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Helix-Sense-Selective Polymerization of Achiral Phenylacetylenes with Two *N*-Alkylamide Groups to Generate the One-Handed Helical Polymers Stabilized by Intramolecular Hydrogen Bonds

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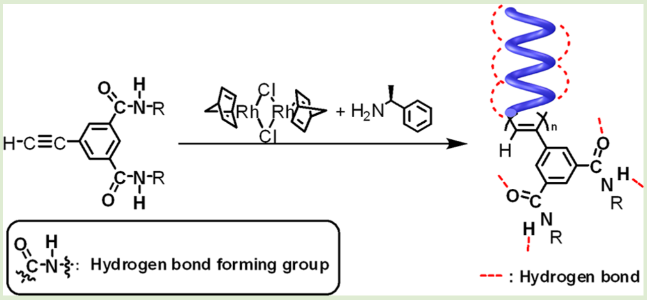
Supporting Information



ABSTRACT: In this study, we investigated the helix-sense-selective polymerizations of newly synthesized achiral phenylacetylenes having two *N*-alkylamide groups, such as 3,5-bis(dodecylamide)phenylacetylene (**DAPA**), 3,5-bis(octylamide)phenylacetylene (**OAPA**), and 3,5-bis(butylamide)phenylacetylene (**BAPA**), by using a chiral rhodium catalyst system ($[Rh(nbd)Cl]_2$-(*R*)-(+)-1-phenylethylamine [(*R*)-PEA]). Poly(**BAPA**) was insoluble in any solvents. On the other hand, poly(**DAPA**) and poly(**OAPA**) were soluble in toluene, THF, and $CHCl_3$, and the obtained polymers showed intense circular dichroism signals at the absorption region of the main chain in the UV−vis region. This result suggested those polymers were present in helical conformations with an excess of one-handed screw sense. The chiral helix structures of the formed polymers were stable in toluene at room temperature for a long time because of intramolecular hydrogen bonds. This result is the second example about polyacetylenes with one-handed helical conformation stabilized by intramolecular hydrogen bonds.

Recently, considerable number of studies have been conducted on synthesis of one-handed helical polyacetylenes due to their interesting application such as chiral sensor, optical resolution, microelectronic device, organic magnetic material, and so on.[1−6]

Now, two major synthetic strategies have been developed, that is, the first is asymmetric induced polymerization (**AIP**) in which chiral-substituted acetylenes are used as monomer.[7−13] The second is helix-sense-selective polymerization (**HSSP**) in which achiral acetylene monomers and other chiral sources such as initiators,[14−17] additives,[18−20] and a polymerization field[21−23] are used.

One-handed helical poly(substituted acetylenes) synthesized by **AIP** have two chiral sources, that is, chiral side groups and a one-handed helical main chain. This fact often causes complications in the understanding of their chiral behavior and chiral functions. Recently we reported modified **AIP** (**AIP-RIM**) to obtain one-handed helical poly(substituted acetylene)s having no chiral side groups.[24−26] This method is as follows: a chiral monomer was used in **AIP** followed by desubstitution of the chiral groups from a one-handed helical polymer membrane.

On the other hand, **HSSP** is a very important and simple method for the synthesis of one-handed helical polyacetylenes. Yashima and co-workers intensively have been investigating the induction of an excess of one-handed helical conformation of polyacetylenes by use of acid−base interaction or host−guest complexation.[18−20] Akagi et al. reported that the synthesis of a one-handed helical unsubstituted polyacetylene by polymerization of acetylene in chiral liquid crystalline phase induced by chiral dopant.[1,21−23] Recently, we have succeeded in the **HSSP** of achiral phenylacetylenes using $[Rh(nbd)Cl]_2$ in the presence of optically active 1-phenylethylamine (PEA) as cocatalyst.[14] For example, polymerization of 4-dodecyloxy-3,5-bis(hydroxymethyl)phenylacetylene (DHPA) by $[Rh(nbd)Cl]_2$-(*R*)-PEA gave the corresponding polymer, which showed large Cotton effects in the CD spectrum attributed to one-handed helical conformation in solution. This is the first example of one-handed helical substituted polyacetylenes having no other chiral moieties in the side or end groups, the conformation of which in solution is kinetically stabilized by intramolecular hydrogen bonds.

This catalyst system, $[Rh(nbd)Cl]_2$-(*R*)-PEA, is very simple and both compounds are commercially available. Furthermore, the polymerization procedure is very easy. The method is clearly valuable, but unfortunately a monomer type that is applicable to **HSSP** is limited.[27] Therefore, we had our mind set on exploring a new monomer type applicable to **HSSP** to expand the universality of the chiral catalyst system we found.

Here we will report on the new achiral phenylacetylene monomers for helix-sense-selective polymerization by $[Rh(nbd)Cl]_2$-(*R*)- or (*S*)-PEA. The monomers shown in Scheme

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Scheme 1. Helix-Sense-Selective Polymerization of Two *N*-Alkylamide Groups Containing Phenylacetylenes

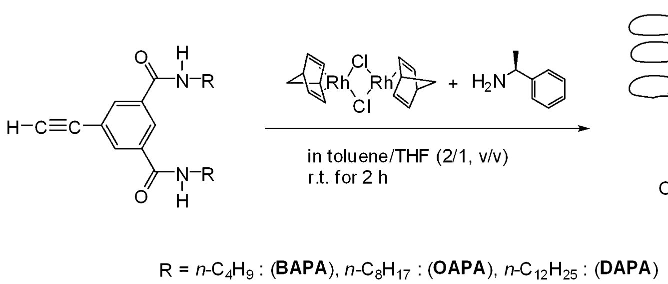


Table 1. Polymerization Results of Two *N*-Alkylamide Groups Containing Phenylacetylenes[a]

no.	monomer	[monomer] / [[Rh(nbd)Cl]$_2$]	[(*R*)-PEA] / [[Rh(nbd)Cl]$_2$]	yield (%)	M_w[b] (×10^7)	M_w/M_n	$[\theta]_{350}$[c] (×10^3 deg·cm^2/dmol)
1	**OAPA**	500	1	89	2.27	1.31	−4.59
2		500	250	90	2.49	1.34	−9.55
3		200	200	78	1.78	2.29	−7.34
4	**DAPA**	500	1	60	6.71	1.73	−2.33
5		300	300	83	2.77	1.66	−9.55
6	**BAPA**	100	100	21	[d]	[d]	[d]

[a] Polymerized in toluene/THF (2/1, v/v) at room temperature for 2 h; $[M]_0$ = 0.080 M. [b] Estimated by GPC (eluent: $CHCl_3$, polystyrene standard). [c] Determined by circular dichroism (CD) spectrum in toluene (c = 1.00 × 10^{-3} M). [d] Insoluble.

1 have two *N*-alkylamide groups at the 3,5-positions on the phenyl ring for intramolecular hydrogen bonds.

The new three achiral phenylacetylenes having two *N*-alkylamide groups, such as 3,5-bis(dodecylamide)-phenylacetylene (**DAPA**), 3,5-bis(octylamide)phenylacetylene (**OAPA**), and 3,5-bis(butylamide)phenylacetylene (**BAPA**), were synthesized with reference to the literature methods (see Supporting Information). [Rh(nbd)Cl]$_2$ (Aldrich) and (*R*)-(+)-1-phenylethylamine (Tokyo Chemical Industry Co. Ltd.) were used as purchased. All polymerizations were carried out under a dry nitrogen atmosphere in a mixture of toluene and THF (volume ratio of 2:1; a detailed procedure of polymerization has been described in Supporting Information.) Polymers were isolated by precipitation into a large amount of acetone and polymer yields were determined by gravimetry. The molecular weights of polymers were determined by gel permeation chromatography calibrated by standard polystyrene (eluent: THF).

Table 1 shows the results for the polymerization of **OAPA**, **DAPA**, and **BAPA** by [Rh(nbd)Cl]$_2$-(*R*)-PEA at various ratios of (*R*)-PEA/[[Rh(nbd)Cl]$_2$]. All polymerizations in Table 1 were carried out in a mixed solvent of toluene/THF (2:1, volume ratio) because solubility of the monomers into toluene was poor. The [Rh(nbd)Cl]$_2$-(*R*)-PEA catalyst system exhibited high activity in the polymerization of all monomers to afford polymer in good yield, except for **BAPA** (Table 1, run 6). Poly(**BAPA**) was insoluble in common organic solvents because *n*-butyl groups on nitrogen atoms was too short to enhance solubility. Therefore, during the polymerization, poly(**BAPA**) was precipitated and the polymerization was terminated. **OAPA** and **DAPA** had two *n*-octyl and *n*-dodecyl groups, respectively, afforded light-brown polymers as solid, and the obtained polymers were soluble in THF, $CHCl_3$, and toluene, and insoluble in acetone, methanol, DMF, diethyl ether, DMSO, benzene, and hexane. Poly(**OAPA**) and poly(**DAPA**) were extremely high molecular weight (M_w > 1.5 × 10^7) and relatively narrow molecular-weight-distribution (M_w/M_n = 1.3−2.3).

Poly(**OAPA**) and poly(**DAPA**) obtained by [Rh(nbd)Cl]$_2$-(*R*)-PEA showed a large Cotton signal in the range of main chain absorption (Table 1, runs 1−3 and 4, 5, respectively, Figure 1), indicating that both polymers exist in excess one-handed helical conformation.[8] Therefore, it was ascertained that [Rh(nbd)Cl]$_2$-(*R*)-PEA catalyst could lead to the helix-sense-selective polymerization of **OAPA** and **DAPA**.

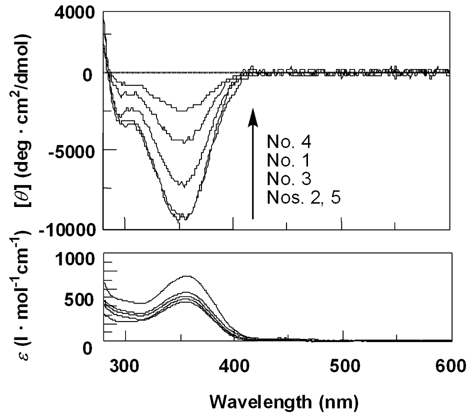


Figure 1. CD and UV−vis spectra of poly(**OAPA**) and poly(**DAPA**) in toluene (the numbers correspond to those in Table 1).

By the way, interesting solvent effects on the **HSSP** were observed. Table 2 shows the **HSSP** results of **DAPA** in $CHCl_3$ and a mixture of $CHCl_3$ and toluene. Polymer yields and molecular weights were similar to those of the polymerization in THF system in Table 1. On the other hand, molar ellipticity, [*θ*], was an opposite sign and relatively small (Figure S1). Similar inversion phenomenon due to solvent polarity was reported by Sanda et al. about poly(propargylamide) carrying L-glutamic acid and azobenzene.[28] But our polymers in this study have no chiral pendant groups. Therefore, kinetic stabilities for P-helix and M-helix should be the same. Hence, the reason why helices with the opposite helix sense were formed in different

Table 2. Solvent Effects on Helix-Sense-Selective Polymerization of **DAPA** by $[\mathrm{Rh(nbd)Cl}]_2$-(R)-PEA[a]

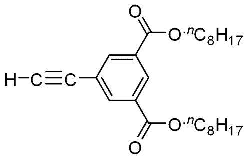
no.	solvent	yield (%)	M_w[b] ($\times 10^7$)	M_w/ M_n	$[\theta]_{350}$[c] ($\times 10^3$ deg·cm^2/dmol)
1	$CHCl_3$	83	3.15	3.59	+3.10
2	toluene/$CHCl_3$ (2:1, v/v)	74	7.48	1.43	+1.18
3	toluene/$CHCl_3$ (2:1, v/v)	78	3.49	1.28	+1.28

[a] Polymerized at room temperature for 2 h; $[M]_0 = 0.080$ M, [**DAPA**]/$[[\mathrm{Rh(nbd)Cl}]_2] = 165$, [($R$)-PEA]/$[[\mathrm{Rh(nbd)Cl}]_2] = 80$. [b] Estimated by GPC (eluent: $CHCl_3$, polystyrene standard). [c] Determined by circular dichroism (CD) spectrum in toluene ($c = 1.00 \times 10^{-3}$ M).

polymerization solvents should be due to the difference in the chirality of the Rh complex formed in given solvents. Detailed chiral structures of the Rh complexes in various solvents are now under investigation.

The chiral structure of poly(**OAPA**) and poly(**DAPA**) in this study were stable in toluene at room temperature for a long period of time (ca. 2 months). Moreover, even when the xylene solution of the polymers was heated to 110 °C, only a slight decrease was detected in CD (Figures S2–S4). 3,5-Bis(octyloxycarbonyl)phenylacetylene (**OEPA**; Chart 1) was synthesized, which has no hydrogen-bond formable group, and polymerized under the same **HSSP** conditions. However, the obtained polymer did not show the Cotton signal. This result indicates that two amide groups in **OAPA** and **ODPA** are essential for **HSSP** and the one-handed helical conformation of poly(**OAPA**) and poly(**ODPA**) is maintained by an intramolecular hydrogen bond between two alkyl amide groups. To confirm this further, we measured the solid- and solution-state IR spectra of poly(**OAPA**). In the solid state and solution state (in toluene), poly(**OAPA**) showed the amide $\nu_{C=O}$ at 1638 and 1645 cm^{-1}, respectively. Furthermore, the peaks of C═O stretching of the amide of **OAPA** (dilute condition: 50 mM) were observed at 1682 cm^{-1}, which was 37 cm^{-1} lower wavenumbers than those of poly(**OAPA**). These results indicate that the amide groups of the polymer form intramolecular hydrogen bonds in toluene.[28−31]

Chart 1. Phenylacetylene Monomers without Hydrogen Bond Formable Groups (**OEPA**)



As mentioned above, the one-handed helical structure of the polymers in this study was very stable in toluene at room temperature for a long period. While on the other hand, in $CHCl_3$, the chiral structure easily collapsed. Figure 2 shows a time-profile of CD and UV–vis spectrum of poly(**DAPA**) in $CHCl_3$. In $CHCl_3$, the Cotton signal gradually decreased, and after 30 min, about a 40% reduction occurred, and then after 550 min, the Cotton signal was completely disappeared. As Cotton signal decreased, in UV–vis spectra an absorption maximum red-shifted from 350 to 450 nm. These results indicate that intramolecular hydrogen bonds in the one-handed helical polymer were easily broken in $CHCl_3$ to form a random coil polymer with longer effective conjugated length.

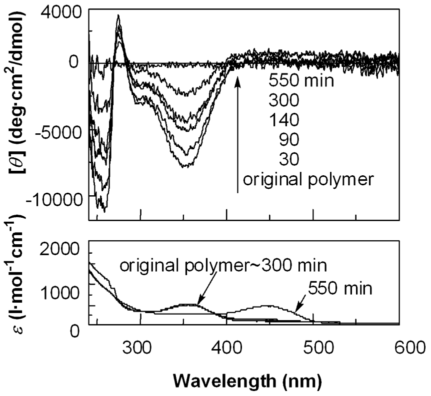


Figure 2. Aging effect on CD and UV–vis spectra of poly(**DAPA**) polymerized in toluene/THF(2/1, v/v) (measured in $CHCl_3$).

In summary, three achiral phenylacetylenes having two N-alkylamide groups (**DAPA**, **OAPA**, **BAPA**) were newly designed for synthesis of one-handed helical polyacetylenes. Poly(**BAPA**) was insoluble in common organic solvents. **HSSP** of **DAPA** and **OAPA** by $[\mathrm{Rh(nbd)Cl}]_2$-(R)-(+)-1-phenylethylamine was successful and gave stable one-handed helical polymers in solution in which conformation was maintained by intramolecular hydrogen bonds of two N-alkylamide groups. Interestingly, solvent effect on the sign of Cotton signal was observed. That is, the polymers synthesized in a mixture of toluene/THF showed the Cotton signal with minus sign, on the other hand, polymerization in toluene/$CHCl_3$, gave a polymer with the plus Cotton signals. The chiral helix structures of poly(**OAPA**) and poly(**DAPA**) were stable in toluene at room temperature for a long time because of intramolecular hydrogen bonds. On the other hand, in $CHCl_3$, hydrogen bonds were unstable and the one-handed helical conformation was broken. The polymer was synthesized by **HSSP** in a mixture of toluene/THF or $CHCl_3$ and toluene/$CHCl_3$. Investigation of detailed secondary structures and **HSSP** of a series of achiral phenylacetylenes with amide-type hydrogen bonds forming groups such as urea and carbamate functionality are now in progress.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures for monomer synthesis, characterization, and polymerization technique. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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