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Articles

Polyaddition of 2,7-Diethynyl-9,9-dioctylfluorene Using Regio- and Stereoselective Alkyne Dimerization Catalysts

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ABSTRACT: Three geometrical isomers of poly(9,9-dioctyl-2,7-fluorene ethynylene vinylene) [poly(**1**)] having (*E*)-, (*Z*)-, and *gem*-vinylene units have been prepared in high regio- and stereoselectivities by polyaddition of 2,7-diethynyl-9,9-dioctylfluorene (**1**) catalyzed by three kinds of transition metal catalysts. Thus, a palladium catalyst (**2**), in situ generated from $Pd(OAc)_2$, 1,3-dimesitylimidazolinium chloride (SIMes·HCl), and Cs_2CO_3, efficiently catalyzes the (*E*)-selective reaction, giving (*E*)-rich poly(**1**) in over 99% selectivity, whereas the reaction using a catalytic amount of $RuCl_2({=}C{=}CHPh)(PPr^i_3)_2$ (**3**) in the presence of *N*-methylpyrrolidine forms (*Z*)-rich poly(**1**) in over 92% selectivity. On the other hand, a rhodium catalyst $[RhCl(PMe_3)_2]_2$ (**4**) forms poly(**1**) bearing *gem*-vinylene linkages in 94% selectivity. The regio- and stereochemical courses well preserve the catalyst nature of **2**−**4** observed in dimerization reactions of arylacetylenes as prototypes of the present polyaddition processes. All polymers exhibit emission property and high thermal stability.

Introduction

Poly(phenylenevinylene) (PPV) and related π-conjugated polymers have attracted a great deal of recent interest owing to their remarkable electrooptical properties such as photo- and electroluminescence.[1] These properties are known to be significantly affected by stereoregularity of the polymer backbone. For example, it has been documented that the (*E*)/(*Z*) ratio of vinylene linkages governs luminescence efficiency of PPV, which is an essential factor in applying the polymers to light-emitting devices.[2,3] Consequently, stereochemical control of polymer frameworks is among the principal subjects in the synthesis of π-conjugated polymers.

Transition metal-catalyzed organic transformations have proven to be powerful tools of constructing well-defined architecture of macromolecules.[4] In this context, regio- and stereoselective addition to alkyne substrates must be utilized as a particularly simple and efficient means of synthesizing π-conjugated polymers bearing vinylene linkages, while synthetic studies in this approach have been extremely limited.[5−8] Recently, Mori et al. reported stereoselective synthesis of (*E*)- and (*Z*)-poly(*p*-phenylene dimethylsilylene vinylene)s via rhodium-catalyzed polyaddition of *p*-bis(dimethylsilyl)benzene to *p*-diethynylbenzene.[6]

In this paper, we describe new polyaddition systems based on catalytic dimerization of arylacetylenes (Scheme 1).[7,8] Thus, it has been found that polyaddition of 2,7-diethynyl-9,9-dioctylfluorene (**1**) proceeds in highly regio- and stereocontrolled ways on the choice of catalysts, affording the polymers with (*E*)-, (*Z*)-, and *gem*-vinylene linkages in over 92% selectivities. Although π-conjugated polymers of this type have been previously prepared by palladium-catalyzed polycondensation,[9] geometrical control around vinylene linkage has remained almost unexplored.

Results and Discussion

The present polymerization is based on transition-metal-catalyzed dimerization of arylacetylenes,[10,11] which may form three geometrical isomers of diarylbutenynes (see the products in eq 1). To accomplish the regio- and stereoselective synthesis of poly(**1**), we have needed the catalysts leading to (*E*)-, (*Z*)-, and *gem*-isomers of butenyne. Nolan et al. have developed a highly (*E*)-selective catalyst (**2**), which is prepared in situ from $Pd(OAc)_2$, 1,3-dimesitylimidazolinium chloride (SIMes·HCl), and Cs_2CO_3 and converts phenylacetylene into (*E*)-1,4-diphenyl-1-buten-3-yne in 97% selectivity.[11b] Goldman et al. have reported that $[RhCl(PMe_3)_2]_2$ (**4**) causes perfectly *gem*-selective dimerization of phenylacetylene.[12] On the other hand, as for the dimerization of arylacetylenes, (*Z*)-selective catalysts with high catalytic activity have been limited.[11a,13] We therefore examined several transition-metal catalysts and found a vinylideneruthenium complex $RuCl_2({=}C{=}CHPh)(PPr^i_3)_2$ (**3**)[14] in combination with *N*-methylpyrrolidine to serve as a particularly effective catalyst (eq 1).[15] Thus, the dimerization of phenylacetylene in CH_2Cl_2 in the presence of **3** (1 mol %) and *N*-methylpyrrolidine (20 mol

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Scheme 1

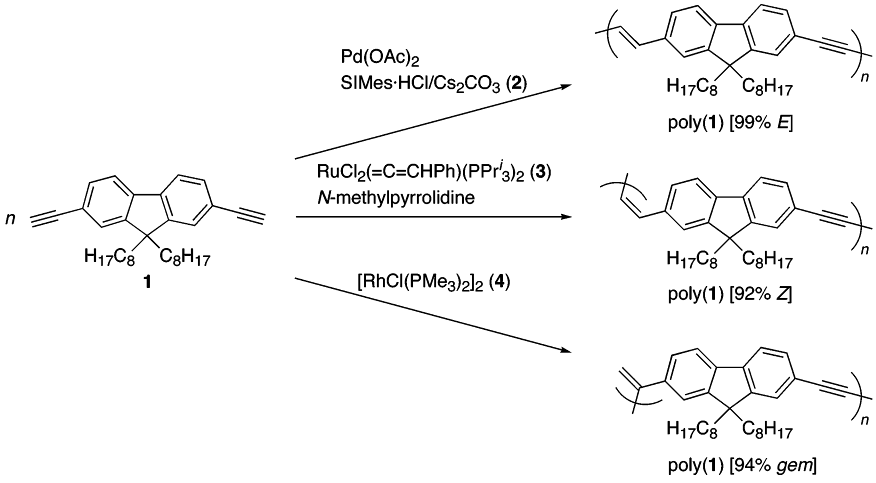
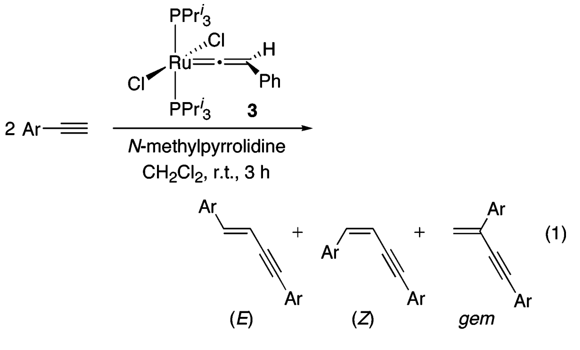


Table 1. Polyaddition of 1 Catalyzed by 2−4

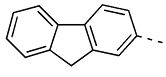
entry	catalyst	condition	yield[a] (%)	$M_{n,NMR}$[b]	n_{av}[b]	$M_{n,GPC}$[c]	M_w/M_n[c]	(*E*):(*Z*):*gem*[b]
1[d]	**2**	50 °C, 10 min	99	6200	14.1	14000	2.35	99:<1:<1
2[d]	**2**	50 °C, 3 min	62	2400	5.5	3400	1.52	99:<1:<1
3[e]	**3**	r.t., 24 h	87	1900	4.3	2500	1.81	2:94:4
4[e]	**3**	70 °C, 24 h	87	2600	5.9	3400	2.10	5:92:3
5[f]	**4**	r.t., 2 h	>99	3900	8.9	5400	2.58	<6:<1:94
6[f]	**4**	50 °C, 2 h	>99	5600	12.8	11900	2.22	5:2:93

[a] Isolated yield. [b] Determined by ^{1}H NMR spectroscopy. [c] Determined by GPC based on polystyrene standards. [d] Solvent: *N*,*N*-dimethylacetamide. Initial concentration: [**1**] = 0.10 M, [Pd(OAc)$_2$] = 1.0 mM, [SIMes·HCl] = 2.0 mM, [Cs$_2$CO$_3$] = 0.40 M. [e] Solvent: 1,2-dichloroethane. Initial concentration: [**1**] = 0.10 M, [**3**] = 5.0 mM, [*N*-methylpyrrolidine] = 20 mM. [f] Solvent: benzene. Initial concentration: [**1**] = 0.10 M, [**4**] = 5.0 mM.

%) was accomplished in 3 h at room temperature to give (*Z*)-1,4-diphenyl-1-buten-3-yne in 96% selectivity. 2-Ethynylfluorene was also dimerized smoothly at room temperature, giving the corresponding (*Z*)-enyne in 90% selectivity. The addition of *N*-methylpyrrolidine to the system is of particular importance to develop the high catalytic activity. This component very probably promotes the elimination of β-hydrogen of the vinylidene ligand and the chlorido ligand in **3** as HCl to generate a catalytically active alkynylruthenium species.[16] The catalytic activity was rather sensitive to the sorts of phosphine ligands, and **3** having bulky and basic triisopropylphosphines exhibited the best performance of the vinylideneruthenium complexes examined.[17]



(1)

Ar	yield	(*E*):(*Z*):*gem*
Ph	>99%	1:96:3
	98%	0:90:10

Having the (*E*)-, (*Z*)-, and *gem*-selective catalysts **2**−**4** in hand, we next examined polyaddition of 2,7-diethynyl-9,9-dioctylfluorene (**1**) (Scheme 1). π-Conjugated polymers bearing fluorene units are highly expected as blue-light-emitting materials.[1a,18] The results are listed in Table 1. The polymerization using **2** [i.e., Pd(OAc)$_2$ (1 mol %), SIMes·HCl (2 mol %), Cs$_2$CO$_3$ (4 equiv)] proceeded in *N*,*N*-dimethylacetamide at 50 °C for 10 min. The reaction mixture was poured into a large quantity of MeOH to give a 99% yield of (*E*)-rich poly(**1**) as a yellowish-brown powder (entry 1), whose molecular weight (M_n) and average degree of polymerization (n_{av}) were estimated to be 6200 and 14.1, respectively, by end-group analysis using ^{1}H NMR spectroscopy. The GPC analysis indicated $M_{n,GPC}$ of 14 000, the value of which is significantly larger than the $M_{n,NMR}$ value, probably due to overestimation resulting from the rigid-rod structure of poly(**1**).[19] The molecular weight was reduced to 2400 by shortening the reaction time to 3 min (entry 2).

Next, the polymerization was carried out in the presence of **3** (5 mol %) and *N*-methylpyrrolidine (20 mol %) in 1,2-dichloroethane at room temperature. After 24 h, the dark orange solution with fluorescence was subjected to silica gel column chromatography eluted with CH$_2$Cl$_2$ to remove the ruthenium catalyst. Concentration of the eluate to dryness afforded (*Z*)-rich poly(**1**) as an orange oily material in 87% yield (entry 3). This reaction also proceeded in high (*Z*)-selectivity at 70 °C (entry 4). The polymerization catalyzed by rhodium complex **4** proceeded in benzene at room temperature for 2 h to give *gem*-rich poly(**1**) with $M_{n,NMR}$ of 3900, which was isolated as a reddish-black solid in almost quantitative yield by precipitation with MeOH (entry 5). The molecular weight increased at 50 °C (entry 6).

All the polymers thus obtained were soluble in common organic solvents such as THF, CHCl$_3$, and toluene

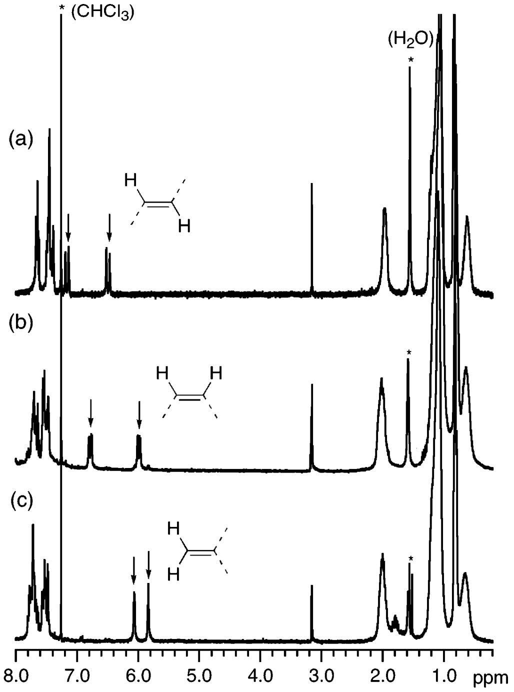


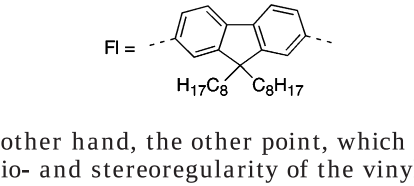
Figure 1. ^{1}H NMR spectra (300 MHz, CDCl$_3$) of (a) (*E*)-, (b) (*Z*)-, and (c) *gem*-rich poly(**1**)s isolated from the reaction system of entries 2, 4, and 5 in Table 1, respectively. The arrows mark vinylic proton signals.

Table 2. Optical Data of (*E*)-, (*Z*)-, and *gem*-Rich Poly(1)s

polymer [$M_{n,NMR}$, (*E*):(*Z*):*gem*]	UV λ_{max}[a] (nm)	FL λ_{max}[a] (nm)	Φ_F[b]
(*E*)-rich poly(**1**) [6200, 99:<1:<1]	419	455[c]	0.31
(*E*)-rich poly(**1**) [2400, 99:<1:<1]	410	452[c]	0.37
(*Z*)-rich poly(**1**) [2600, 5:92:3]	373	452[d]	0.42
gem-rich poly(**1**) [3900, <6:<1:94]	342	375[e]	0.32
gem-rich poly(**1**) [5600, 5:2:93]	345	377[e]	0.27

[a] UV−vis absorption and fluorescence (FL) spectra were recorded in a dilute CHCl$_3$ solution at room temperature. [b] The FL quantum yield (Φ_F) was estimated by using quinine sulfate in 1 N H$_2$SO$_4$ as a standard. [c] Excited at 410 nm. [d] Excited at 380 nm. [e] Excited at 340 nm.

and were stable in air. The structural analysis was made by NMR and IR spectroscopy. There are two points to be clarified about the microstructure of the polymer backbone. One is the sequential arrangement of the π-conjugated units. Thus, we must consider at least two types of arrangements of fluorene, ethynylene, and vinylene units, as illustrated in the following diagram. Despite several attempts using the model compounds, however, we could not obtain any crucial information on this point.



On the other hand, the other point, which is related to the regio- and stereoregularity of the vinylene linkages, was clearly investigated by ^{1}H NMR spectroscopy. As seen from Figure 1, the vinylic proton signals of (*E*)-, (*Z*)-, and *gem*-vinylene groups appeared separately at δ 7.17 and 6.49 ($^3J_{HH}$ = 16.4 Hz), δ 6.78 and 5.99 ($^3J_{HH}$ = 12.0 Hz), and δ 6.06 and 5.83 ($^3J_{HH}$ = 0.0 Hz), respectively. The peak integration provided the (*E*):(*Z*):*gem* ratio of vinylene linkages in each polymer, as listed in Table 1. Thus, the (*E*)-, (*Z*)-, and *gem*-selective nature of catalysts **2**−**4** was well preserved in the polymerization of **1**, respectively. The signal at around δ 3.16 observed in all spectra is assigned as C≡CH protons of polymer termini. All polymers exhibited a C≡C stretching band at around 2360 cm^{-1} in the IR spectra. The (*E*)-rich poly(**1**) also showed an absorption peak at 944 cm^{-1} in medium intensity, which is assignable to C−H bending vibration of the (*E*)-CH=CH group.

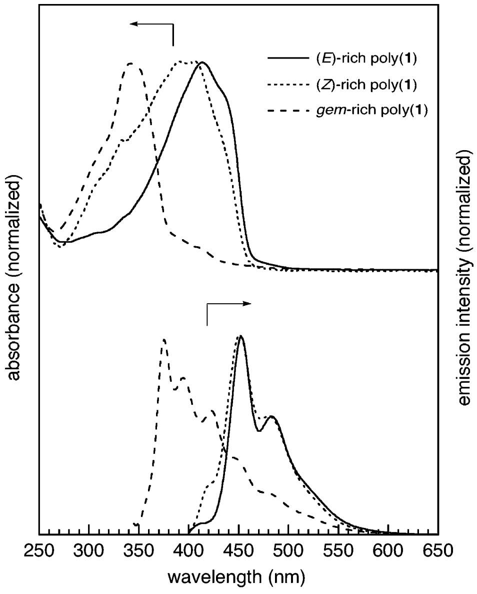


Figure 2. UV−vis absorption and fluorescence (FL) spectra (CHCl$_3$) of (*E*)-, (*Z*)-, and *gem*-rich poly(**1**)s isolated from the reaction system of entries 2, 4, and 5 in Table 1, respectively. The spectra are normalized for comparison.

The dependence of optical properties of poly(**1**)s on the structures of the polymer backbone was investigated by UV−vis absorption and fluorescence (FL) spectroscopy. Table 2 summarizes the results. Figure 2 compares the spectra of the polymers with similar molecular weights ($M_{n,NMR}$ = 2400−3900, entries 2, 4, and 5 in Table 1) under equivalent conditions. In the absorption spectra, the π−π* transition of the (*E*)-rich poly(**1**) was observed at 410 nm (λ_{max}), the value of which was red-shifted as compared with that of (*Z*)-rich poly(**1**) (λ_{max} = 373 nm). This tendency is consistent with the general observation that the (*E*)-vinylene unit forms a longer π-conjugated system than the (*Z*)-vinylene unit.[3] On the other hand, both polymers exhibited almost identical FL spectra with the emission maximum at 452 nm and a shoulder peak at 480 nm. Interestingly, the FL quantum yield of the (*Z*)-rich polymer (Φ_F = 0.42) was slightly higher than that of the (*E*)-rich poly(**1**) (Φ_F = 0.37). A similar phenomenon has been reported for (*E*)- and (*Z*)-rich poly(phenylenevinylene)s.[3] The absorption and emission maxima of *gem*-rich poly(**1**) were both observed at much shorter wavelengths than those of the (*E*)- and (*Z*)-rich ones.[20]

Besides the emission property, poly(**1**)s exhibited excellent thermal stability. Thermogravimetric analysis (TGA) under a nitrogen atmosphere revealed that the temperatures for 5% weight loss of poly(**1**)s were in excess of 500 °C irrespective of their main-chain structures. This value is significantly higher than those of typical fluorene-based π-conjugated polymers.[21]

In conclusion, we have succeeded in regio- and stereocontrolled synthesis of poly(fluorene ethynylene vinylene)s using catalytic polyaddition process. The structure of vinylene units clearly reflects the nature of catalysts observed in the prototype dimerization reactions of arylacetylenes. This finding should be useful for further designing of more efficient catalysts for the polyaddition approach to π-conjugated polymers.

Experimental Section

General Experimental Procedure and Materials. All manipulations were performed under a nitrogen atmosphere using conventional Schlenk techniques. Nitrogen gas was purified by passing successively through the columns of an activated copper catalyst (BASF, R3-11) and P_2O_5 (Merck, SICAPENT). IR spectra were recorded on a JASCO FT/IR-410 instrument. NMR spectra were recorded on a Varian Mercury 300 (^{1}H NMR, 300.11 MHz; ^{13}C NMR, 75.46 MHz) spectrometer. Chemical shifts are reported in δ (ppm), referred to the ^{1}H (of residual protons) and ^{13}C signals of deuteration solvents. GLC analysis was performed on a Shimadzu GC-14B instrument equipped with a FID detector and a capillary column CBP-1 (25 m × 0.25 mm). Gel permeation chromatography (GPC) was carried out on a JASCO GPC assembly consisting of a model PU-980 pump, a model RI-1530 refractive index detector, and three GPC gel columns (Shodex KF-801, KF-803L, KF-805L). Polystyrene standards were used for calibration, and THF was used as the mobile phase with a flow rate of 1.0 mL/min. The UV−vis absorption and fluorescence spectra were recorded on a JASCO V-560 spectrophotometer and a FP-750 spectrofluorometer, respectively. Thermogravimetric analysis (TGA) was conducted under a nitrogen atmosphere on a Rigaku TAS-300 thermal analyzer at a heating rate of 10 °C/min.

Dichloromethane and 1,2-dichloroethane were dried over CaH_2 and distilled prior to use. Benzene was dried and distilled from Na/benzophenone ketyl. $RuCl_2(=C=CHPh)(PPr^i{}_3)_2$ (**3**) was prepared from $[RuCl_2(p\text{-cymene})]_2$, triisopropylphosphine, and phenylacetylene according to the literature.[14] 2-Ethynylfluorene and 2,7-diethynyl-9,9-dioctylfluorene were synthesized by Sonogashira coupling reactions of the corresponding iodoarenes with ethynyltrimethylsilane followed by desilylation with potassium carbonate in methanol.[22] 1,3-Dimesitylimidazolinium chloride (SIMes·HCl) was synthesized according to the literature.[23] All other chemicals were obtained from commercial suppliers and used without further purification.

Dimerization of Arylacetylenes Catalyzed by $RuCl_2(=C=CHPh)(PPr^i{}_3)_2$ (3) in the Presence of *N*-Methylpyrrolidine. To a solution of phenylacetylene (204 mg, 2.00 mmol) and anisole (40 mg, internal standard for GLC analysis) in CH_2Cl_2 (2.0 mL) were added **3** (12 mg, 20 μmol) and *N*-methylpyrrolidine (34 mg, 0.40 mmol) successively. The mixture was stirred at room temperature for 3 h. GLC analysis revealed the formation of (*Z*)-$PhCH=CHC\equiv CPh$ in 96% yield, along with small amounts of (*E*)- (1%) and *gem*-isomers (3%). Volatile materials were removed by pumping to give dark orange oil, which was subjected to flash column chromatography over silica gel eluted with hexane. Evaporation of the eluate afforded a colorless oil of $PhCH=CHC\equiv CPh$ ((*E*):(*Z*):*gem* = 1:96:3), which was pure for elemental analysis (203 mg, >99%). The NMR data were consistent with those reported.[24] The dimerization of 2-ethynylfluorene was similarly carried out.

Identification Data for (*Z*)-1,4-Bis(2-fluorenyl)but-1-en-3-yne. ^{1}H NMR ($CDCl_3$): δ 8.25 (br s, 1H, Ar), 7.98−7.95 (m, 1H, Ar), 7.83−7.78 (m, 4H, Ar), 7.70 (br s, 1H, Ar), 7.56−7.54 (m, 3H, Ar), 7.44−7.30 (m, 4H, Ar), 6.79 (d, J = 11.9 Hz, 1H, CH=CH), 5.96 (d, J = 11.9 Hz, 1H, CH=CH), 3.96, 3.94 (each s, 4H, CH_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 143.8, 143.6, 143.3, 143.2, 142.1, 142.0, 141.4 (each s, Ar), 138.7 (s, CH=CH), 135.4, 130.6, 130.3, 128.0, 127.9, 127.2, 127.0, 126.9, 125.2, 125.1, 120.2, 120.1, 120.0 (each s, Ar), 106.7 (s, CH=CH), 96.9, 88.9 (each s, $C\equiv C$), 36.9, 36.8 (each s, CH_2). Anal. Calcd for $C_{30}H_{20}$: C, 94.70; H, 5.30. Found: C, 94.47; H, 5.31.

Polymerization of 2,7-Diethynyl-9,9-dioctylfluorene (1) Catalyzed by $Pd(OAc)_2$/SIMes·HCl/Cs_2CO_3 (2). A typical procedure is as follows (entry 1 in Table 1). To a solution of **1** (70 mg, 0.16 mmol) in *N*,*N*-dimethylacetamide (1.6 mL) were successively added $Pd(OAc)_2$ (0.36 mg, 1.6 μmol), SIMes·HCl (1.1 mg, 3.2 μmol), and Cs_2CO_3 (209 mg, 0.640 mmol). The mixture was stirred at 50 °C for 10 min, during which the initially deep green solution gradually darkened. The resulting fluorescent solution was immediately poured into vigorously stirred MeOH (150 mL). The yellowish-brown solid of (*E*)-rich poly(**1**) thus precipitated was collected by filtration and washed with MeOH (69 mg, 99%). IR (KBr): 3310, 2925, 2853, 2362, 1463, 944, 811 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.67−7.62, 7.50−7.39 (each m, Ar), 7.17, 6.49 (each d, J = 16.4 Hz, CH=CH), 3.16 (s, terminal $C\equiv CH$), 2.05−1.88, 1.25−0.55 (each m, CH_2 and CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 107.6 (s, CH=CH), 93.2, 89.7 (each s, $C\equiv C$); only characteristic peaks were reported due to complexity of the spectrum.

Polymerization of 1 Catalyzed by 3/*N*-Methylpyrrolidine. A typical procedure is as follows (entry 3 in Table 1). To a solution of **1** (70 mg, 0.16 mmol) in 1,2-dichloroethane (1.6 mL) were successively added **3** (4.8 mg, 8.0 μmol) and *N*-methylpyrrolidine (2.7 mg, 32 μmol). The mixture was stirred at room temperature. The reaction progress was followed by TLC. After 24 h, the resulting dark orange fluorescent solution was directly subjected to flash column chromatography eluted with CH_2Cl_2. The eluate was evaporated and dried under vacuum overnight to afford (Z)-rich poly(**1**) as an orange oil (61 mg, 87%). IR (KBr): 3310, 2926, 2854, 2360, 1466, 890, 822 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.85−7.46 (m, Ar), 6.78, 5.99 (each d, J = 12.0 Hz, CH=CH), 3.15 (s, terminal $C\equiv CH$), 2.20−1.85, 1.35−0.50 (each m, CH_2 and CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 106.6 (s, CH=CH), 97.8, 89.3 (each s, $C\equiv C$); only characteristic peaks were reported due to complexity of the spectrum.

Polymerization of 1 Catalyzed by $[RhCl(PMe_3)_2]_2$ (4). A typical procedure is as follows (entry 5 in Table 1). A solution of **1** (266 mg, 0.606 mmol) and **4** (18 mg, 31 μmol) in benzene (1.2 mL) was stirred at room temperature for 2 h. The reaction progress was followed by TLC. The resulting dark red solution was poured into vigorously stirred MeOH (150 mL). The reddish-black solid of *gem*-rich poly(**1**) thus precipitated was collected by filtration and dried under vacuum (265 mg, >99%). IR (KBr): 3309, 2925, 2852, 2360, 1465, 1211, 947, 822 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.81−7.48 (m, Ar), 6.06, 5.83 (each s, CH=CH), 3.16 (s, terminal $C\equiv CH$), 2.13−1.61, 1.35−0.50 (each m, CH_2 and CH_3). $^{13}C\{^1H\}$ NMR analysis was infeasible due to low solubility.

Fluorescence (FL) and Quantum Yield Measurements. All emission studies were performed at room temperature in optically dilute solutions with absorption maxima less than 0.1 to avoid the inner filter effect. The solutions for the measurement were freshly prepared by dissolving the polymer into spectroscopic grade $CHCl_3$. The quantum yields were measured relative to quinine sulfate in 1 N H_2SO_4 assuming a quantum yield of 0.546 when excited at 350 nm. Corrections for refractive indices and differences between the excitation light intensities of different wavelengths were applied.

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