Synthesis of Poly(1-chloro-2-arylacetylene)s with High Cis-Content and Examination of Their Absorption/Emission Properties

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Received 29 August 2016; accepted 6 October 2016; published online 2 November 2016
DOI: 10.1002/pola.28397

ABSTRACT: A series of 1-chloro-2-arylacetylenes [Cl-C≡C-Ar, Ar = C_6H_5 (**1**), C_6H_4-*p*-*i*Pr (**2**), C_6H_4-*p*-O*i*Pr (**3**), C_6H_4-*p*-NHC(O)O*t*Bu (**4**), and C_6H_4-*o*-*i*Pr (**5**)] were polymerized using (tBu_3P)PdMeCl/silver trifluoromethanesulfonate (AgOTf) and $MoCl_5/SnBu_4$ catalysts. The corresponding polymers [poly(**1**)–poly(**5**)] with weight-average molecular weights of 6,500–690,000 were obtained in 10–91% yields. THF-insoluble parts, presumably high-molecular weight polymers, were formed together with THF-soluble polymers by the Pd-catalyzed polymerization. The Pd catalyst polymerized nonpolar monomers **1** and **2** to give the polymers in yields lower than the Mo catalyst, while the Pd catalyst polymerized polar monomers **3** and **4** to give the corresponding polymers in higher yields. The ^{1}H NMR and UV–vis absorption spectra of the polymers indicated that the cis-contents of the Pd-based polymers were higher than those of the Mo-based polymers, and the conjugation length of the Pd-based polymers was shorter than that of the Mo-based polymers. Pd-based poly(**5**) emitted fluorescence most strongly among poly(**1**)–poly(**5**). © 2016 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2017**, *55*, 382–388

KEYWORDS: catalysts; conjugated polymers; fluorescence; polyacetylenes; UV–vis spectroscopy

INTRODUCTION Polyacetylenes are a family of macromolecules that triggered intense research in the area of conjugated polymers after discovery of high conductivity in doped-polyacetylene films.[1] The most stable members of polyacetylene family are disubstituted acetylene derived polymers and therefore these polymers are the most suitable for industrial applications.[2] In addition, disubstituted acetylene polymers display other outstanding properties such as selective gas permeability, stimuli responsiveness, helix formation, electroluminescence (EL), and photoluminescence (PL).[3]

Numerous studies have been performed regarding PL of substituted polyacetylenes to constitute a base of knowledge that allow us to synthesize acetylene polymers featuring high emission efficiencies.[4,5] Monosubstituted acetylene polymers emit weak PL, while disubstituted acetylene polymers such as poly[(alkyl)C≡CAr] and poly[Ar′C≡CAr] emit intense blue–green PL.[4,5] There are also various reports concerning the effect of alkyl chain length, bulkiness and electronic properties of substituents on the emission properties of the acetylene polymers.[4] The PL efficiency can also be further enhanced by introducing emissive groups such as silole, biaryl, and carbazolyl to the side chains of the substituted polyacetylenes.[3,6] In spite of a large amount of studies on the relationship between polymer structures and PL/EL properties of disubstituted acetylene polymers, there is no systematic study presenting the effect of geometry (variation of cis/trans content) of the main chain on the polymer properties, because disubstituted acetylene polymers were only synthesized by the early transition metal catalysts, wherein the stereoregularity is uncontrollable due to no cis/trans selectivity of the metathesis reaction.

Recently, we presented a series of bulky monophosphine-ligated Pd catalysts that can polymerize 1-chloro-2-(4-*tert*-butyl)phenylacetylene to yield a polymer with a higher cis-content than that of the analogue polymer synthesized by a Mo catalyst.[7] No cis-stereoregulated disubstituted acetylene polymers had been synthesized previous to our study. Consequently, there was no paper analyzing the effect of stereoregularity on the properties of disubstituted acetylene polymers. Chen and a coworker also succeeded in polymerizing disubstituted acetylenes using *N*-heterocyclic carbene-ligated Pd complexes in conjunction with sodium tetrakis(3,5-bis(trifluoro-methyl)phenyl)borate.[8] In this article, we disclose the polymerization of 1-chloro-2-arylacetylenes [Cl-C≡C-Ar, Ar = C_6H_5 (**1**), C_6H_4-*p*-*i*Pr (**2**), C_6H_4-*p*-O*i*Pr (**3**), C_6H_4-*p*-NHC(O)O*t*Bu (**4**) and C_6H_4-*o*-*i*Pr (**5**)] by employing (*t*Bu_3P)PdMeCl/AgOTf and $MoCl_5/SnBu_4$[9] catalytic systems, and the influence of cis/trans contents on the properties of the polymers formed.

EXPERIMENTAL

Materials

The reagents were used as received from commercial suppliers (Aldrich and Wako) without further purification. Tri-tert-butylphosphine was received from Nippon Chemical Industrial Co. and used without further purification. ClC≡CC_6H_5,[10] HC≡CC_6H_4-*o*-*i*Pr,[11] HC≡CCC_6H_4-*p*-NHC(O)O*t*Bu[12] and (*t*Bu_3P)PdMeCl[13] were synthesized according to the procedures in the literature. The solvents used for the air and moisture sensitive procedures were purified employing standard procedures.

Synthesis and Instrumentation

All air and moisture sensitive manipulations were performed under argon using standard Schlenk techniques. ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra were recorded on a JEOL ECA-400 spectrometer, wherein the chemical shifts were referenced to TMS ($\delta = 0.00$ ppm) or $CHCl_3$ ($\delta = 7.26$ ppm) as an internal standard. IR spectra were measured on a JASCO FT/IR-4100 spectrophotometer using the KBr method. Elemental analysis was performed at the Microanalytical Center of Kyoto University. High-resolution mass spectra were obtained with a JEOL JMS-MS700 (EI), Thermo Fisher Scientific Exactive (ESI, APCI) spectrometer or a Thermo Fisher triple quadrupole mass spectrometer in a positive ion mode. The weight-average molecular weights (M_w) and the polydispersity indices (PDI) of the polymers were determined on a JASCO SEC system equipped with Shodex columns KF805 × 3 (molecular weight limit = 4×10^6) eluted with THF at 40 °C using polystyrene standards for calibration. UV–vis absorption and fluorescence spectra were recorded on JASCO V-550 and FP-750 spectrometers, respectively.

Synthesis of Monomers

Synthesis of 1-chloro-2-(4-isopropyl)phenylacetylene (**2**). 1-Bromo-4-isopropylbenzene (10.0 g, 50.2 mmol), $(CH_3CN)_2PdCl_2$ (390 mg, 1.5 mmol), *t*Bu_3P (609 mg, 3.0 mmol), CuI (191 mg, 1.0 mmol), and HN*i*Pr_2 (8.4 mL, 60.2 mmol) were placed in a round-flask provided with a three-way stopcock under Ar. 1,4-Dioxane (50 mL) was added to the mixture, and the resulted solution was cooled to 0 °C. Then, trimethylsilylacetylene (5.92 g, 60.2 mmol) was added to the mixture dropwise, and the resulting mixture was stirred at room temperature overnight. The solution was diluted with Et_2O (70 mL) and washed with saturated NH_4Cl aq. (2 × 50 mL), saturated $NaHCO_3$ aq. (2 × 50 mL) and saturated aqueous NaCl (2 × 50 mL). The organic phase was dried with anhydrous $MgSO_4$, filtrated, and concentrated on a rotatory evaporator. The residue was purified by silica gel flash chromatography using hexane as eluent to obtain [(4-isopropylphenyl)ethynyl]trimethylsilane as a yellow liquid in 92% yield (9.98 g, 46.1 mmol). The ^{1}H and ^{13}C NMR spectra were in agreement with those reported in the literature.[14]

Next, CCl_4 (120 mL) was fed to a mixture of [(4-isopropylphenyl)ethynyl]trimethylsilane (4.98 g, 23.0 mmol) and K_2CO_3 (3.18, 23.0 mmol) under N_2. A solution of tetra-*n*-butylammonium fluoride in THF (1.0 mol/L, 46 mL, 46.0 mmol) was added to the resulting mixture, and allowed to stir at room temperature overnight. The reaction mixture was diluted with Et_2O (60 mL) and washed with 1 M HCl solution (2 × 50 mL), saturated $NaHCO_3$ aq. (2 × 50 mL) and saturated aqueous NaCl (2 × 50 mL). The organic phase was dried over anhydrous $MgSO_4$, filtrated, and concentrated on a rotary evaporator. The residual mass was purified by preparative HPLC eluted with $CHCl_3$ to obtain a light yellow oil in 99% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 (d, $J = 8.0$ Hz, 2H; Ar), 7.19 (d, $J = 8.0$ Hz, 2H; Ar), 2.91 (sep, $J = 8.0$ Hz, 1H; CH of iPr), 1.26 (d, $J = 8.0$ Hz, 6H; CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.6, 132.0, 126.5, 119.4, 69.5, 67.1, 34.05, 23.7.

Synthesis of 1-chloro-2-(4-isopropoxy)phenylacetylene (**3**). This compound was synthesized according to a similar procedure to 2 employing 1-iodo-4-isopropoxybenzene instead of 1-bromo-4-isopropylbenzene. Product **3** was obtained as a red oil in 74% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 (d, $J = 8.7$ Hz, 2H; Ar), 6.81 (d, $J = 8.7$ Hz, 2H; Ar), 4.56 (sep, $J = 6.0$ Hz, 1H; OCH), 1.34 (d, $J = 6.0$ Hz, 6H; CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.2, 133.4, 115.7, 113.8, 69.9, 69.4, 66.2, 21.9. HR-MS (ESI): m/z calcd for $C_{11}H_{11}ClO$: 194.0489, found 194.0489.

Synthesis of 1-chloro-2-(*N*-Boc-amino)phenylacetylene (**4**). This compound was synthesized by a modified procedure reported in the literature.[9(e)] The details are as follows. HC≡CC_6H_4-*p*-NHC(O)O*t*Bu (2.0 g, 9.2 mmol), potassium carbonate (2.4 g, 11.0 mmol), and CCl_4 (9 mL) were fed into a flask equipped with a three-way stopcock after flushing with Ar. Then, a solution of tetra-*n*-butylammonium fluoride in THF (1.0 mol/L, 0.5 mL, 0.5 mmol) was added to the mixture. After stirring the resulting mixture at 45 °C overnight, MeOH (5 mL) and $CHCl_3$ (40 mL) were added to the mixture. The resulting solution was washed with 1 M hydrochloric acid (2 × 50 mL) and then with water (50 mL). The organic phase was dried with anhydrous magnesium sulfate and the solvent was evaporated. The crude product was purified by preparative HPLC to yield the desired product (0.5 g, 2.0 mmol) as a light yellow crystalline solid in 21% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29–7.37 (m, 4H; Ar), 6.52 (s, 1H; NH), 1.51 (s, 9H; CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.3, 138.7, 132.8, 118.0, 116.3, 81.0, 69.2, 67.0, 28.3; HR-MS (ESI): m/z calcd for $C_{13}H_{14}ClNO_2 + NH_4$: 269.1051 [M]; found 269.1057; ELEM ANAL calcd (%) for $C_{13}H_{14}ClNO_2$: C, 62.03; H, 5.61; N, 5.56; Cl, 14.08; found: C, 61.75; H, 5.55; N, 5.50; Cl, 14.12.

Synthesis of 1-chloro-2-(2-isopropyl)phenylacetylene (**5**). This compound was synthesized in a similar manner to a procedure in the literature.[9(e)] The details are as follows. $HC{\equiv}CC_6H_4$-*o*-*i*Pr (1.4 g, 9.7 mmol), potassium carbonate (1.6 g, 11.6 mmol), and CCl_4 (9.7 mL) were fed into a flask equipped with a three-way stopcock under nitrogen gas. Then, a solution of tetra-*n*-butylammonium fluoride in THF (1.0 mol/L, 0.5 mL, 0.5 mmol) was added to the mixture. After stirring the resulting mixture at 45 °C overnight, MeOH (1 mL) and $CHCl_3$ (40 mL) were added to the mixture. The resulting solution was washed with 1 M hydrochloric acid (2 × 40 mL) and then with water (40 mL). The organic phase was dried with anhydrous magnesium sulfate and the solvent was evaporated. The crude product was purified by preparative HPLC to yield the desired product as a colorless oil in 15% yield. ^1H NMR (400 MHz, $CDCl_3$): δ 7.40–7.42 (m, 1H; Ar), 7.25–7.32 (m, 2H; Ar), 7.10–7.14 (m, 1H; Ar), 3.40 (m, $J = 6.8$ Hz, 1H; CH of *i*Pr), 1.27 (d, $J = 6.8$ Hz, 6H; CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.1, 132.8, 128.8, 125.5, 125.0, 120.8, 70.9, 68.3, 31.6, 23.2. HR-MS (ESI): *m/z* calcd for $C_{11}H_{11}Cl$: 178.0549 [M]; found 178.0541; ELEM ANAL calcd (%) for $C_{11}H_{11}Cl$: C, 73.95; H, 6.21; Cl, 19.84; found: C, 74.06; H, 6.36; C, 20.03.

Polymerization

Polymerization by Pd Catalyst

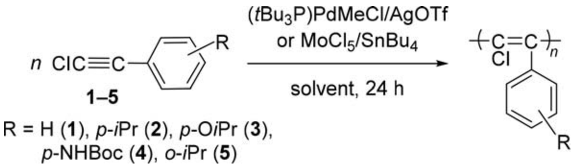
Monomers **1**–**5** were polymerized employing the standard Schlenk techniques following the same procedure. Typical procedure: Monomer **2** (200 mg, 1.12 mmol) was fed into a Schlenk tube, and toluene (280 mL) was added to the monomer. In another Schlenk tube, a catalyst solution was prepared by stirring 1.0 equivalent of (tBu$_3$P)PdMeCl (16.0 mg, 0.04 mmol) with 1.2 equivalents of AgOTf (14.0 mg, 0.05 mmol) in toluene (560 mL) at 50 °C. After 30 min, the catalyst solution was filtrated and a portion of the catalyst solution (280 mL) was added to the monomer solution. After stirring at 80 °C for 24 h, CH_3COOH (100 mL) was added to the mixture, and the reaction mixture was poured into MeOH (200 mL) to precipitate a solid, which was separated by filtration. The MeOH-insoluble solid was washed with THF until the washing solution became colorless. The THF solution used for washing was evaporated, and the solid obtained was dissolved in a small amount of $CHCl_3$ (0.5 mL), reprecipitated with $Et_2O/MeOH = 1/3$ (80 mL), and dried under vacuum to obtain a yellow solid.

Polymerization by Mo Catalyst ($MoCl_5/SnBu_4$)

The polymerization of monomers **2**–**5** followed a similar procedure employing the standard Schlenk techniques. Typical procedure: Monomer **2** (200 mg, 1.12 mmol) and toluene (560 mL) were placed under Ar. In a separate Schlenk tube, a solution of Mo catalyst was prepared by stirring $MoCl_5$ (12 mg, 0.04 mmol) and $SnBu_4$ (14 mL, 0.04 mmol) in toluene (1.12 mL). A portion of the Mo catalyst solution (560 mL) was added to the monomer solution, and the resulting mixture was kept at 30 °C for 24 h. The reaction mixture was poured in MeOH. The solid product was obtained after filtration and vacuum drying.

RESULTS AND DISCUSSION

The polymerization of 1-chloro-2-arylacetylenes **1**–**5** was carried by two type of catalysts, (tBu$_3$P)PdMeCl/AgOTf[7] and $MoCl_5/SnBu_4$[9] (Scheme 1). As summarized in Table 1, the Pd catalyst polymerized monomer **1** to yield the corresponding polymer [poly(**1**)-Pd] with an M_w of 6,500 (entry 1) in 30% while the Mo catalyst yielded a polymer [poly(**1**)-Mo] with an M_w of 690,000 in 91% (entry 2).[9(c)] Both the yield and M_w of poly(**1**)-Pd were lower than those of poly(**1**)-Mo. A similar trend was observed in the polymerization of monomer two substituted with a para-isopropyl group (entries 3 and 4). However, the Pd catalyst polymerized monomer **3** substituted with a para-isopropoxy group to give poly(**3**) with a higher M_w in a higher yield than the Mo catalyst (entries 5 and 6). The PDI of poly(**3**)-Pd was small (1.58), while that of poly(**3**)-Mo was large (3.13), indicating that the polymerization using the Pd catalyst proceeded in a more controlled manner than that using the Mo catalyst. The lower yield of poly(**3**)-Mo is attributable to the presence of an ether oxygen atom in **3**, which possibly coordinates to the Mo catalyst resulting in decrease of catalytic activity. The yield of poly(**3**)-Pd was not low compared with those of poly(**1**)-Pd and poly(**2**)-Pd presumably due to the low oxophilicity of Pd compared with Mo. The difference of sensitivity between the Pd and Mo catalysts towards polar groups was clearly evidenced by the polymerization of polar monomer **4** bearing a para-carbamate substituent. The Pd catalyst polymerized **4** to yield a polymer ($M_w = 9{,}100$) in 21% yield (entry 7). In contrast, the Mo catalyst yielded no polymer, and **4** was quantitatively recovered from the reaction mixture after evaporating the solvent (entry 8), indicating the higher oxophilicity of Mo than that of Pd resulting in deactivation of the Mo catalyst.



SCHEME 1 Polymerization of 1-chloro-2-arylacetylenes **1**–**5** by (tBu$_3$P)PdMeCl/AgOTf and $MoCl_5/SnBu_4$.

Next, the polymerization of monomer **5** substituted with an ortho-isopropyl group was examined using the Pd and Mo catalysts. The Pd catalyst polymerized monomer **5** to yield poly(**5**) in 77% (entry 9), while the Mo catalyst yielded poly(**5**) as low as 10% (entry 10). The low yield of poly(**5**)-Mo is reasonable because Mo catalysts cannot polymerize sterically hindered acetylene monomers efficiently.[3(f)] It is likely that the ortho-isopropyl group of **5** sterically hampers the Mo catalyst to decrease the activity. The Pd catalyst performed better in the polymerization of **5** probably because it has plenty of room at the coordination site due to the T-shape tricoordinated structure in contrast to crowded tetracoordinated common Pd catalysts.[7]

We compared the difference of the properties between the polymers synthesized by the polymerization using the Pd and Mo catalysts. The Pd-based polymers were partly insoluble in common organic solvents including THF, $CHCl_3$, CH_2Cl_2, benzene, toluene, and MeOH. It is likely that the THF-insoluble fractions are high molecular weight polymers featuring high cis-contents formed by the polymerization via

TABLE 1 Polymerization of **1**–**5** by (tBu$_3$P)PdMeCl/AgOTf or MoCl$_5$/SnBu$_4$[a]

Entry	Monomer	Cat	Solvent	$[M]_0$ (M)	Temp (°C)	Yield[b] (%)	Content of insoluble fraction[c] (%)	M_w[d]		PDI[d]
1	**1**	Pd	toluene	2.0	80	30	22	6,500		1.62
2[e]	**1**	Mo	toluene	1.0	30	91	0	690,000		–
3	**2**	Pd	toluene	2.0	80	31	18	20,600	(81%)	2.11
4	**2**	Mo	toluene	1.0	30	74	0	90,500		2.31
5	**3**	Pd	toluene	2.0	80	34	24	42,700	(86%)	1.58
6	**3**	Mo	toluene	1.0	30	26	0	34,500	(85%)	3.13
7	**4**	Pd	$CHCl_3$	0.8	60	21	16	9,100	(86%)	1.91
8	**4**	Mo	$CHCl_3$	0.8	60	–	–	–		–
9	**5**	Pd	toluene	2.0	80	77	49	18,300	(89%)	1.99
10	**5**	Mo	toluene	1.0	30	10	0	13,600	(84%)	1.62

[a] Conditions: time 24 h. $[\text{monomer}]_0/[\text{Pd}] = [\text{monomer}]_0/[\text{Mo}] = 50$, $[\text{AgOTf}]/[\text{Pd}] = 1.2$, $[\text{Mo}]/[\text{Sn}] = 1.0$.

[b] MeOH-insoluble part. The Pd-based polymers were reprecipitated with MeOH/Et$_2$O = 2/1.

[c] Insoluble part in common organic solvents including THF, $CHCl_3$, CH_2Cl_2, benzene, toluene, and MeOH.

[d] THF-soluble part estimated by SEC eluted with THF calibrated by polystyrene standards. The quantities in parentheses are the area ratios of the peaks whose data are listed. The other parts were lower M_w products.

[e] Data taken from ref. 9(c).

the coordination-insertion mechanism in a manner similar to Rh-catalyzed polymerization of monosubstituted acetylenes,[7] as well as the reports suggesting low solubility of substituted cis-cisoidal polyacetylenes.[3(e),15] In fact, both the THF-soluble and insoluble parts exhibited similar IR spectroscopic patterns. Morokuma and coworkers have reported the formation of cis-stereoregulated substituted polyacetylenes by the coordination-insertion mechanism.[16] However, the Mo-based polymers were completely soluble in THF, presumably due to the low stereoregularity of the main chain originated the polymerization via the metathesis mechanism.[3]

The difference of structures between the polymers synthesized by Mo and Pd catalysts was also suggested by ^{1}H NMR spectroscopy, in particular at the region of the aromatic protons. For instance poly(**2**)-Pd displayed a signal around 6.64 ppm and a shoulder around 6.85 ppm, while poly(**2**)-Mo displayed two broad signals with almost the same intensity around 6.88 and 6.68 ppm (Fig. 1). However, the chemical shift of the signal assignable to the isopropyl group remained practically unaffected regardless of the catalyst employed. The shape of the aromatic proton signal was also dependent on the catalysts employed in the cases of poly(**3**) and poly(**5**), especially in the latter (Figs. 2 and 3).

In the ^{13}C NMR spectra of poly(**2**) and poly(**3**), no C≡C carbon signals of the monomers but broad C=C carbon signals assignable to the main chains were observed around 137–139 ppm. Unfortunately, no clear information was obtained regarding the stereoregularity of the polymers (Figs. 4 and 5) due to the broad main chain carbon signals in the ^{13}C NMR spectra of the polymers. No significant difference was observed between the signals of the aryl and isopropyl groups. The poor solubility of poly(**5**)-Pd prevented us from measuring the ^{13}C NMR spectrum. The IR spectra of the polymers also confirmed the

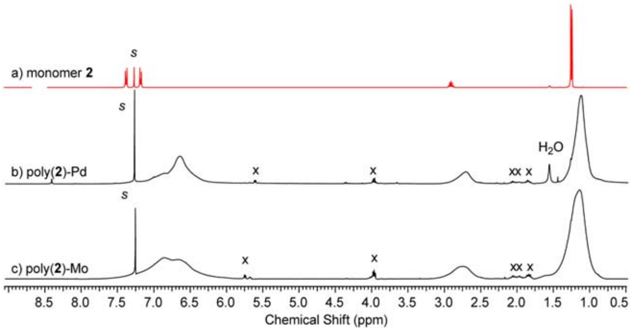


FIGURE 1 ^{1}H NMR spectra of (a) monomer **2**, (b) poly(**2**) synthesized by the polymerization using (tBu$_3$P)PdMeCl/AgOTf (Table 1, entry 3), (c) poly(**2**) synthesized using MoCl$_5$/SnBu$_4$ (Table 1, entry 4). All the spectra were measured in $CDCl_3$ at room temperature (*s*: solvent, x: impurity). [Color figure can be viewed at wileyonlinelibrary.com]

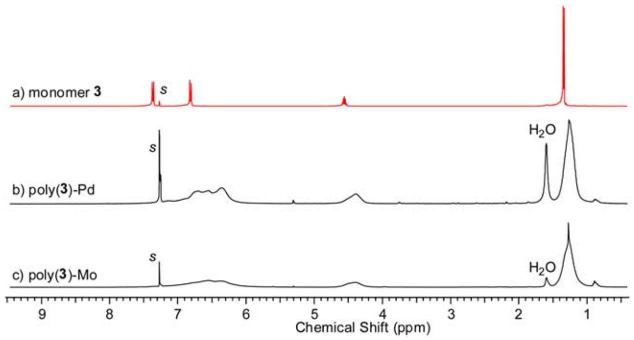


FIGURE 2 ^{1}H NMR spectra of (a) monomer **3**, (b) poly(**3**) synthesized by the polymerization using (tBu$_3$P)PdMeCl/AgOTf (Table 1, entry 5), (c) poly(**3**) synthesized using MoCl$_5$/SnBu$_4$ (Table 1, entry 6) measured in $CDCl_3$ at room temperature (*s*: solvent). [Color figure can be viewed at wileyonlinelibrary.com]

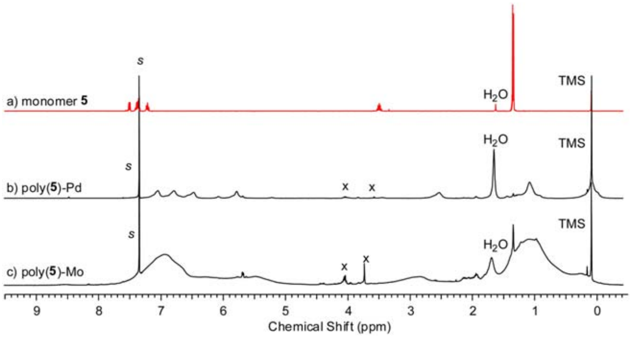


FIGURE 3 ^{1}H NMR spectra of (a) monomer **5**, (b) poly(**5**) synthesized by the polymerization using (tBu$_3$P)PdMeCl/AgOTf (Table 1, entry 9), (c) poly(**5**) synthesized by MoCl$_5$/SnBu$_4$ (Table 1, entry 10) measured in CDCl$_3$ at room temperature (*s*: solvent, x: impurity). [Color figure can be viewed at wileyonlinelibrary.com]

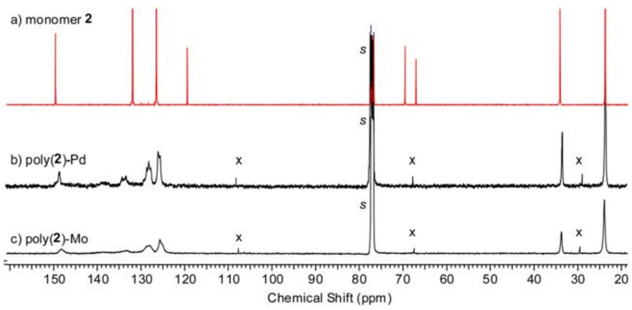


FIGURE 4 ^{13}C NMR spectra of (a) monomer **2**; (b) poly(**2**) synthesized by the polymerization using (tBu$_3$P)PdMeCl/AgOTf (Table 1, entry 3) and, (c) poly(**2**) synthesized using MoCl$_5$/SnBu$_4$ (Table 1, entry 4) measured in CDCl$_3$ at room temperature (*s*: solvent, x: impurity). [Color figure can be viewed at wileyonlinelibrary.com]

complete consumption of the C≡C bond of the acetylene monomers, i.e., no signal characteristic to the C≡C stretching band around 2221 cm^{-1} (Figs. 6–8) was observed. Intense C—Cl stretching absorption bands were observed around 750–835, suggesting no significant loss of Cl atom from the polymers.

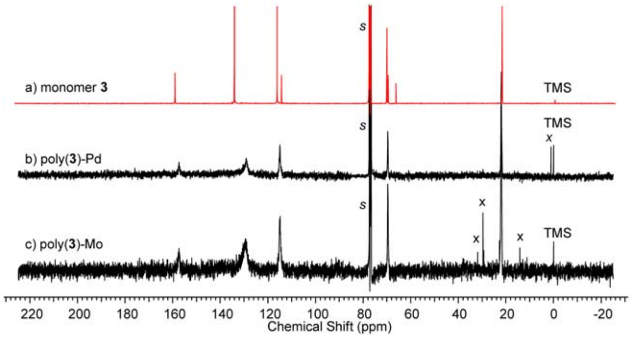


FIGURE 5 ^{13}C NMR spectra of (a) monomer **3**; (b) poly(**3**) synthesized by the polymerization using (tBu$_3$P)PdMeCl/AgOTf (Table 1, entry 5), (c) poly(**3**) synthesized by MoCl$_5$/SnBu$_4$ (Table 1, entry 6) measured in CDCl$_3$ at room temperature (*s*: solvent, x: impurity). [Color figure can be viewed at wileyonlinelibrary.com]

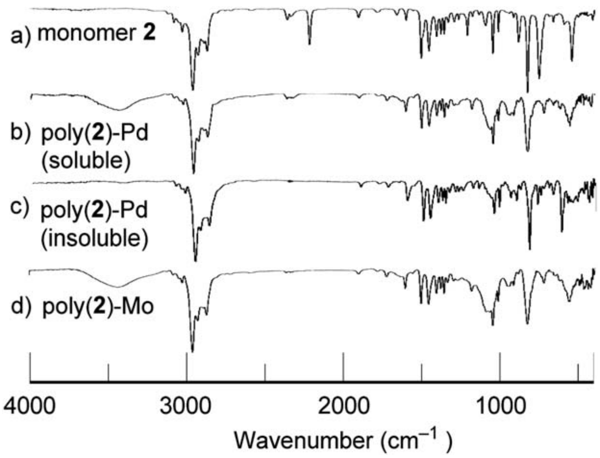


FIGURE 6 IR spectra of (a) monomer **2**; (b) poly(**2**) synthesized by the polymerization using (tBu$_3$P)PdMeCl/AgOTf (Table 1, entry 3), (c) insoluble fraction of poly(**2**) synthesized using (tBu$_3$P)PdMeCl/AgOTf (Table 1, entry 3), (d) poly(**2**) synthesized using MoCl$_5$/SnBu$_4$ (Table 1, entry 4) measured by the KBr pellet method.

The optical properties of the polymers were analyzed to examine the difference arising from the catalysts used in the polymerization. The UV–vis spectroscopic analysis revealed the shorter absorption length of Pd-based poly(**2**), poly(**3**) and poly(**5**) than those of the corresponding Mo-based polymers as shown in Figure 9(a–c), tops. In particular, the $\lambda_{\max}$ of poly(**5**)-Pd (337 nm) was observed at a considerable shorter wavelength position than that of poly(**5**)-Mo (382 nm). The color difference between the two polymers was clearly noticed by naked eye, dark yellow (Pd-based polymer) and orange (Mo-based polymer). The lower absorption wavelength of the Pd-based polymers than that of the Mo-based counterparts is

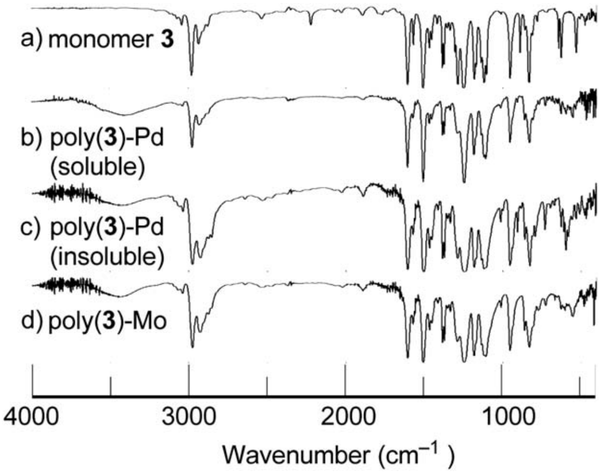


FIGURE 7 IR spectra of (a) monomer **3**; (b) poly(**3**) synthesized by the polymerization using (tBu$_3$P)PdMeCl/AgOTf (Table 1, entry 5), (c) insoluble fraction of poly(**3**) synthesized using (tBu$_3$P)PdMeCl/AgOTf (Table 1, entry 5), (d) poly(**3**) synthesized using MoCl$_5$/SnBu$_4$ (Table 1, entry 6) measured by the KBr pellet method.

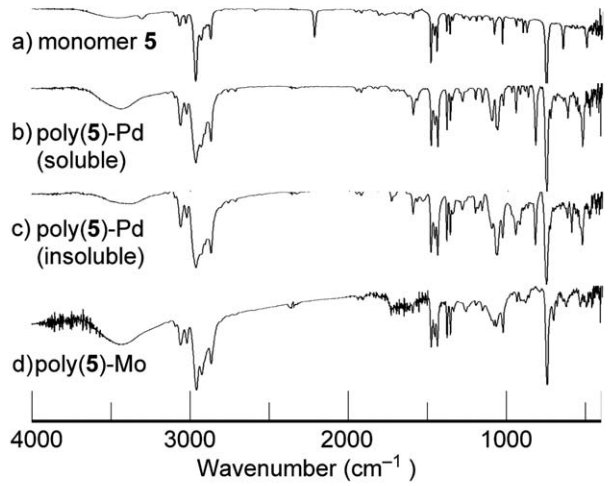


FIGURE 8 IR spectra of (a) monomer **5**, (b) poly(**5**) synthesized by the polymerization using (tBu$_3$P)PdMeCl/AgOTf (Table 1, entry 9), (c) insoluble fraction of poly(**5**) synthesized using (tBu$_3$P)PdMeCl/AgOTf (Table 1, entry 9), (d) poly(**5**) synthesized using MoCl$_5$/SnBu$_4$ (Table 1, entry 10) measured by the KBr pellet method.

attributable to a shorter conjugation length, presumably originates from the higher cis-contents of the Pd-based polymers.[7]

Figure 9(a–c), bottoms show the emission spectra of poly(**2**), poly(**3**), and poly(**5**). As summarized in Table 2, para-substituted poly(**2**) and poly(**3**) emitted fluorescence with small quantum yields ($\Phi_{\mathrm{emi}} = 0.7–1.1\%$) regardless of the catalyst employed in the polymerization. Interestingly, ortho-substituted poly(**5**)-Pd emitted fluorescence with a moderate quantum yield ($\Phi_{\mathrm{emi}} = 14.0\%$), while poly(**5**)-Mo did with a small value ($\Phi_{\mathrm{emi}} = 0.7\%$). The ortho-substitution and high cis-content are effective to enhance the fluorescence emission. No relevant tendency was observed between the molecular weights and fluorescence (Table 2, entries 5 and 6).

TABLE 2 Fluorescence Quantum Yields of Poly(**2**), Poly(**3**), and Poly(**5**) Synthesized by the Polymerization using (tBu$_3$P)PdMeCl/AgOTf and MoCl$_5$/SnBu$_4$[a]

Entry	Monomer	Catalyst	Φ_{emi}[b] (%)
1	**2**	Pd	1.1
2	**2**	Mo	1.1
3	**3**	Pd	0.7
4	**3**	Mo	1.9
5	**5**	Pd	14.0
6[c]	**5**	Pd	11.5
7	**5**	Mo	0.7

[a] Samples synthesized in Table 1.

[b] Calculated from the emission spectra of the polymers excited at 320 nm measured in THF using anthracene as a standard in EtOH ($\Phi_{\mathrm{emi}} = 0.27$). The values were corrected using the refractive indices of THF and EtOH.

[c] Fraction separated from poly(**5**)-Pd Et$_2$O-soluble part (Table 1) employing preparative HPLC.

CONCLUSIONS

In this article, we have demonstrated the polymerization of 1-chloro-2-arylacetylenes **1**–**5** with various substituents using Pd and Mo catalysts, and the properties of the formed polymers. The Pd catalyst outperformed the Mo catalyst for the polymerization of monomers **3**–**5** substituted with polar groups. The ^{1}H NMR spectra suggested the difference of stereostructures between the Pd- and Mo-based polymers. The UV–vis spectra indicated a higher cis-content of the Pd-based polymers than that of the Mo-based polymers. The Pd-based

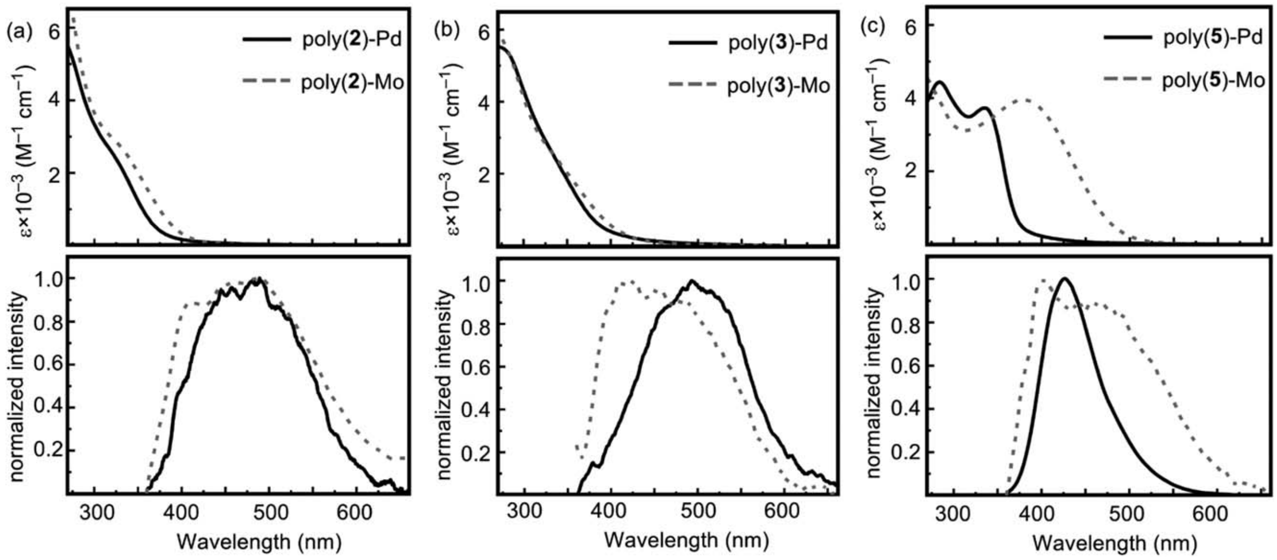


FIGURE 9 UV–vis absorption (tops) and emission (bottoms) spectra of (a) poly(**2**), (b) poly(**3**), and (c) poly(**5**) synthesized by the polymerization using (tBu$_3$P)PdMeCl/AgOTf (solid line) and MoCl$_5$/SnBu$_4$ (dotted line) measured in THF at room temperature ($c = 0.02$ mM). Excitation wavelength: 320 nm.

cis-rich polymer derived from an ortho-substituted monomer emitted fluorescence with a higher intensity than that of the Mo-based counterpart. As far as we know, this is the first study on the relationship between the main chain stereoregularity and absorption-emission properties of disubstituted acetylene polymers.

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