Supplementary Information for

Salicylaldiminate/Pd(trifluoroacetate)2 [SalAld/Pd(tfa)2] Initiating System for C1

Polymerization of Diazoacetate: Generation of Active Initiator from Ordinary Reagents

with Facile Procedures

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Experimental Section

Materials

Tetrahydrofuran (THF, Kanto Chemical, >99.5%, dehydrated Super Plus grade) was used after passage through solvent purification columns (Nikko Hansen & Co., Glass Contour MINI). Diethyl ether ((Kanto Chemical, >99.5%, dehydrated), 1,4-dioxane (Kanto Chemical, >99.5%, super dehydrated), *N,N*-dimethylformamide (Kanto Chemical, >99.5%, super dehydrated), chloroform (Junsei Chemical, 99%), dichloromethane (FUJIFILM Wako Pure Chemical, Guaranteed Reagent), methanol (Yoneyama Yakuhin Kogyo, 99%; Kanto Chemical, >99.8%, super dehydrated), palladium(II) acetate [Pd(OAc)₂, Sigma-Aldrich, 98%], palladium(II) trifluoroacetate [Pd(tfa)₂, Tokyo Chemical Industry, >98.0%], sodium tetraphenylborate (NaBPh₄, Tokyo Chemical Industry, >99.5%), sodium hydride (NaH, Nacalai Tesque, with approx. 40% paraffin liquid), 2,6-di-*t*-butyl-4-methylphenol (**8**, FUJIFILM Wako Pure Chemical, >98.0%), hydrochloric acid (Nacalai Tesque, 35–37%), Na₂SO₄ (Nacalai Tesque, >98.5%), and CaH₂ (Nacalai Tesque, >90.0%) were used as received.

Synthesis of ligands and monomers

Salicylaldimines 1-7 were prepared from the corresponding salicylaldehydes and anilines by a similar procedure reported in the literature.¹

Methyl diazoacetate (MDA) and ethyl diazoacetate (EDA) were prepared according to the literature,² and dried over CaH₂ and stored as a dichloromethane solution. The concentrations of MDA and EDA were determined with trichloroethylene (Katayama Chemical) as an internal standard by using ¹H NMR spectroscopy. Benzyl diazoacetate (BDA) and cyclohexyl diazoacetate (*c*HDA) were synthesized according to the general procedure reported by Fukuyama and co-workers.³ The characterization data for BDA³ and *c*HDA⁴ were reported in the literature. *Caution!* Extra care must be taken for syntheses and handling of the diazoacetabelyl compounds because of their potential explosiveness.

Preparation of (SalAld)₂Pd from 4 and Pd(OAc)₂.

This complex was prepared following the reported procedure for the preparation of analogous (SalAld)₂Pd complexes.^{5,6}

Under a N₂ atmosphere, a dehydrated MeOH (12 mL) solution of $Pd(OAc)_2$ (0.112 g, 0.499 mmol) was placed in a round-bottomed flask equipped with a three-way cock. A MeOH solution (10 mL) of salicylaldimine **4** (0.280 g, 0.996 mmol) was added to the solution, and the mixture was heated under reflux for 2 h, during which a solid was formed in the mixture. After the mixture was cooled to room temperature, the solid was isolated by filtration followed washing with MeOH. Drying of the solid under reduced pressure afforded (SalAld)₂Pd as a yellowish brown solid in 73% yield (0.242 g, 0.36 mmol).

¹H NMR (500 MHz, CDCl₃, δ): 7.54 (s, 1H, CH=N), 7.33 (t, J = 7.5 Hz, 1H, Ar–H), 7.20 (m, 1H, Ar–H), 7.08 (m, 2H, Ar–H), 6.43 (t, J = 7.5 Hz, 1H, Ar–H), 5.99 (d, J = 8.5 Hz, 2H, Ar–H), 3.52 [sept, J = 7.5 Hz, 2H, CH(CH₃)₂], 1.30 [d, J = 7.0 Hz, 6H, CH(CH₃)₂], 1.16 [d, J = 6.5 Hz, 6H, CH(CH₃)₂].

¹³C NMR (125 MHz, CDCl₃, δ): 165.6 [Ar, quaternary (q.)], 162.7 (Ar), 144.9 (Ar, q.), 142.4 (Ar, q.), 134.8 (Ar), 134.3 (Ar), 126.7 (Ar), 122.8 (Ar), 120.9 (Ar), 119.5 (Ar, q.), 114.3 (Ar), 28.4 [*C*H(CH₃)₂], 24.4 [*C*H(*C*H₃)₂], 23.4 [*C*H(*C*H₃)₂].

Anal. Calcd for C₃₈H₄₄N₂O₂Pd: C, 68.41; H, 6.65; N, 4.20. Found: C, 68.12; H, 6.70; N, 4.35.

Polymerization procedure

As a representative example, the polymerization procedures for run 6 in Table 2 is described.

Under a N₂ atmosphere, salicylaldimine **4** (28.1 mg, 0.100 mmol) was reacted with NaH (2.40 mg, 0.100 mmol) in THF (3.0 mL) at room temperature for 1 h to yield a SalAld solution. Under a N₂ atmosphere, a THF (1.3 mL) solution of Pd(tfa)₂ (8.31 mg, 0.0250 mmol) was placed in a Schlenk tube and cooled to -78 °C. Then, at -78 °C, the SalAld solution was added dropwise to the Schlenk tube containing the Pd(tfa)₂ solution using a syringe and the mixture was warmed to room temperature and stirred for 3 h. After a CH₂Cl₂ solution of EDA (3.25 M, 0.77 mL, 2.5 mmol) was added at room temperature, the mixture was heated to 50 °C and stirred for 13 h at the temperature. After volatiles were removed under reduced pressure, 1 M HCl/MeOH solution (10 mL), 1 M HCl aqueous solution (10 mL), and CHCl₃ (20 mL) were added to the residue, and the mixture was transferred to a separatory funnel, with which the organic layer was washed with 1 M HCl, H₂O, and brine, and dried over Na₂SO₄. After Na₂SO₄ was removed by filtration, the volatiles were removed under reduced pressure, and the residual solid was subjected to purification with preparative recycling SEC (eluent: CHCl₃) to yield polyEDA' (107 mg, 50 % yield).

Other polymerizations were carried out in similar procedures, except for the polymerization of BDA and cHDA, where the monomer was added as a THF solution to a solution of an initiator.

Measurements

The molar mass distributions of EDA and *c*HDA polymers were measured via SEC in THF (flow rate = 1.0 mL/min) at 40 °C on polystyrene gel columns [Styragel HR4 and Styragel HR2 (Waters, molar-mass exclusion limit = 600 kDa and 20 kDa for polystyrene, respectively)] connected to a pump (JASCO, PU-4180), a column oven (JASCO, CO-2065 Plus), an ultraviolet detector (JASCO, UV-4075), and a refractive index detector (JASCO, RI-2031 Plus). The molar mass distributions of MDA polymers were measured via SEC in chloroform (flow rate = 1.0 mL/min) at 40 °C on polystyrene gel columns [TSKgel G4000H_{XL} (Tosoh, molar-mass exclusion limit = 400 kDa for polystyrene) and GPC K-802.5 (Shodex, molar-mass exclusion limit = 20 kDa for polystyrene)] connected to a pump (Shimadzu, LC-6AD), a column oven (JASCO, CO-2065 Plus), an ultraviolet detector (Shimadzu, RID-20A). The number-average molar mass (M_n) and dispersity [D; weight-average molar mass/number-average molar mass (M_w/M_n)] were calculated from the chromatographs on the basis of six poly(methyl methacrylate) (PMMA) standards (Shodex M-75; $M_p = 2400-212000$, D < 1.1) and dibutyl sebacate (molar mass = 314.5).

The absolute molecular weight of the polymers was determined by SEC coupled with multiangle light scattering (SEC-MALS) on a Dawn HELEOS II 8+ (Wyatt Technology; $\lambda = 661.5$ nm). The refractive index increment (dn/dc) values were measured assuming 100% mass recovery.

Purification by preparative recycling SEC was performed on a JAI LC-918R equipped with a combination of JAIGEL-3H and JAIGEL-2H (Japan Analytical Industry, molar mass exclusion limit = 70 kDa and 5 kDa for polystyrene, respectively; column size = $600 \text{ mm} \times 20 \text{ mm}$ i.d.) using chloroform as eluent at a flow rate of 3.8 mL/min at room temperature.

 1 H (500 MHz) and 13 C (126 MHz) NMR spectra of polymers were recorded on a Bruker Avance III HD 500 spectrometer in CDCl₃ at 50 °C.

Elemental analyses were performed on a YANAKO CHN Corder MT-5.



Figure S1. ¹H NMR spectra of the polyEDA's obtained with **1** (run 2 in Table 1), **2** (run 3 in Table 1), **3** (run 4 in Table 1), **5** (run 7 in Table 1), **6** (run 8 in Table 1), and **7** (run 9 in Table 1).



¹H NMR (500 MHz, CDCl₃, δ): 7.54 (s, 1H, CH=N), 7.33 (t, *J* = 7.5 Hz, 1H, Ar–H), 7.20 (m, 1H, Ar–H), 7.08 (m, 2H, Ar–H), 6.43 (t, *J* = 7.5 Hz, 1H, Ar–H), 5.99 (d, *J* = 8.5 Hz, 2H, Ar–H), 3.52 [sept, *J* = 7.5 Hz, 2H, CH(CH₃)₂], 1.30 [d, *J* = 7.0 Hz, 6H, CH(CH₃)₂], 1.16 [d, *J* = 6.5 Hz,

6H, CH(CH₃)₂].

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Figure S2. ¹H (upper) and ¹³C (lower) NMR spectra of (SalAld)₂Pd (SalAld of 4).

References

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