the steric hindrance may not favor the attack at this position.

Effect of the Concentration of Monomers. Under similar polymerization conditions, the molecular weight of the polymer was monitored by GPC after the designated reaction time (Figure 2), and the number average molecular weight ($\bar{M}_n$) was found to increase gradually, as is usual for step-growth polymerization, and reached 15 000, after reaction for 54 h.

As expected, the molecular weight of the polymer was effected by the feed ratio of **2a**/**1** and the highest

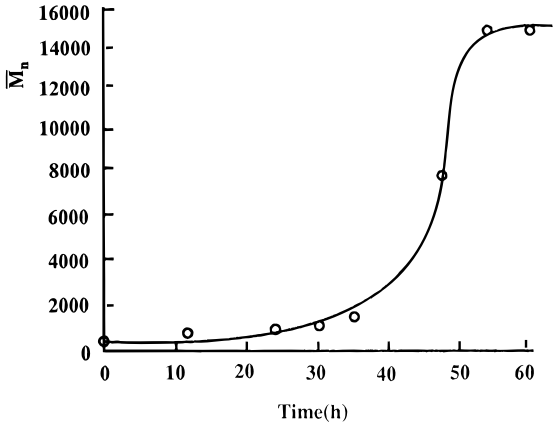


Figure 2. Time vs $\bar{M}_n$ in the coupling polymerization of **1**, **2a**, and **3** (1.5 mol % Pd cat.).

Table 1. Effect of Stoichiometry of Monomers[a]

run	amount, g **1** (mmol)	 **2a** (mmol))	[**1**]/[**2a**] ratio	% yield[b]	$\bar{M}_n$ ($\bar{M}_w/\bar{M}_n$)[c]
1	0.084 (0.52)	0.305 (0.75)	0.69	89	2900 (2.01)
2	0.103 (0.63)	0.305 (0.75)	0.84	96	4500 (2.19)
3	0.122 (0.75)	0.305 (0.75)	1.00	100	11000 (2.02)
4	0.136 (0.84)	0.305 (0.75)	1.12	100	10000 (2.82)
5	0.156 (0.96)	0.305 (0.75)	1.28	100	5900 (2.02)

[a] Reaction conditions: Pd(OAc)$_2$-2dppe, 1.5 mol % vs **2a**; NaCH(CO$_2$Et)$_2$, 3 mmol in 4.5 mL of 1,4-dioxane at 80 °C for 2 days. [b] Insoluble in methanol/water (v/v = 1/1). [c] Estimated by GPC (THF, PSt std).

Table 2. Effect of the Concentration of Palladium Catalyst[a]

run	Pd cat., mol %[b]	% yield[c]	$\bar{M}_n$ ($\bar{M}_w/\bar{M}_n$)[d]
1	0.5	46	1300 (1.2)
2	1.5	97	11100 (3.8)
3	2.5	100	8600 (3.3)
4	3.5	95	8400 (2.5)
5	5	100	6100 (2.0)
6	10	100	3300 (1.5)

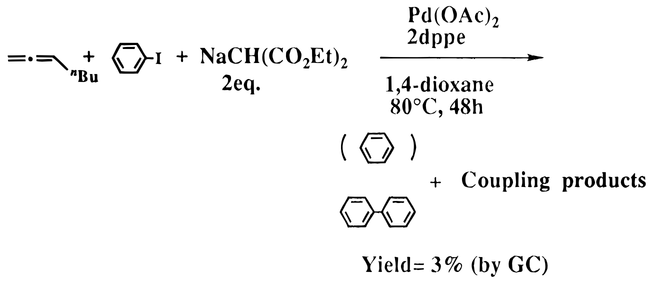
[a] Reaction conditions: **1**, 0.75 mmol; **2a**, 0.75 mmol; NaCH(CO$_2$Et)$_2$, 3 mmol in 4.5 mL of 1,4-dioxane at 80 °C for 2 days. [b] Pd(OAc)$_2$-2dppe. [c] Insoluble in methanol/water (v/v = 1/1). [d] Estimated by GPC (THF, PSt std).

molecular weight was obtained when the polymerization was carried out with a stoichiometric amount of **1** and **2a** (Table 1). According to the amount of the nucleophile **3**, the molecular weight of the resulting polymer was not effected when more than 2 equiv of **3** was used for the reaction. This result may indicate that the nucleophile does not attack the arylpalladium complex but the π-allylpalladium complex.

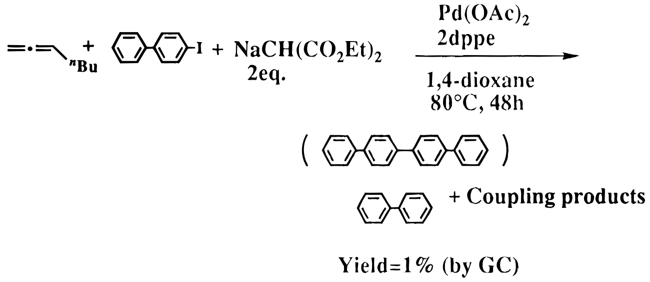
Effect of the Concentration of the Catalyst. Interestingly, the concentration of the palladium catalyst was found to effect the molecular weight of the polymer (Table 2). Though the amount of catalyst should effect the rate of polymerization, it may not affect the degree of polymerization. However, a considerable decrease of the molecular weight was observed when the concentration of palladium catalyst was increased (runs 2−6).[11] These results may indicate that some side reactions caused by the palladium catalyst may take place during the polymerization.

Perry et al. have described two side reactions in the carbonylative coupling reaction[12] (i.e., reduction of aryl halides and homocoupling of aryl halides). In order to clarify similar possibilities in the present system, the following model reactions were carried out. When the reaction of iodobenzene, *n*-butylallene, and **3** was carried out for 2 days under the conditions similar to the polymerization, biphenyl (i.e., homocoupling product of aryl halide) was detected in 3% yield by GC besides the main products (Scheme 3). By using 4-iodobiphenyl instead of iodobenzene under the same conditions, biphenyl (i.e., the reduced products of aryl halide) was detected in 1% yield by GC (Scheme 4).[13] It is well-known that arylpalladium intermediates react with various nucleophiles.[14] In the present system, however, this type of reaction did not take place. In fact, the reaction using iodobenzene and **3** without *n*-butylallene did not produce phenyl diethyl malonate (Scheme 5). The absence of this side reaction is most probably the reason for the independence of the amount of **3** upon the degree of polymerization (*vide supra*). As described in the polymerization using the Suzuki coupling reaction,[15] phosphine ligands on arylpalladium might react with the aryl moieties to form an aryl phosphonium salt that would bring about the termination. From the direct observation of the ^{31}P-NMR spectrum of the reaction mixture obtained under the same condition outlined in Table 2, run 5 (i.e., the polymerization using 5 mol % of palladium catalyst), a peak was observed at 25.4 ppm that cannot be attributed to the catalyst system nor the free ligand. The relative intensity of this peak was ca. 10% of all the observed peaks. A phosphonium salt independently prepared from triphenylphosphine and 1,2-dibromoethane showed a peak at 24.9 ppm in the ^{31}P-NMR spectrum which is very close to the peak observed in the polymerization mixture.

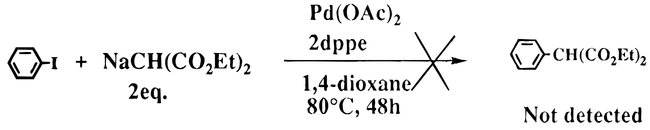
Scheme 3



Scheme 4



Scheme 5



From the experiments mentioned above, side reactions (reduction, homocoupling, and phosphonium formation) are found to exist in the present coupling polymerization (Scheme 6).

Polymerization with Various Aryl Dihalides. Polymerizations of **1** and **3** were carried out with various aryl dihalides (**2a**−**e**) in the presence of Pd(OAc)$_2$-2dppe

Scheme 6

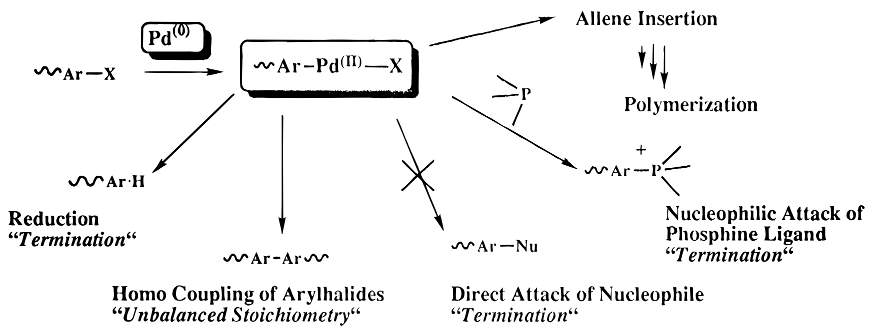
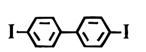
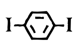
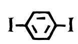
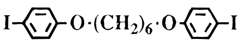
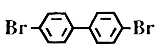
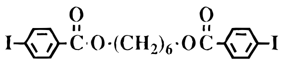


Table 3. Coupling Polymerizations of 1 and 3 with Various Aryl Dihalides (2a–e)[a]

Run	X-Ar-X		Time(days)	Yield(%)[b]	$\overline{M}_n$ ($\overline{M}_w/\overline{M}_n$)[c]	*E* :*Z* :*exo*[d]
1		(2a)	2	100	11100(3.8)	80:14: 6
2		(2b)	2	87	2400(1.3)	89: 8: 3
3			4	93	10000(3.1)	87:10: 3
4		(2c)	2	92	8300 (3.3)	84:12: 4
5		(2d)	2	99	13700(3.9)	81:10: 9
6		(2e)	7	88 [e]	1700(1.4)	——

[a] Reaction conditions: **1**, 0.75 mmol; **2**, 0.75 mmol; Pd(OAc)$_2$-2dppe, 1.5 mol %; NaCH(CO$_2$Et)$_2$, 3 mmol in 4.5 mL of 1,4-dioxane at 80 °C. [b] Insoluble in methanol/water (v/v = 1/1). [c] Estimated by GPC (THF, PSt std). [d] Determined by ^{1}H-NMR. [e] Without precipitation.

(1.5 mol %) (Table 3). In place of **2a**, 4,4′-dibromobiphenyl (**2d**) also produced a polymer (**4d**) having a structure identical to **4a**. The molecular weight of **4d** was almost the same as that of **4a** prepared from a diiodide (**2a**). The result can be explained by the fact that the oxidative addition in Scheme 2 is generally a fast step in this kind of coupling reaction when aryl bromides or aryl iodides were used.[16] A polymer (**4c**, $\overline{M}_n$ = 8000) was obtained quantitatively from an aryl halide (**2c**) connected with the ether group after the reaction for 2 days. In the case of 1,4-diiodobenzene (**2b**), the polymerization required much longer reaction time in comparison with that for **2a**. In fact, the polymerization of **2b** for 2 days resulted in the formation of oligomers ($\overline{M}_n$ = 2400), while the molecular weight increased ($\overline{M}_n$ = 10 000) after the longer reaction time (4 days). From model reactions with various *p*-substituted aryl halides under the polymerization conditions, aryl iodides bearing electron-donating groups were consumed faster than those bearing electron-withdrawing groups (Figure 3).[17] Thus, the first aryl iodide moiety in **2b** (i.e., *p*-iodophenyl moieties) is expected to be less reactive than the second one (i.e., *p*-vinylphenyl moieties) for the coupling reaction. In the case of an aryl diiodide linked by ester moieties (**2e**), the polymerization took place much slower and $\overline{M}_n$ of the resulting polymer (**4e**) did not increase even after reacting for 7 days. The slower polymerization can be explained similarly. That is, both aryl iodide moieties in **2e** are less reactive for the coupling reaction because of the ester substituent.

Regardless of the aryl halide used, all the polymers were found to contain double bonds quantitatively that were mainly composed of *E*-units (>80%) accompanied by *Z*-units and *exo*-methylene units.

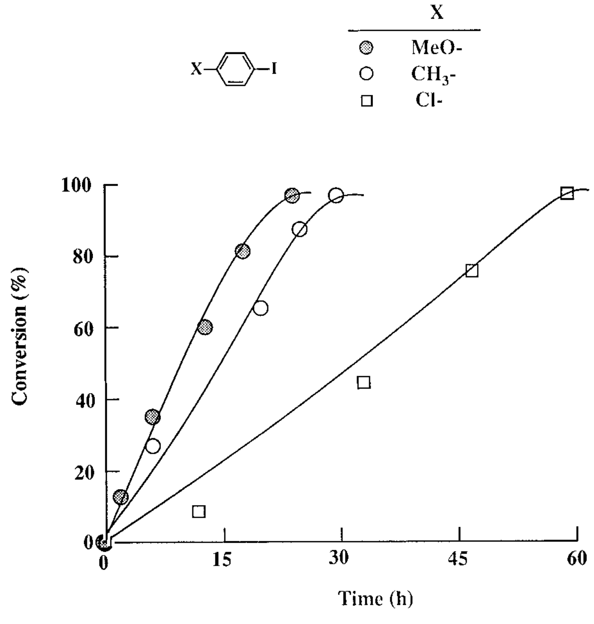


Figure 3. Time vs conversion of various aryl halides in model reactions with *n*-hexylallene.

By using the present polymerization system, various three building blocks may be incorporated into the structure of the polymer at the same time. Further applications of the present polymerization method for the synthesis of functional materials are now in progress.

References and Notes

(1) (a) Leland, J.; Boucher, J.; Anderson, K. *J. Polym. Sic., Polym. Ed.* **1977**, *15*, 2785. (b) Yokozawa, T.; Ito, N.; Endo, T. *Chem. Lett.* **1988**, 233. (c) Aggour, Y. A.; Tomita, I.; Endo, T. *Makromol. Chem.* **1993**, *194*, 3323.

(2) Takahashi, T.; Yokozawa, T.; Endo, T. *Makromol. Chem.* **1991**, *192*, 1207.

(3) Tomita, I.; Kondo, Y.; Takagi, K.; Endo, T. *Macromolecules* **1994**, *27*, 4413.

(4) (a) Tsuji, J. *Organic Synthesis with Palladium Compounds*; Springer-Verlag: Berlin, 1980. (b) Heck, R. F. *Palladium Reagents in Organic Synthesis*; Academic Press: London, 1985.

(5) (a) Ahmar, M.; Cazes, B.; Gore, J. *Tetrahedron Lett.* **1984**, *25*, 4505. (b) Shimizu, I.; Tsuji, J. *Chem. Lett.* **1984**, 233. (c) Trost, B. M. *Acc. Chem. Res.* **1980**, *13*, 385. (d) Trost, B. M. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1173. (e) de Meijere, A.; Meyer, F. E. *Angew. Chem., Int. Ed. Engl.* **1994**, *33* 2379.

(6) (a) Yoneyama, M.; Kakimoto, M.; Imai, Y *Macromolecules* **1988**, *21*, 1908. (b) *Idem., ibid.* **1989**, *22*, 2593.

(7) Patai, S. *The Chemistry of Ketenes, Allenes, and Related Compounds*; Elsevier Scientific Publishing Company: New York, 1981. Brandsma, L.; Verkruijsse, H. D. *Synthesis of Acetylenes, Allenes and Cumulenes*; Preface Ltd., New York, 1981.

(8) Although, the formation of an *exo*-isomer was not mentioned in ref 5a, the peaks at 5.30 and 5.06 ppm are illustrative of the existence of the *exo*-isomer.

(9) The small peaks appeared at 1.9 and 2.9 ppm in the ^{1}H-NMR spectrum (Figure 1) can be attributed to the protons of methylenes adjacent to the *Z*-isomeric double bond.

(10) Trost, B. M. *Tetrahedron* **1977**, *33*, 2615.

(11) The polymerization was also carried out using $Pd_2(dba)_3 \cdot CHCl_3$-2dppe (1.5 mol %) as a catalyst. Although the polymer was obtained in 98% yield, the molecular weight of the polymer was lower ($\bar{M}_n$ = 2,900) than that obtained by the Pd(II) catalyst.

(12) Perry, J. R; Wilson, D. B. *Macromolecules* **1993**, *26*, 1503.

(13) In this case, the homocoupling product, terphenyl, should be also produced; however, it did not appear with GC because of its high boiling point.

(14) Uno, M.; Sato, K.; Masuda, M.; Ueda, W.; Takahashi, S. *Tetrahedron Lett.* **1985**, *26*, 1553.

(15) Wallow, T. I.; Novak, B. M. *ACS Polym. Prep.* **1993**, *34*, 1008.

(16) (a) Fauvarque, J.-F.; Pflüger, F.; Troupel, M. *J. Organomet. Chem.* **1981**, *208*, 419. (b) Amatore, C.; Pflüger, F. *Organometallics* **1990**, *9*, 2276.

(17) The para-substituents probably affected the rate-determining step (the insertion of allene moieties or the nucleophilic attack), because the preceding oxidative addition is known to be a very fast step and to become faster as the electron-withdrawing character of substituent is increased. See, ref 16.

MA9504431