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Synthesis of Stereoregular Telechelic Poly(phenylacetylene)s: Facile Terminal Chain-End Functionalization of Poly(phenylacetylene)s by Terminative Coupling with Acrylates and Acrylamides in Rhodium-Catalyzed Living Polymerization of Phenylacetylenes

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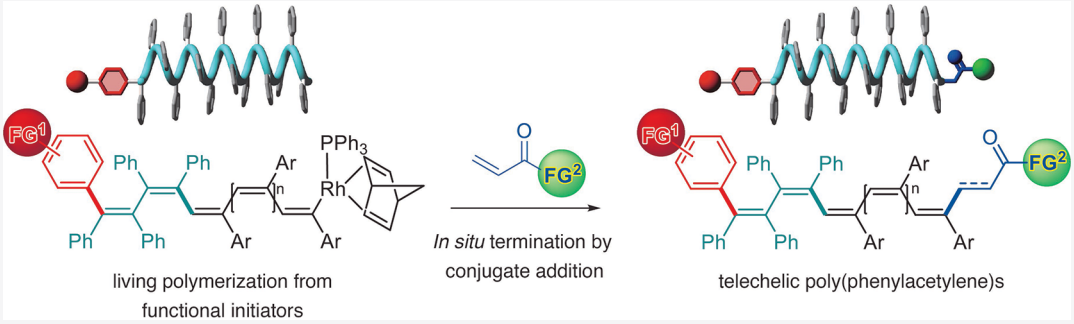

ABSTRACT: Various α,β-unsaturated carbonyl compounds, such as acrylates and acrylamides, were quantitatively introduced to the terminal chain end of poly(phenylacetylene)s by C−C bond formation with terminal organorhodium(I) species formed in the living polymerization of phenylacetylenes with a rhodium-based multicomponent catalytic system that we have recently developed, when these carbonyl compounds were used as terminating reagents. This enables the facile and versatile synthesis of stereoregular telechelic poly(phenylacetylene)s with various functional groups at both the initial and terminal chain ends because the components of aryl boronic acid derivatives used as initiators in our multicomponent catalytic system are quantitatively introduced to the initiating end of the resulting polymer.

INTRODUCTION

Poly(phenylacetylene)s are important π-conjugated polymers as promising candidates of new functional materials because of the properties of their rigid π-conjugated polyene backbones, including optoelectronic properties, high gas permeability, and liquid crystallinity.[1] Moreover, many polyacetylenes including poly(phenylacetylene)s form a helical conformation, for which the helix sense can be controlled by introducing chiral groups into the pendants, using noncovalent interactions with chiral compounds, or using a chiral catalyst during the polymerization reaction. These helical polyacetylenes with a controlled helix sense have potential applications to functional chiral materials such as chiral recognition materials, asymmetric catalysts, nonlinear optical materials, and ferroelectric liquid crystals.[2]

Poly(phenylacetylene)s are usually synthesized by transition-metal-catalyzed polymerization of the corresponding phenylacetylene monomers.[3] Coordination−insertion polymerization of phenylacetylenes by rhodium(I) catalysts is widely used as a reliable method for synthesis of poly(phenylacetylene)s because the catalysts are highly tolerant toward various functional groups and usually produce highly stereoregular polymers with a *cis* geometry,[3c] which has been reported to be a prerequisite for the formation of a helical conformation of the polyacetylene backbone.[4] Furthermore, well-controlled living polymerization of phenylacetylenes by rhodium catalysis has been developed.[5] In representative seminal works, Noyori[6] and Masuda[7] independently reported well-controlled living polymerization of phenylacetylenes by well-defined rhodium(I) complexes derived from the commercially available bicyclo[2.2.1]hepta-2,5-diene rhodium(I) chloride dimer [Rh(nbd)Cl]$_2$. In the polymerization of phenylacetylenes using Noyori's system consisting of the rhodium(I) complex Rh(C≡CPh)(nbd)(PPh$_3$)$_2$ and 4-(dimethylamino)pyridine (DMAP), an initiating end functionalization of poly(phenylacetylene)s is virtually impossible because it is

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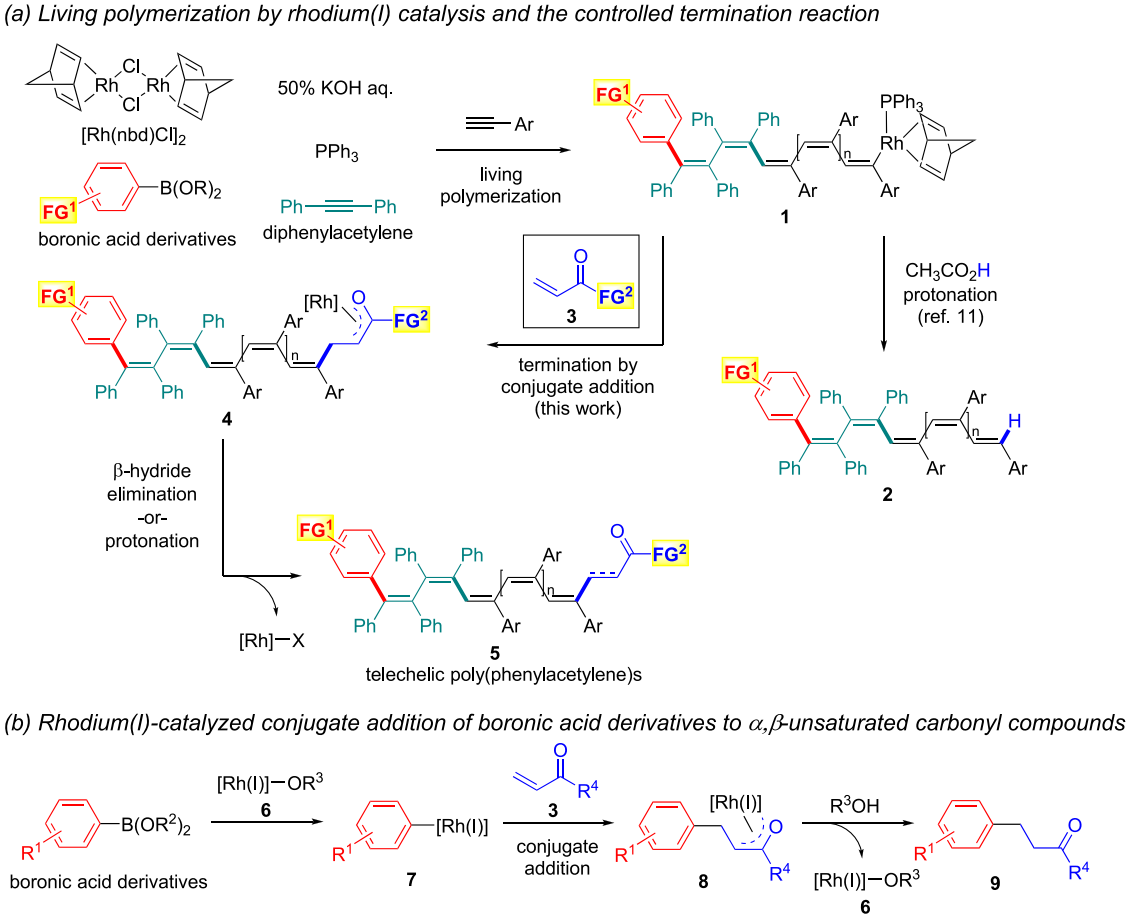

Figure 1. Living polymerization of phenylacetylenes by our multicomponent catalytic system and the controlled termination reaction (a) and rhodium(I)-catalyzed conjugate addition of aryl boronic acid derivatives to α,β-unsaturated carbonyl compounds (b).

presumed that a hydrogen atom is introduced to an initiating end of the polymer from a rhodium hydride species formed *in situ*.[6c] In contrast, in Masuda's system consisting of the rhodium(I) complex [(nbd)Rh{C(Ph)=CPh$_2$}(PAr$_3$)] and PPh$_3$, the triphenylvinyl group on the Rh complex is introduced to the initiating end of poly(phenylacetylene)s.[8] However, versatile functionalization of an initiating end of the polymer by this catalytic system seems to be difficult because functionalized triphenylvinyl lithium reagents, which are precursors of the active rhodium complex, are not easily accessible reagents.[7c,9,10]

Very recently, we developed a new method for well-controlled living polymerization of phenylacetylenes using a multicomponent catalytic system composed of [Rh(nbd)Cl]$_2$, aryl boronic acid derivatives, diphenylacetylene, 50% aqueous KOH and PPh$_3$ (Figure 1a).[11] This method enables a facile and versatile initiating end functionalization of poly(phenylacetylene)s because the aromatic residues of the aryl boronic acids used are introduced to an initiating end of poly(phenylacetylene)s along with at least two molecules of diphenylacetylene. The isolated polymer has a hydrogen atom at the terminal chain end, as depicted as structure **2** in Figure 1a when the terminal rhodium(I) species **1** is protonated by acetic acid added as a quenching reagent after the polymerization. If another phenylacetylene monomer is added instead of acetic acid after consumption of the first monomer, block copolymers are synthesized because the rhodium(I) species **1** at a polymer terminal chain end retains polymerization activity. However, to the best of our knowledge, effective terminal chain end functionalization of poly(phenylacetylene)s by end-capping reagents (terminators), except for a proton, of living polymerization has not been reported.

In organic synthesis, organoboronic acid derivatives are widely used as building blocks in rhodium-catalyzed C−C bond formation reactions.[12] Rhodium-catalyzed conjugate addition reactions between organoboronic acid derivatives and α,β-unsaturated carbonyl compounds are some of the most powerful tools (Figure 1b).[13] Mechanistically, organoboronic acid derivatives can work as nucleophiles through transformation to the corresponding organorhodium(I) species **7** by transmetalation with a hydroxy (R^3 = H) or alkoxy (R^3 = alkyl) rhodium(I) catalyst **6**. The formed organorhodium(I) species **7** add to α,β-unsaturated carbonyl compounds **3** by a coordination−insertion mechanism to form rhodium(I) enolate intermediates **8**. Water or alcohols are typically added to the catalytic system to close the catalytic cycle by protonation of enolates **8**, which are converted to the corresponding saturated carbonyl products **9** with regeneration of the rhodium(I) catalyst **6**.

We envisioned the application of this conjugate addition reaction to the living rhodium(I) species **1** at the terminal end of poly(phenylacetylene)s formed in the polymerization of phenylacetylenes using our multicomponent catalytic system. If the rhodium(I) species **1** causes an addition reaction to various α,β-unsaturated carbonyl compounds **3**, the corresponding rhodium(I) enolates **4** would be produced by C−C bond

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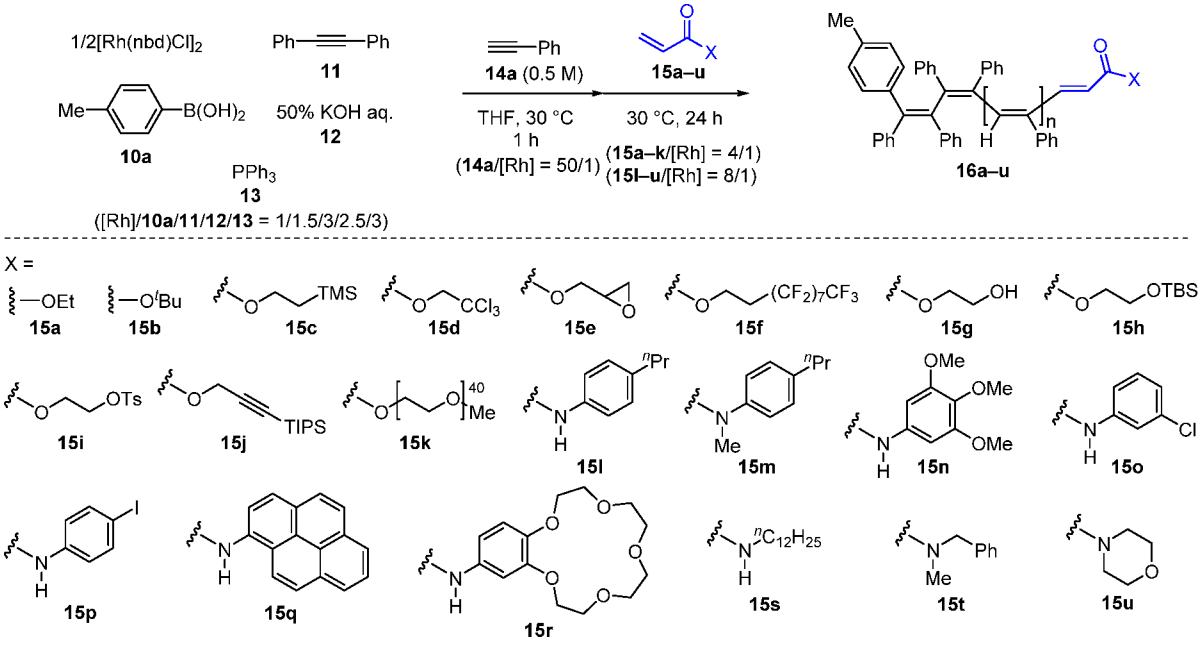
Table 1. Results of Terminal Chain End Functionalization of Poly(phenylacetylene) Using Acrylates and Acrylamides as Terminators[a]



entry	15	yield (%)[b]	M_n[c]	M_w/M_n[c]	degree of chain end functionalization (%)[d]
1	**15a**	>95	5100	1.04	>95
2[e]	**15a**	>95	9100	1.04	>95
3	**15b**	>95	4900	1.03	>95
4	**15c**	>95	5000	1.03	>95
5	**15d**	>95	4900	1.03	>95
6	**15e**	>95	4800	1.04	>95
7	**15f**	86	6000	1.04	>95
8	**15g**	>95	5200	1.02	75
9	**15h**	87	4800	1.04	>95
10	**15i**	>95	5800	1.04	>95
11	**15j**	90	5200	1.04	>95
12[f]	**15k**	92	34600[g]	1.38[g]	>95
13	**15l**	>95	5300	1.04	>95
14	**15m**	>95	6000	1.03	>95
15	**15n**	85	4700	1.05	>95
16	**15o**	86	5500	1.04	>95
17	**15p**	>95	4800	1.04	>95
18	**15q**	>95	5800	1.04	>95
19	**15r**	90	4900	1.04	>95
20[h]	**15s**	>95	5100	1.08	90
21	**15t**	>95	5200	1.05	>95
22	**15u**	>95	5700	1.02	>95

[a]Typical conditions: $[Rh(nbd)Cl]_2$ (0.02 mmol), **10a** (0.06 mmol), **11** (0.12 mmol), **12** (0.10 mmol), **13** (0.12 mmol) in THF (0.4 mL) for 5 min at 0 °C, then **14a** (2.0 mmol) in THF (3.6 mL) for 1 h at 30 °C, and then **15a–u** (0.16 or 0.32 mmol) for 24 h at 30 °C. [b]Methanol-insoluble part. [c]Determined by SEC using TSKgel $G4000H_{XL}$ + $G3000H_{XL}$ + $G3000H_{XL}$ as columns on the basis of polystyrene standards (THF, 40 °C). [d]Determined by ^1H NMR analysis. [e]**14a**/[Rh] = 100. [f]**14a**/[Rh] = 500/1. [g]Determined by SEC using Shodex KF-805L as a column on the basis of polystyrene standards (THF, 40 °C). [h]**15s**/[Rh] = 16/1.

formation (Figure 1a). Finally, the rhodium species is eliminated by *β*-hydride elimination *in situ* (Mizoroki–Heck type reaction) or protonation by quenching the reaction mixture (conjugate addition type reaction).[14] In any case, the *α,β*-unsaturated carbonyl compounds **3** are introduced to the terminal end of the polymer to provide telechelic poly(phenylacetylene)s **5** having functional groups at both ends.[15]

Herein we report a facile method for terminal chain end functionalization of poly(phenylacetylene)s using *α,β*-unsaturated carbonyl compounds such as acrylates and acrylamides as terminators of the rhodium-catalyzed living polymerization of phenylacetylenes. This terminal chain end functionalization method allows, for the first time, the synthesis of stereoregular telechelic poly(phenylacetylene)s because the substituents of the aryl boronic acids used as initiators are introduced into the initiating chain end of the resulting polymer in our rhodium-based multicomponent catalytic system.[11]

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RESULTS AND DISCUSSION

We designed a model system of living polymerization of phenylacetylene (**14a**) with a multicomponent catalytic system composed of $[Rh(nbd)Cl]_2$, 4-methylphenylboronic acid (**10a**), diphenylacetylene (**11**), a 50% (w/v) aqueous solution of KOH (**12**), and PPh_3 (**13**) (**14a**/[Rh] = 50/1, [Rh]/**10a**/**11**/**12**/**13** = 1/1.5/3/2.5/3) to test terminal end functionalization using α,β-unsaturated carbonyl compounds.[11] To the polymerization mixture was directly added 4 equiv of ethyl acrylate (**15a**) to the rhodium catalyst after the living polymerization had been conducted for 1 h at 30 °C in THF, and the resultant mixture was further stirred for 24 h at 30 °C. A 50-mer polymer having a narrow molecular weight distribution (M_w/M_n = 1.04) was quantitatively obtained as a methanol-insoluble part (entry 1 in Table 1).

The ^{1}H NMR spectrum of the obtained polymer showed sharp signals based on poly(phenylacetylene), indicating that high *cis* stereoregularity (>95%) is kept even after the termination reaction for 24 h (Figure 2).[1a,3b,4a] Moreover,

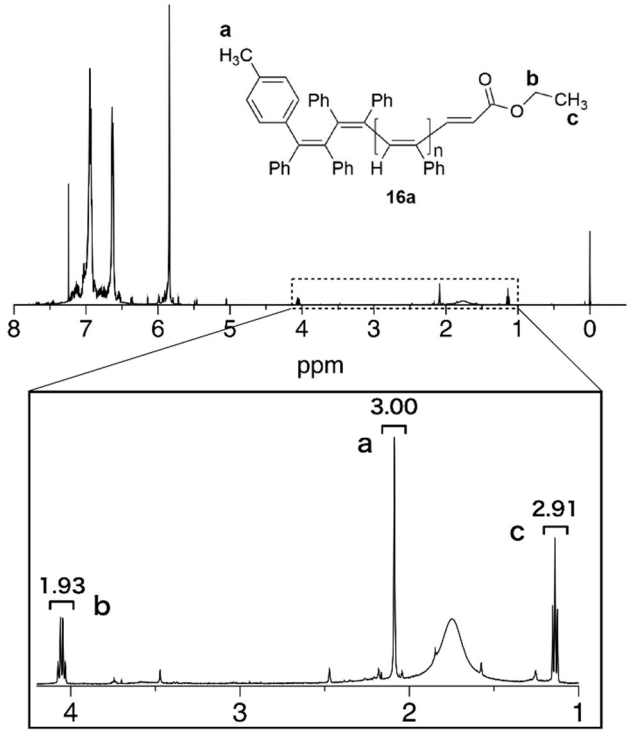

Figure 2. ^{1}H NMR spectrum of **16a** (entry 1 in Table 1) in $CDCl_3$ at room temperature.

clear signals assignable to an ethyl ester were observed at 1.13 and 4.05 ppm, for which the integration values were 3H and 2H, respectively, in comparison with 3H of a methyl group of a 4-methylphenyl group at the initiating end of the polymer. This means that **15a** was quantitatively introduced to the terminal end of the polymer. On the other hand, signals of methylene groups were absent, suggesting that the polymer **16a** having an α,β-unsaturated ester was produced by β-hydride elimination of a rhodium species in situ (Mizoroki–Heck type reaction). This structure was confirmed by APCI-TOF-MS of **16a** having a low molecular weight (M_n = 2900, M_w/M_n = 1.03), which was synthesized by living polymerization at a low feed ratio of the monomer to the initiator (**14a**/[Rh] = 25/1). As shown in Figure 3a, a series of peaks

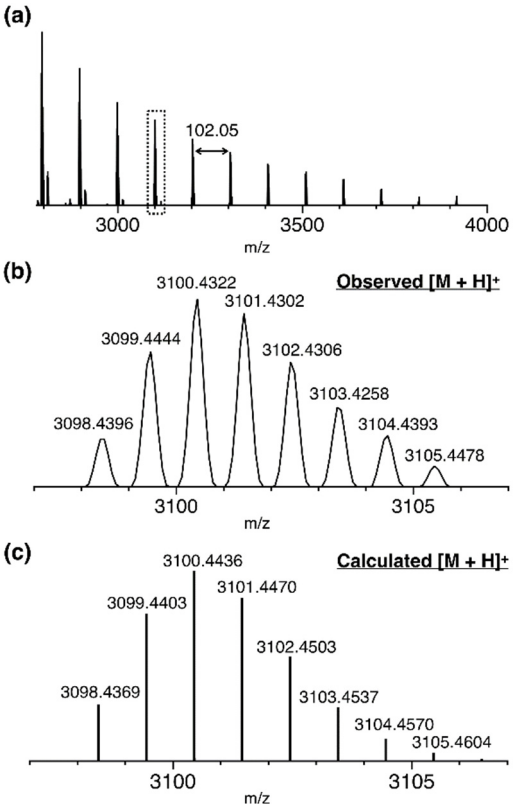

Figure 3. High-resolution APCI-TOF-MS spectrum of **16a** (M_n = 2900, M_w/M_n = 1.03) (a), the expanded spectrum of **16a** (n = 25) (b), and the calculated spectrum of **16a** (n = 25) (c).

based on the polymer was detected up to m/z 4000 in the HRMS spectrum, and each peak has a difference of m/z 102 corresponding to a phenylacetylene repeating unit. For instance, a peak at m/z 3098.4396 corresponds to $C_{240}H_{185}O_2^+$ $[M + H]^+$ (calcd 3098.4369), which can be assigned as a structure composed of 25-mer poly(phenylacetylene) (n = 25, $C_{200}H_{150}$), one 4-methylphenyl group (C_7H_7), two diphenylacetylene units ($C_{14}H_{10} \times 2$), and a terminal ethyl acrylate moiety ($C_5H_7O_2$) (Figure 3b,c). Molecular ions based on a polymer having a hydrogen atom instead of an ethyl acrylate moiety were not detected in the spectrum, strongly supporting full introduction of ethyl acrylate to the terminal end of the polymer. We tried to reduce the amount of ethyl acrylate (**15a**) used to 2 equiv to the rhodium catalyst, but ^{1}H NMR analysis of the obtained polymer indicated incomplete introduction (83% chain end functionalization) of **15a** to the polymer terminal end in 24 h. This termination reaction using **15a** was hardly affected by the degree of polymerization of the polymer (entry 2 in Table 1).

Next, we focused on terminal end functionalization of poly(phenylacetylene)s using various terminators under the same living polymerization conditions. Typically, the introduction rate of terminators was estimated from integral values of characteristic signals in ^{1}H NMR spectra of the isolated polymers. *tert*-Butyl, 2-trimethylsilylethyl, and 2,2,2-trichloroethyl acrylates (**15b–d**) were quantitatively introduced to the terminal end of the polymer as in the case of ethyl acrylate (**15a**) (entries 3–5 in Table 1), and they are beneficial for further functionalization of the polymer because different conditions can be used in hydrolysis depending on the situation. Characteristic functional groups such as epoxide and

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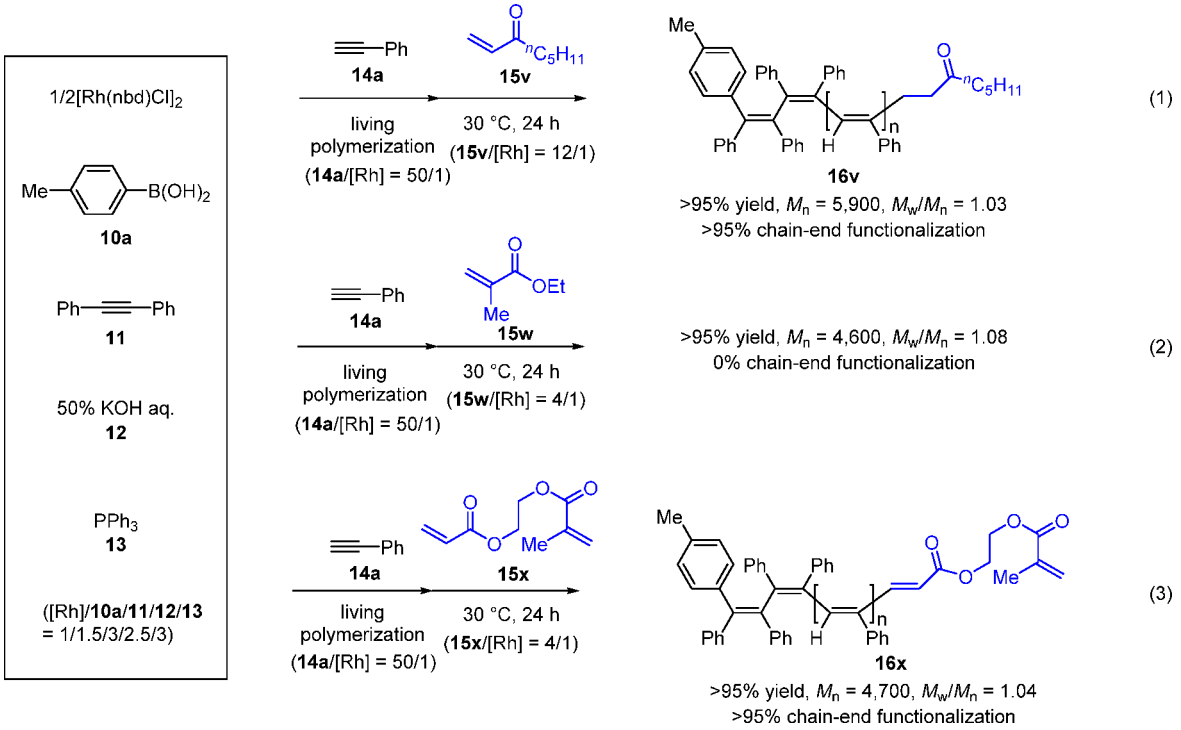
Scheme 1. Termination Reaction of the Living Polymerization of Phenylacetylene (14a) with α,β-Unsaturated Ketone 15v, Methacrylate 15w, and Acrylate 15x Having a Methacrylate Moiety[a]



[a]The yield was calculated from the methanol-insoluble part. M_n and M_w/M_n values were determined by SEC using TSKgel G4000H_{XL} + G3000H_{XL} + G3000H_{XL} as columns on the basis of polystyrene standards (THF, 40 °C). The degree of chain end functionalization (%) was determined by ^{1}H NMR analysis.

fluorous groups could be readily introduced using acrylates **15e** and **15f** (entries 6 and 7 in Table 1). Acrylate **15g**, having a free hydroxyl group, was incompletely introduced (75% chain end functionalization) (entry 8 in Table 1), while acrylate **15h** having a TBS-protected hydroxyl group was quantitatively introduced to the polymer terminal end (entry 9 in Table 1). These results clearly indicate that a free hydroxyl group inhibits rhodium-mediated addition to acrylates, but the reason is unclear. Tosyl-protected acrylate **15i** was also introduced to the polymer terminal end, and it would be useful for further transformation by S_N2 substitution reactions (entry 10 in Table 1). A useful alkyne moiety could be introduced to the polymer terminal end using acrylate **15j** (entry 11 in Table 1). Acrylate **15k** having a polyethylene glycol chain (40-mer) was quantitatively introduced to the polymer terminal end, indicating that the synthesis of a heteroblock copolymer is possible by the present method (entry 12 in Table 1). The broadened molecular weight distribution of the obtained polymer is probably due to tailing in the SEC chromatogram, and this was caused by the introduced polyethylene glycol chain because an aliquot of the polymerization solution before addition of **15k** provided a polymer having a narrow molecular weight distribution (M_n = 49000, M_w/M_n = 1.12).

Our interest turned to end functionalization using acrylamides instead of acrylates because various acrylamides are also easily accessible by condensation between acryloyl chloride and functionalized amines. When 4 equiv of *N*-(4-*n*-propylphenyl)acrylamide (**15l**) to the rhodium catalyst was used as a model terminator, **15l** was introduced to the polymer terminal end in only 60% chain end functionalization, unlike the case for acrylates. This is probably because the electrophilicity of acrylamides is lower than that of acrylates. However, quantitative introduction of **15l** to the polymer terminal end was achieved by increasing the amount of **15l** to 8 equiv (entry 13 in Table 1). The *N*-methylated analogue **15m** was also quantitatively introduced to the polymer terminal end, indicating that tertiary acrylamides can be used for terminal chain end functionalization (entry 14 in Table 1). The electronic nature of the aromatic ring of acrylamides seems to have little effect on the reactivity in the present termination reaction, because acrylamides **15n** and **15o** having a methoxy group and a chlorine atom, respectively, readily reacted with a living species (entries 15 and 16 in Table 1). An iodine atom of acrylamide **15p** was intact under the present reaction conditions, and this is useful for further functionalization by cross-coupling reactions (entry 17 in Table 1). Since characteristic signals were overlapped with signals of the polymer component in ^{1}H NMR spectra of the polymers obtained by reactions with **15o** and **15p**, estimation of the chain end functionalization was complemented by HRMS analysis (see the Supporting Information). It is notable that pyrene and crown ether moieties were successfully introduced to the polymer terminal chain end using acrylamides **15q** and **15r**, respectively, because such functional groups are often important for the development of functional materials (entries 18 and 19 in Table 1). The secondary aliphatic acrylamide **15s** showed a relatively low reactivity, and 90% chain end functionalization was achieved using an increased amount of **15s** (16 equiv) (entry 20 in Table 1). However, tertiary aliphatic acrylamides **15t** and **15u** worked as good terminators as was the case for aromatic acrylamides to give **16t** and **16u**,

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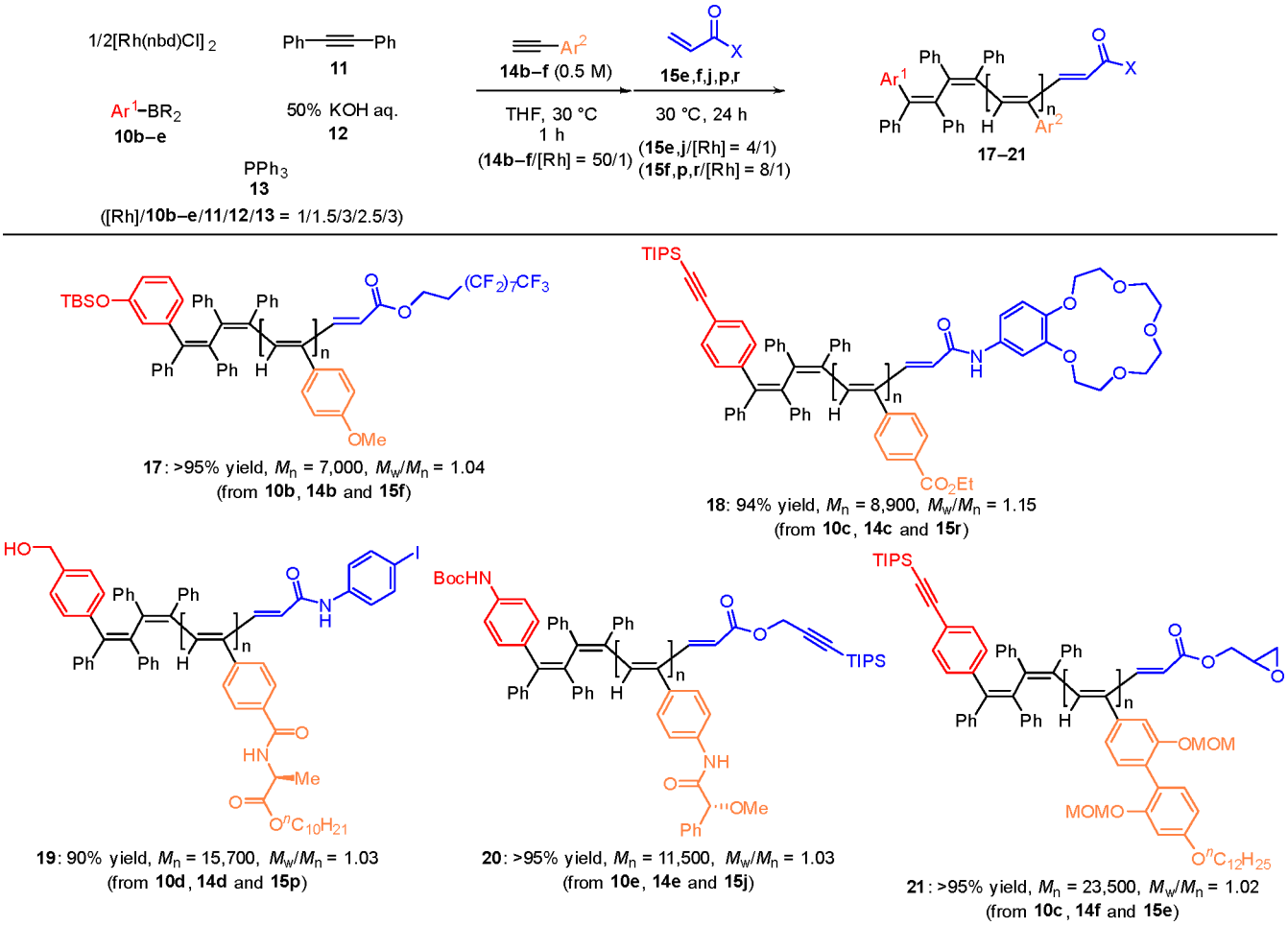

Figure 4. Synthesis of telechelic poly(phenylacetylene)s having functional pendants. The same conditions as those shown in footnote *a* in Table 1 were used unless otherwise noted (see the Supporting Information). The yield was calculated from the methanol-insoluble part. M_n and M_w/M_n values were determined by SEC using TSKgel G4000H_{XL} + G3000H_{XL} + G3000H_{XL} as columns on the basis of polystyrene standards (THF, 40 °C).

respectively, with nearly quantitative chain end functionalization (entries 21 and 22 in Table 1).

We found that α,β-unsaturated ketone **15v** was also introduced to the polymer terminal end, though a larger amount (12 equiv to a rhodium catalyst) of **15v** was required for quantitative introduction (Scheme 1, eq 1). Interestingly, the ^{1}H NMR spectrum of polymer **16v** obtained by this reaction indicated that **15v** was introduced as an α,β-saturated ketone, unlike the cases of acrylates and acrylamides (see the Supporting Information). This indicates that the β-hydride elimination of an intermediary rhodium(I) enolate was suppressed *in situ* probably because an enol form having an O–Rh bond is preferred over a keto form having a C–Rh bond in the isomerization equilibrium of rhodium(I) enolate.[14]

When methyl methacrylate (**15w**) was used as a terminator instead of acrylates under the standard conditions, **15w** was not introduced to the polymer terminal end at all (Scheme 1, eq 2). The contrasting results indicate that the effect of the steric factor of alkenes is significant in the present termination reaction.

Since **15w** did not react with the living species, we tested a chemoselective reaction using the terminator **15x** having both acrylate and methacrylate moieties. As expected, the reaction resulted in perfect chemoselectivity and gave **16x** having an intact methacrylate moiety at the terminal end, which would be useful for further functionalization (Scheme 1, eq 3).

Figure 4 shows examples of the synthesis of telechelic polymers from other functionalized phenylacetylene monomers using a combination of various aryl boronic acid derivatives and terminators. Aryl boronic acid derivatives having protected phenol (**10b**, R = OH), protected alkynyl (**10c**, R = OH), hydroxymethyl (**10d**, R_2 = pin), and protected amino (**10e**, R = OH) substituents were chosen as initiators because these functional groups are useful for further functionalization of the corresponding polymers. Acrylates (**15e**, **15f**, **15j**) and acrylamides (**15p**, **15r**) were used as representative terminators from the viewpoint of usefulness. Telechelic polymers **17**–**21** were synthesized from monomer **14b** having a methoxy group, monomer **14c** having an ester group, and monomers **14d**,[16] **14e**,[17] and **14f**[18] having stimuli-responsive functional groups. These representative examples show the potentially broad scope of monomers in the present method.[19]

Finally, we performed postfunctionalization of the telechelic poly(phenylacetylene)s synthesized by the present method (Scheme 2). For instance, we examined introduction of a cyclodextrin residue into the polymer terminal end by postfunctionalization because its direct introduction to the polymer terminal end by the present termination reaction

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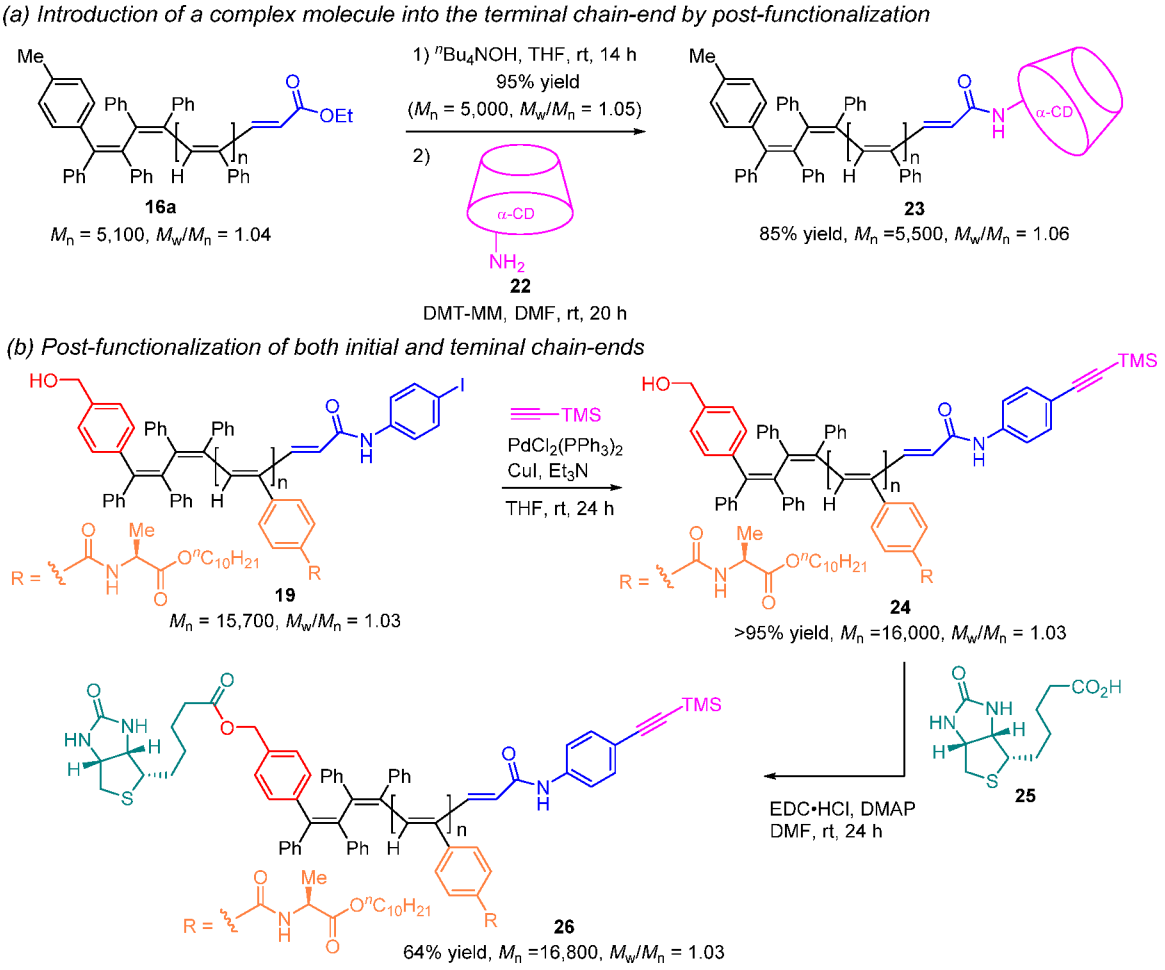
Scheme 2. Postfunctionalization of Telechelic Poly(phenylacetylene)s[a]



[a] M_n and M_w/M_n values were determined by SEC using TSKgel G4000H$_{XL}$ + G3000H$_{XL}$ + G3000H$_{XL}$ as columns on the basis of polystyrene standards (THF, 40 °C).

seems to be very difficult due to multiple hydroxy groups. After basic hydrolysis of the terminal ethyl ester of **16a**, the resultant polymer having a terminal carboxy group was reacted with commercially available 3A-amino-3A-deoxy-(2AS,3AS)-α-cyclodextrin (**22**) using 4-(4,6-dimethoxy-1,3,5-triazin-2-yl)-4-methylmorpholinium chloride (DMT-MM) as a condensing reagent to afford **23** having a cyclodextrin moiety at the terminal end in good yield (Scheme 2a).[20]

Furthermore, postfunctionalization of the telechelic polymer **19** at both chain ends was demonstrated (Scheme 2b). As the first step, an iodine atom at the terminal end of **19** was converted to a protected alkynyl group, which would be useful for further functionalization, by a Sonogashira reaction to give polymer **24**. As the second step, biotin (**25**) was introduced to a hydroxy group at the initiating end of **24** by a condensation reaction using 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC•HCl) to give **26** in good yield.[11]

CONCLUSION

We have developed a method for versatile terminal end functionalization of poly(phenylacetylene)s by collaborating rhodium-catalyzed conjugate addition to α,β-unsaturated carbonyl compounds with living polymerization of phenylacetylenes using a multicomponent catalytic system composed of [Rh(nbd)Cl]$_2$, aryl boronic acid derivatives, diphenylacetylene, 50% aqueous KOH, and PPh$_3$. A variety of easily available acrylates and acrylamides having functionalized groups were quantitatively introduced to the terminal chain end of poly(phenylacetylene)s having high *cis* stereoregularity and a narrow molecular weight distribution. Since the initiating end of poly(phenylacetylene)s is readily functionalized by the component of aryl boronic acid derivatives, the present controlled termination reaction consequently offers a method for the facile synthesis of unprecedented telechelic poly(phenylacetylene)s. The method was applicable to other phenylacetylene monomers having functional groups, and we therefore anticipate that the broad scope of this method will spark the development of novel functional materials based on telechelic poly(phenylacetylene)s.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.1c00150.

Experimental details, characterizations of polymers, supporting data, and NMR spectra (PDF)

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) (a) Simionescu, C.; Percec, V. Progress in polyacetylene chemistry. *Prog. Polym. Sci.* **1982**, *8*, 133−214. (b) Lam, J. W.; Tang, B. Z. Functional polyacetylenes. *Acc. Chem. Res.* **2005**, *38*, 745−754. (c) Aoki, T.; Kaneko, T.; Teraguchi, M. Synthesis of functional π-conjugated polymers from aromatic acetylenes. *Polymer* **2006**, *47*, 4867−4892. (d) Masuda, T. Substituted polyacetylenes. *J. Polym. Sci., Part A: Polym. Chem.* **2007**, *45*, 165−180. (e) Liu, J.; Lam, J. W.; Tang, B. Z. Acetylenic polymers: syntheses, structures, and functions. *Chem. Rev.* **2009**, *109*, 5799−5867. (f) Jin, Y.-J.; Kwak, G. Properties, functions, chemical transformation, nano-, and hybrid materials of poly(diphenylacetylene)s toward sensor and actuator applications. *Polym. Rev.* **2017**, *57*, 175−199.

(2) (a) Rudick, J. G.; Percec, V. Induced helical backbone conformations of self-organizable dendronized polymers. *Acc. Chem. Res.* **2008**, *41*, 1641−1652. (b) Akagi, K. Helical polyacetylene: asymmetric polymerization in a chiral liquid-crystal field. *Chem. Rev.* **2009**, *109*, 5354−5401. (c) Yashima, E.; Maeda, K.; Iida, H.; Furusho, Y.; Nagai, K. Helical polymers: synthesis, structures, and functions. *Chem. Rev.* **2009**, *109*, 6102−6211. (d) Freire, F.; Quinoa, E.; Riguera, R. Supramolecular assemblies from poly(phenylacetylene)s. *Chem. Rev.* **2016**, *116*, 1242−1271. (e) Yashima, E.; Ousaka, N.; Taura, D.; Shimomura, K.; Ikai, T.; Maeda, K. Supramolecular helical systems: helical assemblies of small molecules, foldamers, and polymers with chiral amplification and their functions. *Chem. Rev.* **2016**, *116*, 13752−13990. (f) Maeda, K.; Yashima, E. Helical polyacetylenes induced via noncovalent chiral interactions and their applications as chiral materials. *Top. Curr. Chem.* **2017**, *375*, 72.

(3) (a) Simionescu, C. I.; Percec, V. Thermal cis-trans isomerization of cis-transoidal polyphenylacetylene. *J. Polym. Sci., Polym. Chem. Ed.* **1980**, *18*, 147−155. (b) Furlani, A.; Napoletano, C.; Russo, M. V.; Feast, W. J. Stereoregular polyphenylacetylene. *Polym. Bull.* **1986**, *16*, 311−317. (c) Tabata, M.; Sone, T.; Sadahiro, Y. Precise synthesis of monosubstituted polyacetylenes using Rh complex catalysts. Control of solid structure and π-conjugation length. *Macromol. Chem. Phys.* **1999**, *200*, 265−282. (d) Mayershofer, M. G.; Nuyken, O. Living polymerization of substituted acetylenes. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 5723−5747. (e) Shiotsuki, M.; Sanda, F.; Masuda, T. Polymerization of substituted acetylenes and features of the formed polymers. *Polym. Chem.* **2011**, *2*, 1044−1058.

(4) (a) Simionescu, C. I.; Percec, V.; Dumitrescu, S. Polymerization of acetylenic derivatives. XXX. Isomers of polyphenylacetylene. *J. Polym. Sci., Polym. Chem. Ed.* **1977**, *15*, 2497−2509. (b) Yashima, E.; Huang, S.; Okamoto, Y. An optically active stereoregular polyphenylacetylene derivative as a novel chiral stationary phase for HPLC. *J. Chem. Soc., Chem. Commun.* **1994**, 1811−1812. (c) Percec, V.; Rudick, J. G.; Peterca, M.; Wagner, M.; Obata, M.; Mitchell, C. M.; Cho, W.-D.; Balagurusamy, V. S. K.; Heiney, P. A. Thermoreversible cis-cisoidal to cis-transoidal isomerization of helical dendronized polyphenylacetylenes. *J. Am. Chem. Soc.* **2005**, *127*, 15257−15264. (d) Percec, V.; Rudick, J. G.; Peterca, M.; Heiney, P. A. Nanomechanical function from self-organizable dendronized helical polyphenylacetylenes. *J. Am. Chem. Soc.* **2008**, *130*, 7503−7508.

(5) Seminal reports of living polymerization of acetylenes: (a) Kunzler, J. F.; Percec, V. Living non-conjugated polyacetylenes. *Polym. Bull.* **1987**, *18*, 303−309. (b) Kunzler, J.; Percec, V. Living polymerization of aryl substituted acetylenes by $MoCl_5$ and WCl_6 based initiators: The ortho phenyl substituent effect. *J. Polym. Sci., Part A: Polym. Chem.* **1990**, *28*, 1221−1236. Recent review: (c) Tan, N. S. L.; Lowe, A. B. Polymerizations mediated by well-defined rhodium complexes. *Angew. Chem., Int. Ed.* **2020**, *59*, 5008−5021.

(6) (a) Kishimoto, Y.; Eckerle, P.; Miyatake, T.; Ikariya, T.; Noyori, R. Living polymerization of phenylacetylenes initiated by Rh-(C≡CC_6H_5)(2,5-norbornadiene)[P(C_6H_5)$_3$]$_2$. *J. Am. Chem. Soc.* **1994**, *116*, 12131−12132. (b) Kishimoto, Y.; Miyatake, T.; Ikariya, T.; Noyori, R. An efficient rhodium (I) initiator for stereospecific living polymerization of phenylacetylenes. *Macromolecules* **1996**, *29*, 5054−5055. (c) Kishimoto, Y.; Eckerle, P.; Miyatake, T.; Kainosho, M.; Ono, A.; Ikariya, T.; Noyori, R. Well-controlled polymerization of phenylacetylenes with organorhodium (I) complexes: Mechanism and structure of the polyenes. *J. Am. Chem. Soc.* **1999**, *121*, 12035−12044.

(7) (a) Misumi, Y.; Masuda, T. Living polymerization of phenylacetylene by novel rhodium catalysts. Quantitative initiation and introduction of functional groups at the initiating chain end. *Macromolecules* **1998**, *31*, 7572−7573. (b) Misumi, Y.; Kanki, K.; Miyake, M.; Masuda, T. Living polymerization of phenylacetylene by rhodium-based ternary catalysts, (diene)Rh(I) complex/vinyllithium/phosphorus ligand. Effects of catalyst components. *Macromol. Chem. Phys.* **2000**, *201*, 2239−2244. (c) Miyake, M.; Misumi, Y.; Masuda, T. Living polymerization of phenylacetylene by isolated rhodium complexes, Rh[C(C_6H_5)=C(C_6H_5)$_2$](nbd)(4-XC_6H_4)$_3$P (X = F, Cl). *Macromolecules* **2000**, *33*, 6636−6639. (d) Saeed, I.; Shiotsuki, M.; Masuda, T. Living polymerization of phenylacetylene with tetrafluorobenzobarrelene ligand-containing rhodium catalyst systems featuring the synthesis of high molecular weight polymer. *Macromolecules* **2006**, *39*, 8567−8573. (e) Shiotsuki, M.; Kumazawa, S.; Onishi, N.; Sanda, F. Molecular weight dependence of helical conformation of amino acid-based polyphenylacetylenes. *J. Polym. Sci., Part A: Polym. Chem.* **2011**, *49*, 4921−4925. (f) Kumazawa, S.; Castanon, J. R.; Shiotsuki, M.; Sato, T.; Sanda, F. Chirality amplification in helical block copolymers. Synthesis and chiroptical properties of block copolymers of chiral/achiral acetylene monomers. *Polym. Chem.* **2015**, *6*, 5931−5939.

(8) Kumazawa, S.; Castanon, J. R.; Onishi, N.; Kuwata, K.; Shiotsuki, M.; Sanda, F. Characterization of the polymerization catalyst [(2,5-norbornadiene)Rh{C(Ph)=CPh_2}(PPh_3)] and identification of the end structures of poly(phenylacetylenes) obtained by polymerization using this catalyst. *Organometallics* **2012**, *31*, 6834−6842.

(9) Kanki, K.; Misumi, Y.; Masuda, T. Synthesis of poly(phenylacetylene)-block-poly(β-propiolactone) by use of Rh-cata-

lyzed living polymerization of phenylacetylene. *Inorg. Chim. Acta* **2002**, *336*, 101−104.
(10) Loong Tan, N. S.; Nealon, G. L.; Turner, G. F.; Moggach, S. A.; Ogden, M. I.; Massi, M.; Lowe, A. B. Rh(I)(2,5-norbornadiene)-(biphenyl)(tris(4-fluorophenyl)phosphine): Synthesis, characterization, and application as an initiator in the stereoregular (co) polymerization of phenylacetylenes. *ACS Macro Lett.* **2020**, *9*, 56−60.
(11) Taniguchi, T.; Yoshida, T.; Echizen, K.; Takayama, K.; Nishimura, T.; Maeda, K. Facile and versatile synthesis of end-functionalized poly(phenylacetylene)s: A multicomponent catalytic system for well-controlled living polymerization of phenylacetylenes. *Angew. Chem., Int. Ed.* **2020**, *59*, 8670−8680.
(12) Yoshida, K.; Hayashi, T. In *Modern Rhodium-Catalyzed Organic Reactions*; Evans, P. A., Ed.; Wiley-VCH: Weinheim, Germany, 2005; pp 55−77.
(13) (a) Fagnou, K.; Lautens, M. Rhodium-catalyzed carbon-carbon bond forming reactions of organometallic compounds. *Chem. Rev.* **2003**, *103*, 169−196. (b) Hayashi, T.; Yamasaki, K. Rhodium-catalyzed asymmetric 1,4-addition and its related asymmetric reactions. *Chem. Rev.* **2003**, *103*, 2829−2844. (c) Edwards, H. J.; Hargrave, J. D.; Penrose, S. D.; Frost, C. G. Synthetic applications of rhodium catalysed conjugate addition. *Chem. Soc. Rev.* **2010**, *39*, 2093−2105.
(14) (a) Zou, G.; Wang, Z.; Zhu, J.; Tang, J. Rhodium-catalyzed Heck-type reaction of arylboronic acids with α,β-unsaturated esters: tuning β-hydrogen elimination vs. hydrolysis of alkylrhodium species. *Chem. Commun.* **2003**, 2438−2439. (b) Zou, G.; Guo, J.; Wang, Z.; Huang, W.; Tang, J. Heck-type coupling vs. conjugate addition in phosphine-rhodium catalyzed reactions of aryl boronic acids with α,β-unsaturated carbonyl compounds: a systematic investigation. *Dalton Trans.* **2007**, 3055−3064.
(15) Tasdelen, M. A.; Kahveci, M. U.; Yagci, Y. Telechelic polymers by living and controlled/living polymerization methods. *Prog. Polym. Sci.* **2011**, *36*, 455−567.
(16) (a) Okoshi, K.; Sakurai, S.-i.; Ohsawa, S.; Kumaki, J.; Yashima, E. Control of main-chain stiffness of a helical poly(phenylacetylene) by switching on and off the intramolecular hydrogen bonding through macromolecular helicity inversion. *Angew. Chem., Int. Ed.* **2006**, *45*, 8173−8176. (b) Sakurai, S.-i.; Okoshi, K.; Kumaki, J.; Yashima, E. Two-dimensional surface chirality control by solvent-induced helicity inversion of a helical polyacetylene on graphite. *J. Am. Chem. Soc.* **2006**, *128*, 5650−5651. (c) Okoshi, K.; Kajitani, T.; Nagai, K.; Yashima, E. Uniaxial orientation of a rodlike helical poly-(phenylacetylene) in an electric field. *Macromolecules* **2008**, *41*, 258−261.
(17) (a) Freire, F.; Seco, J. M.; Quiñoá, E.; Riguera, R. Chiral amplification and helical-sense tuning by mono-and divalent metals on dynamic helical polymers. *Angew. Chem., Int. Ed.* **2011**, *50*, 11692−11696. (b) Freire, F.; Seco, J. M.; Quinñoá, E.; Riguera, R. Nanospheres with tunable size and chirality from helical polymer-metal complexes. *J. Am. Chem. Soc.* **2012**, *134*, 19374−19383. (c) Hirose, D.; Isobe, A.; Quiñoá, E.; Freire, F.; Maeda, K. Three-state switchable chiral stationary phase based on helicity control of an optically active poly(phenylacetylene) derivative by using metal cations in the solid state. *J. Am. Chem. Soc.* **2019**, *141*, 8592−8598.
(18) (a) Shimomura, K.; Ikai, T.; Kanoh, S.; Yashima, E.; Maeda, K. Switchable enantioseparation based on macromolecular memory of a helical polyacetylene in the solid state. *Nat. Chem.* **2014**, *6*, 429−434. (b) Ishidate, R.; Shimomura, K.; Ikai, T.; Kanoh, S.; Maeda, K. Macromolecular helicity induction and memory in a poly-(biphenylylacetylene) bearing an ester group and its application to a chiral stationary phase for high-performance liquid chromatography. *Chem. Lett.* **2015**, *44*, 946−948. (c) Ishidate, R.; Sato, T.; Ikai, T.; Kanoh, S.; Yashima, E.; Maeda, K. Helicity induction and memory effect in poly(biphenylylacetylene)s bearing various functional groups and their use as switchable chiral stationary phases for HPLC. *Polym. Chem.* **2019**, *10*, 6260−6268.
(19) We did not use *ortho*-substituted phenylacetylenes as monomers because the corresponding polymers obtained by rhodium-catalyzed living polymerization are often insoluble in most solvents, which makes their NMR and SEC analysis difficult.[6c,11]
(20) Kunishima, M.; Kawachi, C.; Monta, J.; Terao, K.; Iwasaki, F.; Tani, S. 4-(4,6-dimethoxy-1,3,5-triazin-2-yl)-4-methyl-morpholinium chloride: an efficient condensing agent leading to the formation of amides and esters. *Tetrahedron* **1999**, *55*, 13159−13170.

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