Polymerization of Optically Active Disubstituted Acetylene Monomers by Pd Catalyst Bearing Bulky Phosphine Ligand

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ABSTRACT: Chloro- and aryl-substituted acetylene monomers having an optically active group were polymerized by a Pd catalyst [(^tBu₃P)PdMeCl] bearing a bulky phosphine ligand, and by MoCl₅ for comparison. The corresponding disubstituted acetylene polymers with M_n 's = 2000–19,500 and 6900–10,800 were obtained in 29–83% and 11–62% yields when the Pd and Mo catalysts were used, respectively. The formation of polyacetylenes, poly[(*R*)-**1***p*], poly[(*R*)-**1***m*], and poly[(*S*)-**2***p*] were confirmed by SEC and the presence of a Raman scattering peak based on the alternating double bonds of the main chain. Pdbased poly[(*R*)-1*m*] exhibited CD signals around 350 nm assignable to a certain secondary structure, while Mo-based poly[(*R*)-1*m*] did not. © 2017 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. 2017, *00*, 000–000

KEYWORDS: catalysts; conjugated polymers; polyacetylenes; UV-vis spectroscopy

 C_6H_4]₃] (nbd = 2,5-norbornadiene) and [(tfb)Rh{C(Ph)=CPh_2}

INTRODUCTION The polymerization of substituted acetylenes gathers much attention because the formed polymers exhibit high stability,¹ selective gas permeability,^{2–5} liquid crystallinity^{6,7} as well as photoelectric properties.^{8–10} Acetylene polymers substituted with optically active groups commonly adopt chiral secondary structures such as predominantly one-handed helices and chiral aggregates, which are applicable to chiral recognition/resolution, asymmetric catalysis, enantioselective crystallization, etc.¹¹

Substituted acetylenes are commonly polymerized with transition-metal catalysts. When early-transition-metal catalysts including Ta,^{4,5} Mo,^{10,12} Ru,¹³ and W¹⁴ polymerize acetylene monomers via the metathesis mechanism, while latetransition-metal catalysts including Rh, Pd, and Ir complexes¹⁵ polymerize acetylene monomers via the coordination-insertion mechanism. The early-transition-metal catalysts are sensitive to moisture and hetero-atom-containing monomers because of their high Lewis acidity, and polymerize mono- and disubstituted acetylene monomers to give the corresponding polymers with no *cis/trans* selectivity of the double bonds in the main chain. On the contrary, late-transition-metal catalysts are tolerant to moisture and hetero-atom-containing monomers because of their low Lewis acidity, and give polymers with high cis-stereoregularity. Well-defined Rh complex catalysts having -C(Ph)=CPh₂ group such as [(nbd)Rh{C(Ph)=CPh₂}{P(4-F-

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 $(PPh_3)]/PPh_3$ (tfb = tetrafluorobenzobarrelene) polymerize phenyl acetylene in a living fashion.¹⁶⁻¹⁸ Thus the Rh complexes are excellent catalysts for monosubstituted acetylene monomers, but they cannot polymerize disubstituted acetylene monomers presumably due to the large steric hindrance for monomer coordination and insertion processes. It is desirable to develop catalysts for the polymerization of disubstituted acetylene monomers to give highly stereoregular polymers. We have recently found that palladium (Pd) complexes such as [(^tBu₃P)PdMeCl] bearing a bulky alkyl monophosphine ligand show excellent activity in conjunction with silver trifluoromethanesulfonate (AgOTf) for the polymerization of disubstituted acetylene monomers as well as monosubstituted ones, wherein the polymerization progresses via the coordination-insertion mechanism to give polymers with high *cis*-contents.¹⁹ Thus far, optically active polymers of various monosubstituted acetylene monomers having a chiral group are widely synthesized, and the secondary structures were extensively studied.²⁰ On the contrary, only a few examples are reported regarding optically active polymers of disubstituted acetylene monomers. Herein, we wish to report the polymerization of chloro- and aryl-substituted acetylene monomers having an optically active group, by a Pd catalyst [(^tBu₃P)PdMeCl] bearing a bulky phosphine ligand, and by MoCl₅ for comparison. We also report the comparison of chiroptical properties between the Pd- and Mo-based polymers.

1

EXPERIMENTAL

Measurements

¹H (400 MHz), ¹³C (100 MHz) NMR spectra were recorded on a JEOL ECA-400 or a JEOL ECS-400 spectrometer. IR spectra were measured on a JASCO FT/IR-4100 spectrophotometer. Specific rotations were measured on a JASCO DIP-1000 digital polarimeter. Melting points (mp) were measured on a Yanaco micro melting point apparatus. Elemental analysis was done at the analytical center, Faculty of Engineering, Osaka University. Number- and weight-average molecular weights $(M_n \text{ and } M_w)$ of polymers were determined by SEC equipped with a TSK gel α -3000 eluted with a solution of LiBr (10 mM) in N,N-dimethylformamide (DMF) at 40 °C calibrated by polystyrene standards. Raman spectra were measured on a Tokyo Instruments Nanofinder30. Thermogravimetric analysis was performed on a SHIMADZU TGA-50 thermogravimetric analyzer. CD and UV-vis absorption spectra were recorded on a JASCO J-820 spectropolarimeter. POM images were taken by a Nikon ECLIPSE LV100POL polarized optical microscope. The refractive index of thin films spin-coated at about 0.1 μ m thickness on silicon wafers was measured by ellipsometry with a Horiba SmatSE ellipsometer.

Monomer Synthesis

(R)-1-(2-Butoxy)-4-Iodobenzene [(R)-1p-a]

4-Iodophenol (13.98 g, 50.6 mmol), (*S*)-(+)-2-butanol (8.60 g, 116 mmol), and PPh₃ (30.50 g, 116 mmol) were dissolved in THF (300 mL). Diisopropyl azodicarboxylate (DIAD, 61.1 mL, 116 mmol) in THF (100 mL) was added to the solution dropwise under Ar atmosphere at 0 °C. The resulting solution was warmed to room temperature and stirred for 48 h. After evaporating the solvent, Et₂O (50 mL) was added to the residue, and the resulting mixture was filtrated and washed with 1 M HCl aq (50 mL) twice. It was concentrated, and the residual mass was purified by silica gel column chromatography eluted with hexane/ethyl acetate = 4/1 (v/v) to obtain (*R*)-**1***p*-**a** as a clear and colorless liquid (13.98 g). Yield 44%. ¹H NMR (400 MHz, CDCl₃): δ 0.95 (t, *J* = 7.6 Hz, 3H, CH₃), 1.26 (d, *J* = 6.0 Hz, 3H, CH₃), 1.56–1.73 (m, 2H, CH₂), 4.19–4.26 (m, 1H, CH), 6.64–7.53 (m, 4H, Ar).

Trimethylsilyl-4-[(R) – 2-*Butoxy]Phenylacetylene* [(*R*) – 1*p*-*b*] (*R*)-1*p*-a (13.98 g, 50.6 mmol), PdCl₂(PPh₃)₂ (3.58 g, 5.10 mmol), and PPh₃ (5.36 g, 20.4 mmol) were dissolved in a mixture of THF (170 mL) and Et₃N (68.3 mL) under Ar atmosphere. The resulting mixture was stirred at 50 °C for 3 h. After cooling to room temperature, solvent-insoluble products were removed by filtration, and the solvent was evaporated. The residue was purified by column chromatog-raphy on a silica gel eluted with hexane/CHCl₃ (v/v) = 5/1 to obtain (*R*)-1*p*-b as a yellow liquid (8.05 g, 32.6 mmol). Yield 65%. ¹H NMR (400 MHz, CDCl₃): δ 0.22 (s, 9H, TMS), 0.95 (t, *J* = 7.6 Hz, 3H, CH₃), 1.27 (d, *J* = 6.0 Hz, 3H, CH₃), 1.54–1.78 (m, 2H, CH₂), 4.25–4.32 (m, 1H, CH), 6.79–7.38 (m, 4H).



SCHEME 1 Synthesis of monomers. Symbols *p* and *m* in the compound names indicate the *para*- and *meta*-substitutions.

Chloro-4-[(R)-2-Butoxy]Phenylacetylene [(R)-1p]

A solution of 1 M Bu₄NF in THF (18.7 mL, 18.7 mmol) was added to a mixture of (R)-1p-b (8.05 g, 32.6 mmol), K₂CO₃ (4.57 g 32.6 mmol), and CCl₄ (100 mL) under Ar. The resulting mixture was stirred at room temperature overnight. Et₂O (100 mL) was added to the mixture, and the resulting mixture was subsequently washed with 1 M HCl aq (50 mL imes2), saturated NaHCO₃ aq (50 mL \times 2) and saturated NaCl aq (100 mL). The organic layer was separated, dehydrated by anhydrous MgSO₄ and concentrated on a rotary evaporator. The residual mass (1.20 g) was purified by a Japan Analytical Industry preparative HPLC (columns: Shodex GPC K-5001 G and K-5002.5 F) eluted with $CHCl_3$ to obtain (R)-1pas a brown liquid (0.873 g, 4.06 mmol). Yield 73%. $[\alpha]_{\rm D} = 19.7^{\circ} (c = 0.1 \text{ g/dL}, \text{ THF, } 25 \text{ °C}). \text{ IR } (\text{cm}^{-1}): 832, 1249,$ 2221, 2878, 2936, 2974. ¹H NMR (400 MHz, CDCl₃): δ 0.95 (t, J = 7.6 Hz, 3H, CH₃), 1.27 (d, J = 6.4 Hz, 3H, CH₃), 1.55-1.78 (m, 2H, CH₂), 4.25-4.32 (m, 1H, CH), 6.78-7.35 (m, 4H). ¹³C NMR (100 MHz, CDCl₃): δ 9.84, 19.2, 29.2, 66.2, 75.4, 76.8, 77.1, 77.4, 115.8, 133.5, 158.6. Elem. Anal. Calcd for C₁₂H₁₃OCl, C: 69.07%; H 6.28%. Found C: 67.95%, H 6.20%.

Chloro-3-[(R)-2-Butoxy]Phenylacetylene [(R)-1m]

This compound was synthesized in a manner similar to the method with that for (*R*)-**1***p* described above. Yield 65%. [α]_D = 42.2° (*c* = 0.1 g/dL, THF, 25 °C). IR (cm⁻¹): 686, 785, 1286, 1596, 2217, 1878, 1935, 2972. ¹H-NMR (400 MHz, CDCl₃) δ 0.96 (t, *J* = 8.0 Hz, 3H, CH₃), 1.28 (d, *J* = 6.0 Hz, 3H, CH₃), 1.60–1.75 (m, 2H, CH₂), 4.23–4.32 (m, 1H, CH), 6.85–7.24 (m, 4H, Ar), ¹³C NMR (100 MHz, CDCl₃) δ 10.0, 19.5, 29.5, 67.9, 75.0, 76.8, 77.3, 77.7, 117.1, 119.0, 123.2, 124.3, 129.5, 158.2. Elem. Anal. Calcd for C₁₂H₁₃OCl, C: 69.07%; H 6.28%. Found C: 68.26%, H 6.25%.

Chloro-4-[(S)-1-Phenyl-1-Ethoxy]Phenylacetylene [(S)-2p]

This compound was synthesized in a manner similar to the method with that for (*R*)-**1***p* described above. $[\alpha]_D = 2.92^{\circ}$ (*c* = 0.1 g/dL, THF). ¹H NMR (400 MHz, acetone-*d*₆): δ 7.46–7.22 (Ar, 5H), 6.94-6.86 (Ar, 2H), 5.00 (q, 1H, *J* = 6.3 Hz), 1.58 (d, 3H, *J* = 6.3 Hz). ¹³C NMR (100 MHz, acetone-*d*₆): δ 159.4, 143.8, 134.0, 129.4, 128.3, 126.4, 116.9, 114.3, 76.4, 70.2, 66.4, 24.6. IR (KBr): 2985.2, 2975.8, 2927.0, 1604.4,



SCHEME 2 Polymerization of (*R*)-**1**p, (*R*)-**1**m and (*S*)-**2**p using [(^tBu₃P)PdMeCl]/AgOTf and MoCl₅/Bu₄Sn. Symbols p and m in the compound names indicate the *para*- and *meta*-substitutions.

1508.3, 1287.8, 1241.3, 1180.0, 1078.0, 835.7, 763.1, 699.4. Elem. Anal. Calcd for $C_{16}H_{13}$ OCl, C: 74.86%; H 5.10%. Found C: 74.93%, H: 5.03%. MS (EI): m/z 256, 258 (M⁺), 256:258 = 3:1.

Polymerization

Polymerization by Pd Catalyst

Typical procedure: Monomer (R)-1p (234 mg, 1.12 mmol) and toluene (280 mL) were fed into a Schlenk tube under Ar. A catalyst solution was prepared in another Schlenk tube by mixing (^tBu₃P)PdMeCl (16.0 mg, 0.04 mmol) and AgOTf (14.0 mg, 0.05 mmol) in toluene (560 $\mu L)$ and Ar. After 30 min, the catalyst solution was filtrated and a portion of the solution (280 µL) was added to the aforementioned monomer solution. After stirring at 80 °C for 20 h, CH₃COOH (100 mL) was added to the mixture, and the reaction mixture was poured into MeOH (200 mL) to precipitate a solid. It was separated by filtration, and 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 CH₂Cl₂ (0.5 mL), reprecipitated with MeOH (200 mL), and dried under vacuum to obtain a yellow solid.

Spectroscopic Data of the Pd-Based Polymers

Poly[(*R*)-1*p*] IR (cm⁻¹): 3630, 3434, 2966, 2931, 1605, 1507, 1465, 1377, 1248, 1181, 1098, 1028, 923, 803, ¹H-NMR (400 MHz, CDCl₃): δ 7.29-7.21 (m, 4H), 1.55 (s, 2H), 1.34-0.75 (br, m, 2 H). **Poly**[(*R*)-1*m*] IR (cm⁻¹): 3434, 2968, 2933, 2878, 1595, 1485, 1430, 1378, 1261, 1216,



FIGURE 1 Raman spectra of poly[(R)-1p] obtained by the polymerization using Pd (entry 1 in Table 1) and Mo (entry 2 in Table 1) catalysts. [Color figure can be viewed at wileyonlinelibrary.com]

1030, 1003, 877, 796, 696, ¹H-NMR (400 MHz, CDCl₃): δ 7.26 (s 4H), 3.49 (s, 1H), 1.56 (br, 3H). **Poly**[(*S*)-2*p*] IR (cm⁻¹): 3434, 2975, 2927, 1604, 1507, 1449, 1375, 1241, 1175, 1069, 1011, 931, 831, 759, 700, ¹H-NMR (400 MHz, CDCl₃): δ 7.40-7.11 (br, 4H), 3.49 (s, 1H), 1.77-1.43 (br, 3H).

Polymerization by Mo Catalyst

Typical procedure: Monomer (*R*)-**1***p* (209 mg, 1.00 mmol) and toluene (2.5 mL) were fed into a Schlenk tube under Ar. A solution catalyst solution was prepared in another Schlenk tube by mixing MoCl₅ (5.5 mg, 0.02 mmol) and Bu₄Sn (14 μ L, 0.04 mmol) in toluene (2.5 mL). A portion of the Mo catalyst solution (2.5 mL) was added to the aforementioned monomer solution. After stirring at 30 °C for 24 h, the reaction mixture was poured in MeOH (200 mL) to precipitate a solid. It was separated by filtration and vacuum drying.

Spectroscopic Data of the Mo-Based Polymers

Poly[(*R*)-1*p*] IR (cm⁻¹): 3436, 2964, 2933, 2878, 1605, 1507, 1465, 1377, 1261, 1181, 1097, 1025, 923, 801, ¹H-NMR (400 MHz, CDCl₃): δ 7.27-7.20 (br, m 4H), 5.40-4.92 (br, 1H) 1.64-1.45 (br, 3H)

Poly[(*R*)-1*m*] IR (cm⁻¹): 3449, 2964, 2926, 1605, 1508, 1458, 1377, 1261, 1181, 1097, 1025, 923, 801, 499, 468,

Entry	Monomer	Catalyst	[<i>M</i>] ₀ / [Pd or Mo]	[<i>M</i>] ₀ (mol/L)	Yield ^c (%)	M_{n}^{d}	D^{d}
1	(<i>R</i>)- 1 <i>p</i>	[(^t Bu ₃ P)PdMeCI], AgOTf ^a	30	1.3	29 ^c	9600	1.80
2	(<i>R</i>)- 1 <i>p</i>	MoCl₅, Bu₄Sn ^b	50	0.2	15 [°]	8000	1.60
3	(<i>R</i>)- 1 <i>m</i>	[(^t Bu ₃ P)PdMeCI], AgOTf ^a	30	1.3	83 ^c	19,500	_e
4	(<i>R</i>)- 1 <i>m</i>	MoCl₅, Bu₄Sn ^b	50	0.2	11 ^c	6900	1.94
5	(S)- 2p	[(^t Bu ₃ P)PdMeCl], AgOTf ^a	30	1.3	72 ^c	2600	1.83
6	(S)- 2p	[(^t Bu ₃ P)PdMeCl], AgOTf ^a	50	0.2	43 ^c	2000	2.20
7	(<i>S</i>)- 2 <i>p</i>	MoCl₅, Bu₄Sn ^b	50	0.2	62 ^c	10,800	2.13

TABLE 1 Polymerization of (R)-1p, (R)-1m, and (S)-2p

 a [AgOTf]/[Pd] = 1.2 in toluene at 80 $^{\circ}\text{C}$ for 20 h.

 $^{\rm b}$ [Bu₄Sn]/[Mo] = 2.0 in toluene at 80 °C for 24 h.

^c THF-soluble part.



^d Estimated by SEC eluted with DMF, polystyrene calibration.

^e Could not be properly estimated due to the very broad SEC peak.



FIGURE 2 TGA traces of poly [(S)-2p] obtained by polymerization using Pd (red line) and Mo (blue line) catalyst measured in N₂ at a heating rate of 10 °C/min. [Color figure can be viewed at wileyonlinelibrary.com]

¹H-NMR (400 MHz, CDCl₃): δ 7.36–7.16 (br, m 4H), 5.40– 4.92 (br, 1H) 1.80–1.38 (br, 3H). **Poly**[(*S*)–2*p*] IR (cm⁻¹): 3377, 3060, 3024, 2962, 2925, 2871, 1891, 1699, 1607, 1543, 1509, 1450, 1375, 1261, 1173, 1162, 1105, 907, 814, 700, 547 ¹H-NMR (400 MHz, CDCl₃): δ 7.52–7.10 (br, m 9H), 5.40–4.92 (br, 1H) 1.56–1.50 (br, 3H) 1.34–1.06 (br, 1H), 1.06–0.80 (br, 1H).

RESULTS AND DISCUSSION

Monomer Synthesis

Acetylene monomers (R)-**1**p, (R)-**1**m and (S)-**2**p substituted with chloro and optically active aryl groups were synthesized by the Mitsunobu reaction of m-/p-iodophenol and the corresponding optically active alcohols, followed by the Sonogashira-Hagihara coupling reaction with trimethylsilylacetylene, and then reaction with CCl₄ as illustrated in

Scheme 1. We failed to synthesize (R)-2m due to the unsuccessful Sonogashira–Hagihara coupling reaction of (R)-2m-a with trimethylsilylacetylene.

The polymerization of the three monomers was carried out by two types of catalysts, (${}^{t}Bu_{3}P$)PdMeCl/AgOTf and MoCl₅/ Bu₄Sn (Scheme 2). Table 1 lists the results of the polymerization. The Pd catalyst yielded the corresponding disubstituted acetylene polymers with M_{n} 's of 2000–19,500 in 29–83%. On the other hand, the Mo catalyst yielded the corresponding polymers with M_{n} 's of 6900–10,800 in 11–62%.

The Raman spectra of the polymers were measured to obtain information of the structures. As shown in Figure 1, both Pdand Mo-based poly[(R)-**1**p]s exhibited an intense absorption peak around 1600 cm⁻¹ assignable to C—C stretching of the polyacetylene backbone, indicating the proceeding of acetylene polymerization by the both catalysts. In this study, no information could be observed regarding the *cis/trans* content of the double bond of the main chain. *cis*-Polyacetylene derivatives tend to isomerize into *trans*,^{21,22} likely because the *cis*-structure is thermodynamically unfavorable to *trans*one. We have experienced thermally-induced *cis-trans* isomerization of substituted polyacetylene samples during Raman spectroscopic measurement due to the laser beam irradiation, and this study seems to be also the case.

Figure 2 depicts the TGA traces of Pd- and Mo-based poly[(*S*)-**2**p]s. The Pd-based polymer started decomposition around 250 °C, while the Mo-based polymer started decomposition around 200 °C. Judging also from the weight residue (59% and 49%) of the polymers at 500 °C, it is concluded that the Pd-based polymer is thermally more stable than the



FIGURE 3 CD and UV-vis spectra of poly[(R)-1p], poly[(R)-1m] and poly[(S)-2p] obtained by the polymerization using Pd (left: entries 1, 3, 5 in Table 1) and Mo (right: entries 2, 4, 7 in Table 1) catalysts measured in DMF (c = 0.04 mM) at 20 °C. [Color figure can be viewed at wileyonlinelibrary.com]



FIGURE 4 CD and UV-vis spectra of Pd-based poly[(*R*)-1*m*] measured in DMF (c = 0.04 mM) at -10-60 °C. [Color figure can be viewed at wileyonlinelibrary.com]

Mo-based counterpart, presumably due to the higher regularity of the main chain, which will be commented below again. The weight loss at the early stage is attributable to the cleavage of the phenylethoxy group (47% in theoretical) at the side chain and chloro group. (14% in theoretical).

The CD and UV-vis spectra of Pd- and Mo-based polymers were measured in DMF (Fig. 3). Pd-based poly[(R)-1m]

showed a negative CD peak around 360 nm (red line in Fig. 3, left), assignable to the polyacetylene backbone, indicating the presence of a certain chiral secondary structure. On the contrary, no such CD signal was observed in the other polymers. It is likely that the meta substitution and bulkiness of the chiral substituent of poly[(R)-1m] brought about the chiral induction in the main chain.

The UV-vis absorption band edges of the Mo-based polymers were observed at wavelengths ca. 20 nm longer than those of the Pd-based polymers. This result is explainable by the difference of stereo structures between the polymers. Namely, Mo catalyst polymerize acetylene monomers via the metathesis mechanism to give polymers with *cis/trans* = ca. 1/1, while Pd catalyst polymerize acetylene monomers via the coordination-insertion mechanism to give polymers with *high cis*-contents than Mo-based polymers. The conjugation of *trans*-rich polyacetylenes is commonly longer than *cis*-rich polyacetylenes,²¹ and the result of this study is also the case.

Figure 4 depicts the temperature dependence of the CD and UV-vis spectra of Pd-based poly[(R)-**1**m]. The CD intensity decreased as increasing the temperature, indicating the partial deformation of the chiral secondary structure, in a manner similar to optically active disubstituted acetylene polymers synthesized by the polymerization using metathesis catalysts.²³

Figure 5 depicts the POM images of concentrated solutions of Pd- and Mo-based poly[(R)-1m] in THF. Pd-based poly[(R)-1m] showed patterns attributable to liquid crystallinity under the crossed Nicol state [Fig. 5(b)], while Mobased poly[(R)-1m] did not show such pattern [Fig. 5(d)]. It is likely that Pd-based poly[(R)-1m] is highly orientated due



FIGURE 5 POM images of Pd-based poly[(R)-1m] (a, c) and Mo-based poly[(R)-1m] (b, d) solutions in THF (>5 wt%) without (a, b) and with a cross-polarizer (c, d) measured at room temperature. [Color figure can be viewed at wileyonlinelibrary.com]

to the high *cis* stereoregularity. This is also supported by the refractive index of Pd-based poly[(R)-1m] (1.567) higher than that of Mo-based counterpart (1.553).

CONCLUSIONS

In this article, we have demonstrated the polymerization of novel four disubstituted acetylenes using $[({}^{t}Bu_{3}P)PdMeCl]$ and MoCl₅ catalysts. The Pd-based polymers exhibited lyotropic liquid crystallinity as well as shorter UV-vis band edges, higher thermal stability, and refractive index than the Mo-based one, likely due to the higher *cis* stereoregularity of the polyacetylene backbone. Poly[(R)-**1**m] exhibited Cotton effect assignable to the chiral secondary structure.

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