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Synthesis and Conformational Study of Optically Active Poly(phenylacetylene) Derivatives Bearing a Bulky Substituent

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ABSTRACT: Three optically active phenylacetylenes having a chiral carbamoyloxy group at the *para* or *meta* position were synthesized, polymerized, and copolymerized with various optically inactive comonomers with transition metal catalysts such as $[RhCl(NBD)]_2$ (NBD: norbornadiene) in THF in order to explore the role of the bulkiness of side groups on the phenyl moieties during the formation of a helical conformation. $[RhCl(NBD)]_2$ produced high molecular weight polymers and copolymers in THF. The yields and molecular weight of the obtained copolymers were influenced by the bulkiness of the comonomers. All polymers showed broad electronic absorptions up to *ca.* 570 nm, and the ^1H NMR spectra indicated that the polymers had a cis−transoidal structure. The chiral homopolymers and copolymers showed an intense induced CD in the UV−visible region depending on the position of the substituents of the chiral residues and the bulkiness of the achiral comonomers. The polymers having chiral carbamoyloxy groups at the *para* position on the phenyl groups showed very intense induced CD bands in the UV−visible region with negative and positive Cotton effects. The main chain of the polymers seems to be chiral, probably based on a predominant one-handed helical sense. The magnitude of the CD of the copolymers increased with an increase in the bulkiness of the substituents of the comonomers. The polymers with a chiral substituent at the *meta* position showed a very weak induced CD in the UV−visible region. However, a copolymer with the phenylacetylene having a bulky *tert*-butyldiphenylsiloxy group at the *para* position exhibited a very intense induced CD which was almost a mirror image to those of the chiral homopolymers in the 300−450 nm wavelength range. These results suggest that the copolymer may possess a reversed helical structure. The sign and specific rotation at 780 nm of the *para*-substituted polymers and copolymers were also influenced by the bulkiness of the substituents of the comonomers; the specific rotation of the copolymer of **1** or **2** with the phenylacetylene having bulky *tert*-butyldiphenylsiloxy groups at the *para* position showed a specific rotation about 2 times larger than that of the homopolymers. The steric effects of bulky side groups on helical conformation was discussed on the basis of molecular mechanics and molecular dynamics calculations of model polymers.

Introduction

Optically active polymers have aroused wide interest from synthetic, structural, and functional viewpoints. Especially, the synthesis of optically active polymers whose chirality is derived mainly from a one-handed helical structure is one of the major current topics in polymer chemistry.[1] Optically active polyisocyanides,[2] polychloral,[3] polyisocyanates,[4] poly(2,3-quinoxaline)s[5], and poly(triarylmethyl methacrylate)s[1a,6] belong to this category. Among these helical polymers, poly(triarylmethyl methacrylate)s, for instance, poly(triphenylmethyl methacrylate) (PTrMA) with a one-handed helical structure prepared by asymmetric polymerization, possesses the characteristic ability to resolve various racemates as a chiral stationary phase (CSP) for high-performance liquid chromatography (HPLC).[7] The helical conformation of the main chain plays an important role in effective chiral recognition.

Polyacetylenes have been prepared with much interest to develop new functional polymers as conducting materials,[8] nonlinear optical materials,[9] and gas-permeable membranes.[10] Our interest is focused on the structure of the optically active polyacetylenes prepared by the polymerization of acetylenes having a chiral substituent, because they may have a helical structure.[11] Ciardelli *et al.*[11a] and, later, Moore and Grubbs *et al.*[11b] reported that polyacetylenes with a chiral substituent have predominantly a single sense of helix due to the nonplanar conformation of the polyene structure on the basis of the CD analysis of the polyacetylenes. Chiral polyacetylenes with a helical conformation may show prominent chiral recognition. Aoki *et al.*[11d] demonstrated that optically active polyacetylenes worked as enantioselective permeable membranes being capable of separating racemic amino acids and alcohols in water or in methanol.[12] Recently, we have also found that a stereoregular optically active poly(phenylacetylene) prepared from an optically active phenylacetylene derivative having an (*R*)-((1-phenylethyl)carbamoyl)oxy group at the *para* position (**1**) with a rhodium catalyst showed high chiral recognition as a CSP for HPLC and separated many racemates such as Tröger's base, spiropyran derivatives, and racemic alcohols.[13] The stereoregularity and helical conformation of the polymer may play an important role in effective chiral recognition, because a stereoirregular poly(phenylacetylene) having the same chiral side group prepared by a different synthetic route showed poor chiral recognition.[13]

In the present study, three optically active phenylacetylenes (**1**, **2**, and **6**) having a chiral carbamoyloxy group at the *para* or *meta* position were synthesized, polymerized, and copolymerized with various optically inactive comonomers (**3**−**5** and **7**−**9**) with transition metal catalysts such as $[RhCl(NBD)]_2$ (NBD: norbornadiene). The object of this work is to explore the role of the bulkiness of the side groups introduced on the phenyl moieties of a monomer and a comonomer in the formation of a helical conformation which is evaluated through the CD and specific rotation measurements and molecular mechanics and molecular dynamics calculations. Up to now, there has been almost no discussion

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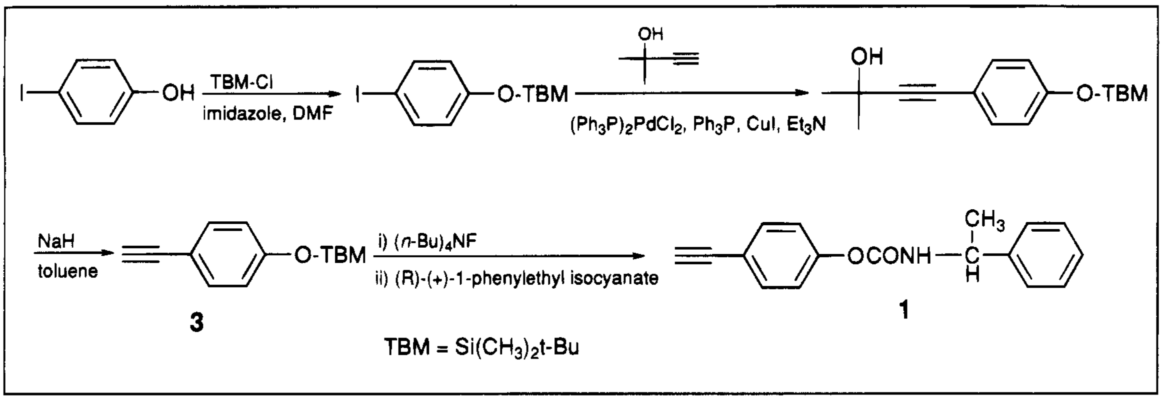
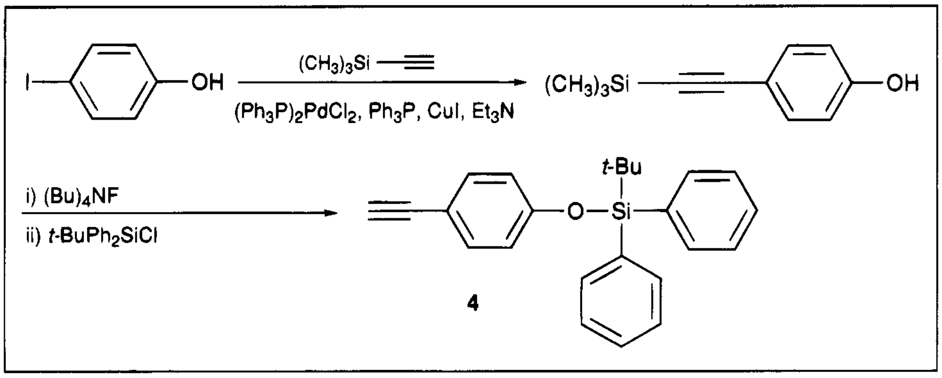
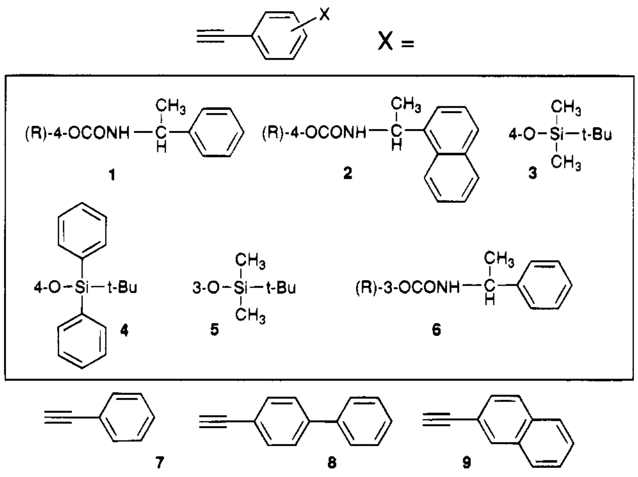
Scheme 1. Synthesis of 1 and 3



Scheme 2. Synthesis of 4



on the effect of bulkiness of substituents during the formation of a helical conformation of polyacetylenes. In the asymmetric synthesis of one-handed helical polymethacrylates with chiral anionic initiators, the bulky triarylmethyl side groups are essential to obtain optically active helical polymers stable in solution, while less bulky polymethacrylates cannot afford helical polymers.[14]



Results and Discussion

Synthesis and Polymerization of Phenylacetylene Derivatives and Structural Characteristics of Polymers. Three optically active phenylacetylenes (**1**, **2**, and **6**) and a variety of achiral phenylacetylenes were prepared without difficulty as outlined in Schemes 1 and 2. The coupling of (trimethylsilyl)acetylene to iodophenol or aromatic halides with a palladium catalyst followed by desilylation of the trimethylsilyl protecting group (Scheme 2) appeared to be a convenient method to prepare hydroxyphenylacetylene or aromatic acetylenes in good yields.[15] The hydroxyphenylacetylene was easily converted to the corresponding carbamates by reaction with commercially available optically active isocyanates. The chiral monomers thus obtained were found to be optically pure based on the chiral HPLC analysis and were characterized by ^{1}H NMR and elemental analysis, which were in fair agreement with their assigned structures. Monomers **3**, **5**,[16] **8**, and **9**[17] are known compounds, and their spectral properties including NMR and MS were consistent with the reported values. Compound **4** was prepared according to Scheme 2, and its formula and structure were confirmed by ^{1}H NMR and elemental analysis.

First, the polymerization of chiral monomer **1** was conducted using WCl_6–Ph_4Sn in toluene at 60 °C, which is known to be an excellent catalyst to polymerize aromatic acetylenes.[18] However, no polymeric products were obtained. The catalyst may be inactivated in the presence of the acidic NH protons of the carbamate groups of **1**. A rhodium catalyst, $[RhCl(NBD)]_2$ (NBD: norbornadiene)] was then examined. This rhodium catalyst has been reported to be effective for the polymerization of monosubstituted acetylenes, especially (substituted-phenyl)acetylenes to afford high molecular weight stereoregular polymers[19] and can polymerize (carbamoyloxy)phenylacetylenes even in a protonic solvent such as methanol.[20] The results of the polymerization and copolymerization of **1**–**9** with the rhodium catalyst are summarized in Table 1.

The polymerization of the chiral acetylene **1** was carried out in anhydrous Et_3N and THF. In Et_3N, the polymerization proceeded rapidly and a yellow polymer precipitated within a few minutes, whereas the reaction system was homogeneous throughout the polymeriza-

Table 1. Polymerization of Optically Active Monomers (M_1) and Copolymerization with Phenylacetylene Derivatives (M_2) with $[Rh(NBD)Cl]_2$ in THF at 30 °C[a]

				polymer		
run	M_1	M_2	time (h)	yield (%)[b]	$[M_1]$ (mol %)[c]	$M_n \times 10^{-4}$ [d]
1	1	—[e]	19	91	100	3.3
2	1	—	1	94	100	32.0
3	1	3	1	79	8.2	39.2
4	1	4	3	30	29.7	56.4
5	1	5	3	73	15.9	117
6	1	7	21	71	9.2	29.5
7	1	8	8	37	—	—
8	1	9	3	39	—	—
9	2	—[f]	2	83	100	5.1
10	2	—	1	90	100	8.6[g]
11	2	3	2	74	11.2	65.5
12	2	4	3.2	38	28.2	64.7
13	2	5	3	52	11.8	103
14	2	7	2	53	13.7	35.0
15	2	8	25	18	—	—
16	2	9	3	59	—	—
17	6	—[e]	1	84	100	5.2
18	6	—	1.5	90	100	75.5
19	6	3	3	79	11.8	62.8
20	6	4	3.5	31	20.4	88.6
21	6	5	3	75	17.2	139
22	6	7	3	71	13.5	34.2
23	6	8	25	61	—	—
24	6	9	3	37	—	—

[a] $[M_1 + M_2] = 0.5$ M, [Rh] = 5 mM, $[M_2]/[M_1] = 9$. [b] Methanol-insoluble fraction. [c] Estimated by ^1H NMR. [d] Determined by GPC (polystyrene standards). [e] In Et_3N. [f] In Et_3N/THF = 4/1 (v/v). [g] THF-soluble part.

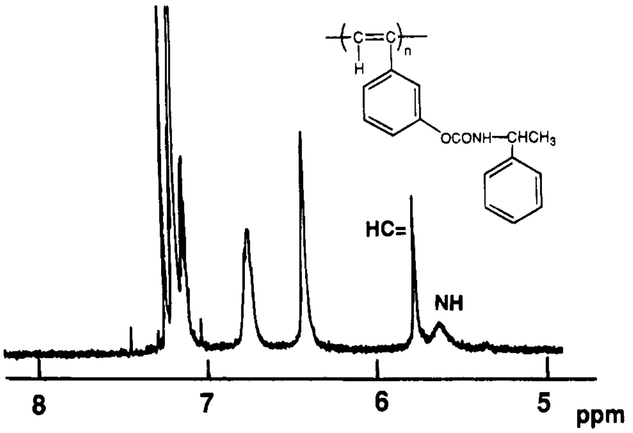


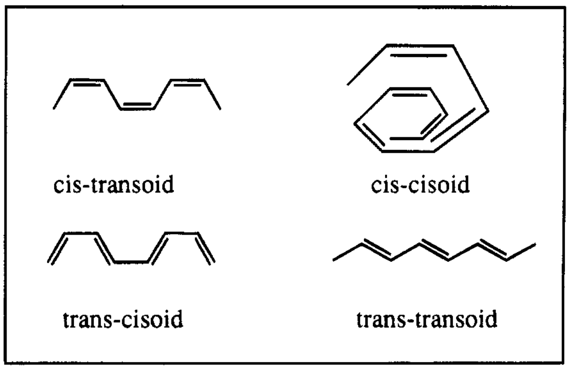
Figure 1. 500 MHz ^1H NMR spectrum of poly-**6** (run 18 in Table 1) in $CDCl_3$ at 60 °C.

Table 2. ^1H NMR and UV–Visible Data of Chiral Poly(phenylacetylene) Derivatives[a]

			^1H NMR	UV–vis		
run[b]	M_1	M_2	=CH (ppm)	λ_{max} (nm)/ϵ	λ_2 (nm)/ϵ	λ_3 (nm)/ϵ
1	1	—	5.4–6.1	250/7820	325/3540	375/3020
3	1	—	5.67	250/6790	325/3440	391/2990
3	1	3	5.77	258/6980	333/4120	407/3140
4	1	4	5.56	260/7750	339/4730	400/3180
5	1	5	5.72	260/5850	—	425/4170
6	1	7	5.83	250/5980	325/3350	388/3200
9	2	—	5.84	268/11860	—	395/3060
11	2	3	5.80	255/8220	330/4580	408/3290
12	2	4	5.60	260/9660	338/5360	400/3690
13	2	5	5.72	263/6320	—	425/4260
14	2	7	5.83	250/6660	323/3670	393/3300
18	6	—	5.78	253/6820	—	405/3880
19	6	3	5.80	250/8760	331/4760	413/3500
20	6	4	5.55	260/8670	336/4760	400/3700
21	6	5	5.72	266/6890	—	425/4870
22	6	7	5.83	245/6840	324/3670	393/3470

[a] ^1H NMR and UV–visible spectra were recorded in $CDCl_3$ and THF, respectively. [b] Run numbers correspond to those in Table 1.

Scheme 3



tion when THF was used as the solvent. The polymerization in THF afforded almost 10 times larger molecular weight homopolymers in higher yields in comparison with the polymerization in Et_3N. Tabata *et al.* claimed that Et_3N was a very useful solvent for the preparation of higher molecular weight and higher cis content poly(phenylacetylene)s compared to THF.[19h] The present results, however, indicate that THF is also a good solvent, especially for the polymerization of phenylacetylenes containing carbamoyl functional groups. Most chiral homopolymers were soluble in THF, chloroform, and acetone, but the poly-**2** obtained in THF was partially soluble in THF and chloroform after isolation. The elemental analyses of all the homopolymers agreed satisfactorily with the calculations.

The stereoregularity of the homopolymers was investigated by ^1H NMR spectroscopy. As an example, the spectrum of poly-**6** obtained in THF is shown in Figure 1, and the ^1H NMR data are summarized in Table 2 together with the UV–visible spectroscopic data. As for the structure of polyacetylenes, there exist at least four possible conformers (Scheme 3): cis–transoid, cis–cisoid, trans–transoid, and trans–cisoid. The chemical shift and line shape of the main chain's olefinic protons and aromatic protons are considered to be sensitive to the conformers.[21] The resonance centered at around 5.8 ppm with a well-resolved sharp line width (Figure 1) can be assigned to the cis–transoidal main chain's olefinic protons, and the cis content is estimated to be 100% by the integral ratio of the olefinic proton resonance and the other aromatic proton resonances based on the literature method for poly(phenylacetylene).[21] Other homopolymers obtained in THF also showed similar sharp olefinic proton resonances (Table 2), but the poly-**1** obtained in Et_3N gave rather broad signals at around 5.4–6.1 ppm. The olefinic proton resonances of homopolymers and copolymers were influenced by the structure of the polymerized monomers and were shifted slightly upfield (0.04–0.24 ppm) as the bulkiness of the comonomers increased. These shifts may reflect a change in electron delocalization on the conjugated olefinic protons. Therefore, the main chain cis–transoidal conformation of the polymers is slightly different depending on the bulkiness of the substituents on the phenyl residues; the consecutive double bonds may be twisted with a different rotational angle. This may result in different electronic transitions and chiroptical properties of the polymers.

Tabata *et al.* reported that a poly(phenylacetylene) having a molecular weight of 350 000 prepared in Et_3N with the same rhodium catalyst gave a well-resolved singlet at 5.82 ppm for the main chain protons, but a poly(phenylacetylene) prepared in THF (molecular weight 35 000) showed a spectrum with a broad line width, suggesting that the cis content of the former polymer was higher than that of the latter polymer.[19h,21] The homopolymers prepared in the present study using THF and Et_3N showed reversed spectral patterns. The relationship between the line broadening of the olefinic proton resonances in ^1H NMR and the stereoregularity of the main chain has been intensively discussed,[21] but no clear explanation has been proposed. In the present cases, the difference in molecular weight between the homopolymers may be responsible in part for the different line widths. Consequently, the homopolymers prepared in THF were found to have an almost complete cis–transoidal structure. Therefore, the copolymerization of the chiral monomers with a series of phenylacetylenes with bulky substituents was conducted only in THF. The feed molar ratio of a comonomer to the chiral monomer was fixed at 9 in all cases (Table 1).

The yields and molecular weights of the copolymers obtained were influenced by the position and bulkiness of the comonomers. Copolymers with the *meta*-substituted comonomer **5** had a very high molecular weight ($>10^6$). The copolymerization with less bulky *para*-substituted phenylacetylenes (**3** and **7**) afforded lower molecular weight copolymers in higher yields in comparison with the copolymerization with the most bulky phenylacetylene **4**, which was copolymerized to give higher molecular weight copolymers. The copolymerizability of the aromatic acetylenes (**8** and **9**) was relatively low and the obtained copolymers were scarcely soluble in common organic solvents such as THF, chloroform, toluene, acetone, and DMF. A similar insoluble poly-**9** was also obtained with halogenated tungsten catalysts.[17]

All polymers showed broad electronic absorptions up to *ca.* 570 nm with an absorption maximum at around 260 ± 10 nm and two peaks between 323 and 425 nm. The wavelengths of these peaks shifted to longer wavelengths by *ca.* 10 nm as the bulkiness of the substituents at the *para* position on the phenyl residue increased as observed for poly-**1**, poly(**1**-*co*-**3**), and poly(**1**-*co*-**4**). Stereoregularity of the obtained copolymers was also examined by ^1H NMR. Rather broad olefinic proton resonances were observed for the copolymers with bulky comonomers (**3** and **4**), while the copolymers with phenylacetylene showed sharp resonances at 5.83 ppm. These differences in line broadening may reflect the mobility of the copolymers; the copolymers with **3** and **4** may have a rigid structure. However, most copolymers had a high cis–transoidal structure based on the literature.[21]

Chiroptical Properties of Polymers. To characterize the chiroptical properties of polyacetylenes having chiral substituents, CD spectroscopy is suitable for detecting a macromolecular asymmetry. The chiral homopolymers and copolymers showed remarkably intense induced CD in the UV–visible region depending on the position of the substituents of the chiral monomers and bulkiness of the achiral comonomers. The CD spectra of a series of homopolymers and copolymers are shown in Figures 2–4. The chiral acetylene monomers do not show any CD bands at wavelengths greater than 260 nm for **1** and **6** and 305 nm for **2**.

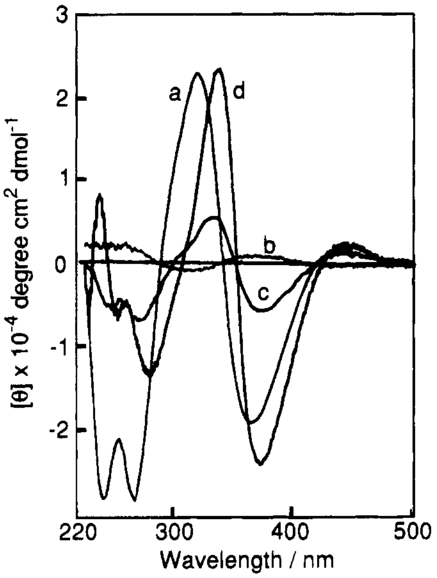


Figure 2. CD spectra of poly-**1** (a, run 2 in Table 1) and copolymers with **7** (b, run 6 in Table 1), **3** (c, run 3 in Table 1), and **4** (d, run 4 in Table 1) in THF at room temperature.

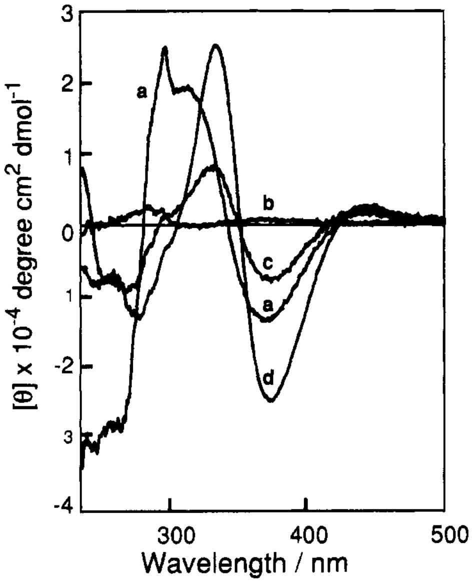


Figure 3. CD spectra of poly-**2** (a, run 9 in Table 1) and copolymers with **7** (b, run 14 in Table 1), **3** (c, run 11 in Table 1), and **4** (d, run 12 in Table 1) in THF at room temperature.

The CD spectra of poly-**1** and its copolymers with various achiral acetylenes are shown in Figure 2. Poly-**1** prepared in THF showed very intense induced CD bands in the UV–visible region with negative and positive Cotton effects (Figure 2a). The CD signals could be assigned to π–π^* electronic transitions of the conjugated polyene chromophors, and, therefore, the main chain of the polymer seems to be chiral, probably due to a predominant one-handed helical sense. The poly-**1** prepared in Et_3N also showed induced CD whose magnitude was almost half of that of the poly-**1** obtained in THF. A similar induced CD was reported for a poly(phenylacetylene) with chiral ester groups at the *para* position.[11d] In order to investigate the effect of stereoregularity of the main chain of poly-**1** on the chiroptical property, the poly(phenylacetylene) was prepared using a different synthetic route. First, 4-(*tert*-butyldimethylsiloxy)phenylacetylene (**3**) was polymerized in toluene at 60 °C using the WCl_6–Ph_4Sn catalyst,[18] followed by desilylation with tetrabutylammonium fluoride. The

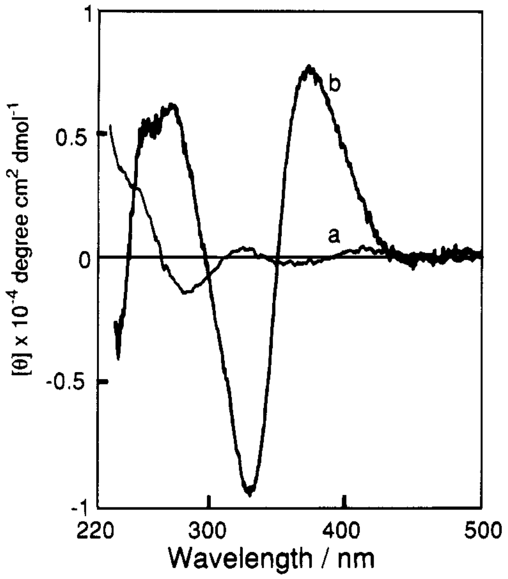


Figure 4. CD spectra of poly-**6** (a, run 18 in Table 1) and copolymer with **4** (b, run 20 in Table 1) in THF at room temperature.

resultant poly(4-hydroxyphenylacetylene) was allowed to react with (*R*)-(+)-1-phenylethyl isocyanate in pyridine to give poly[(*R*)-4-(((1-phenylethyl)carbamoyl)oxy)-phenylacetylene)]. The elemental analysis of the polymer indicated that the (1-phenylethyl)carbamoyl group was almost quantitatively introduced on each hydroxy group. This polymer has the same chiral side groups as poly-**1**, but the ^{1}H NMR showed very broad peaks at 5.5−8.0 ppm, indicating that the polymer is not stereoregular in the main chain configuration.[21] The polymer did not show any significant CD bands in the 500−300 nm range.[13] These results suggest that the regular main chain configuration may be essential for the presence of the helical conformation exhibiting the induced CD.

The magnitude of the CD observed for copolymers of **1** was strongly dependent on the bulkiness of the achiral comonomers; the magnitude of the CD increased with an increase in the bulkiness of the substituents of the comonomers. Poly(**1**-*co*-**7**) showed a very small CD in the range of 300−400 nm and its pattern was almost the mirror image to that of poly-**1**. This indicates that the phenylacetylene sequences incorporated in the main chain could be hardly affected by the neighboring chiral components **1** and, therefore, the induced CD may be attributed to the chiral monomer units, although it still remains unclear why the sign of the Cotton effects of the copolymer was reversed.

Both the copolymers of **1** with *para*-substituted comonomers **3** and **4**, especially poly(**1**-*co*-**4**), showed a very intense induced CD comparable to that of poly-**1**, in spite of a low content of chiral monomer units, and the wavelengths of the two peaks (300−400 nm) shifted *ca.* 10 nm to a longer wavelength. The small amount of chiral monomer units (29.7%) could control the overall chain conformation, and the bulky side groups of the comonomers must be essential to maintain the predominant helical sense of the copolymers induced by the small amounts of chiral monomer units. To discuss the magnitude of the CD of the copolymers, the contents of the chiral monomer units in the copolymers must be taken into consideration. The poly(**1**-*co*-**4**) contained 3.6 times more chiral monomer units than poly(**1**-*co*-**3**), yet the magnitude of the CD bands for poly(**1**-*co*-**4**) at 332 and 375 nm was *ca.* 4.3 times larger than that of poly-(**1**-*co*-**3**). This indicates that the one-handedness in a helix sense of the former copolymer may be higher than that of the latter. Recently, Grubbs *et al.*[11b] reported that chiral polyacetylenes prepared by ring-opening metathesis polymerization of optically active monosubstituted cyclooctatetraene showed an induced CD whose magnitude was comparable to that of previously prepared chiral polyacetylenes having chiral α-branched substituents on every other acetylene residue.[11a] They concluded that the chiral helical conformation imparted to the main chain by the chiral substituents was not greatly influenced by the proximity of the neighboring substituents. However, the present results clearly indicate that the main chain chirality can be affected by the bulkiness of the neighboring monomer units, especially in the poly(phenylacetylene) derivatives. A copolymer of **1** with the *meta*-substituted comonomer **5** did not show an induced CD.

A similar increase in the magnitude of the induced CD was observed for the copolymers of **2** (Figure 3). Poly-**2** bearing (*R*)-((1-(1-naphthyl)ethyl)carbamoyl)oxy groups at the *para* position obtained in THF/Et$_3$N showed a similar induced CD with respect to the pattern as poly-**1**, but the magnitude was slightly smaller. Poly-(**2**-*co*-**4**) showed the most intense induced CD similarly to poly(**1**-*co*-**4**), judging from the content of the chiral monomer units incorporated in the copolymers.

As for poly-**6** having a chiral residue at the *meta* position and its copolymers, their spectroscopic behaviors were very different from those of the *para*-substituted polymers and copolymers (Figure 4). Poly-**6** showed a very weak induced CD in the UV−visible region. The magnitude of the CD over 300 nm was almost one-sixtieth of that of poly-**1** and almost no induced CD was detectable for copolymers with **3**, **5**, and **7**. A similar small ellipticity was previously observed for a chiral poly(phenylacetylene) having chiral ester groups at the *meta* position.[11c] It is not clear why the poly-**6** barely showed an induced CD. A dissymmetric substitution of the chiral residues at the *meta* position on the phenyl groups probably cannot induce a steric factor, which is required to maintain a helical structure. However, interestingly, the poly(**6**-*co*-**4**) exhibited a very intense induced CD, whose magnitude was more intense than that of poly-**6** by a factor of *ca.* 130-fold. Moreover, the CD spectrum was almost a mirror image to those of poly-**1**, poly(**1**-*co*-**4**), and poly(**2**-*co*-**4**) in the 300−450 nm wavelength range. These results indicate that the copolymer poly(**6**-*co*-**4**) possesses a reversed helical structure versus other homopolymers (poly-**1** and poly-**2**) and copolymers [poly(**1**-*co*-**4**) and poly(**2**-*co*-**4**)] and the consecutive helical sequences consisting of **4** units must mainly contribute to the induced CD, because the homopolymer of **6** did not show such an intense CD. Consequently, dramatic effects of the bulkiness of substituents on the formation of the helical structure were observed for the first time.

Attempts to measure optical rotations of poly-**1** using a short-pass quartz cell failed due to the electronic absorption of the polymer near the Na D-line. However, data on optical rotations of the chiral polymers were gained by using a polarimetric detector (Shodex) operated at a wavelength of 780 nm. The polarimetric detector was connected in series to a GPC system including a UV−visible detector (254 nm) and GPC columns (see Experimental Section). Figure 5 presents the GPC chromatograms of poly-**1** (d) and its copolymers

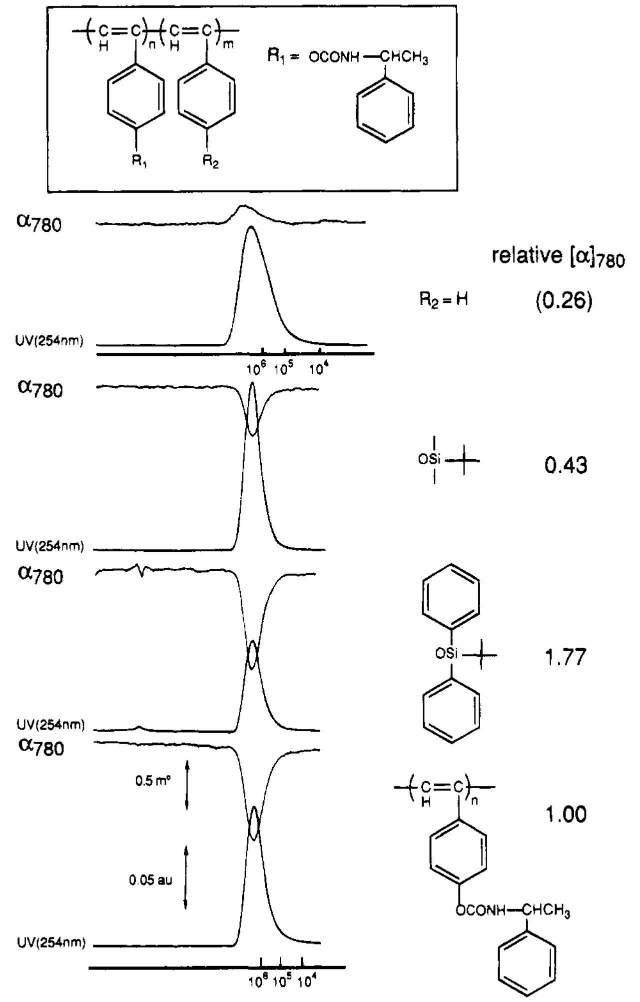


Figure 5. GPC chromatograms of poly-**1** (d, run 2 in Table 1) and copolymers with **7** (a, run 6 in Table 1), **3** (b, run 3 in Table 1), and **4** (c, run 4 in Table 1).

(a, b, and c) monitored with UV and polarimetric detectors. Both curves were unimodal and similar in pattern. The poly-**1** and the copolymers with **3** (b) and **4** (c) were found to show negative rotation in contrast to the positive rotation of monomer **1**, while the poly(**1**-*co*-**7**) showed positive rotation. Such a reversed sign of the optical rotation of these polymers agreed well with the CD data, since only the poly(**1**-*co*-**7**) showed a reversed pattern for the Cotton effect (Figure 2). It is noteworthy that the ratio of the intensity of these two curves directly reflects the specific rotation of the polymer. Therefore, the relative specific rotation ($[\alpha]_{780}$) of a given set of polymers can be estimated by comparison of the intensities and correcting absorbance at 254 nm using the molar extinction coefficient (ϵ) at 254 nm. The results are summarized in Table 3.

The sign and relative specific rotations at 780 nm of the *para*-substituted polymers and copolymers were greatly influenced by the bulkiness of the substituents of the comonomers, and there is a clear tendency as observed in the CD spectra; for instance, the specific rotation of the poly(**1**-*co*-**3**) incorporating only 8.2% chiral units is almost half that of poly-**1** consisting of 100% chiral monomer units, while poly(**1**-*co*-**4**) containing 30% chiral monomer units showed 1.8 times larger specific rotation than that of the homopolymer. The bulky substituents significantly affect the main chain conformation forming a helical structure with a predominant screw sense, which may result in a large negative optical rotation in this case. The same large negative specific rotation was observed for poly(**2**-*co*-**4**).

Table 3. Relative Specific Rotation of Poly(phenylacetylene)s

run[a]	M1	M2	relative $[\alpha]_{780}$[b]
2	1	–	1.00 (−)
3	1	3	0.43 (−)
4	1	4	1.77 (−)
6	1	7	0.26 (+)
9	2	–	1.31 (−)
12	2	4	2.06 (−)
18	6	–	1.11 (+)
20	6	4	0.98 (+)
22	6	7	0.15 (+)

[a] Run numbers correspond to those in Table 1. [b] In THF. The sign of optical rotation is shown in parentheses.

The dramatic effect of such a small amount of chiral monomer during the formation of an excess of one helical sense of a copolymer was demonstrated in the copolymerization of optically active isocyanate with hexyl isocyanate; the obtained copolymer showed optical activity larger than that expected from the content of the feed chiral monomer.[4c]

On the other hand, poly-**6** showing little induced CD revealed a positive rotation whose sign is identical to that of monomer **6**, and other copolymers also showed the same sign with smaller values. As previously mentioned, poly(**6**-*co*-**4**) showed a very intense induced CD with almost a mirror image to those of poly(**1**-*co*-**4**) and poly(**2**-*co*-**4**) that exhibited a negative optical rotation. These results suggest that the positive optical rotation of poly(**1**-*co*-**7**), poly-**6**, and poly(**6**-*co*-**7**) may be mainly derived from the chirality of the side groups because these polymers showed little or no induced CD in the 300–400 nm range. The large positive specific rotation of poly(**6**-*co*-**4**) was comparable to that of poly-**6** and may be responsible for the helical conformation of the main chain.

Computational Studies on a Helical Conformation of Model Polymers. Molecular mechanics and molecular dynamics calculations using the Dreiding force field[22] were carried out for a model polymer of 20 repeated monomer units of **3**, **4**, and **7** in order to gain information regarding the conformation of the poly(phenylacetylene) derivatives prepared in this study. A planar extended backbone conformation has been reported for a trans–transoidal polyacetylene and substituted polyacetylenes,[23] while a helical conformation has been proposed for a few cis–transoidal and cis–cisoidal substituted polyacetylenes.[23a,b]

The rhodium catalyst used in this study may give almost complete cis–transoidal poly(phenylacetylene)s. Therefore, we first constructed cis–transoidal poly(phenylacetylene) (20-mer) as a model polymer for calculations with a different twist angle about a single bond (ϕ = 180–90° at 10° intervals), where ϕ = 180° means a complete cis–transoid with a planar backbone structure. The final minimized energies were similar within a difference of *ca.* 5 kcal/mol for ϕ = 180–110° and were higher for ϕ = 100–90°. When the starting ϕ of the 20-mer was in the 150–110° range, the optimized model polymers converged to a similar left-handed helical structure except for a few monomer units located at the α- and ω-ends, where the sequences had an irregular structure. The calculation of the 20-mer of phenylacetylene under the conditions of ϕ = 250–210°

gave completely reversed helical polymers (in this case right-handed) with almost the same energies because right- and left-handed helical poly(phenylacetylene)s are mirror images. The phenyl rings were twisted out of the backbone by 59−64 ° and the average dihedral angles of the double and single bonds from planarity were 163 ± 6 and 9.6 ± 5° (initial $\phi = 150°$), 162 ± 5 and 12 ± 3° ($\phi = 140°$), 163 ± 4 and 15 ± 2° ($\phi = 130°$), 162 ± 5 and 19 ± 2° ($\phi = 120°$), and 162 ± 3 and 20 ± 2° ($\phi = 110°$), respectively. When the starting model was planar ($\phi = 180°$), the optimized polymer had an irregular structure with both right- and left-handed helices in part as seen in the literature for cis−transoidal poly(phenylacetylene) derivatives.[23c,e] The optimized poly(phenylacetylene) structure (initial $\phi = 140°$) is shown in Figure 6a.

The model polymers (20-mer) of **3** and **4** were also constructed under the initial $\phi = 180–90°$ at 10° intervals and their structures were optimized by molecular mechanics calculations. The most stable model polymers of **3** and **4** were obtained under the initial $\phi = 120$ and 110°, respectively (Figure 6b, c). These polymers had a slightly tight helical conformation; the average dihedral angles of the double and single bonds from planarity were 151 ± 4 and 15 ± 3° for model polymer **3** and 145 ± 3 and 17 ± 3° for **4**.

To explore the steric effect of the side groups on the helical conformation during the molecular dynamics simulations, the dynamics simulations of the model polymers shown in Figure 6 were conducted. The conformation of the helical poly(phenylacetylene) shown in Figure 6a was changed to an irregular conformation only after a 5 ps run; the dihedral angles of the double bonds were in the range −139 to +163°. This indicates that bond rotation occurred in either direction to give an irregular structure. Other two polymer models of **3** and **4** kept their regular helical structures even after 20 ps simulations; the average dihedral angles of the double bonds were 160 ± 7° for model polymer **3** and 158 ± 4° for **4**. For the model polymer **4**, an additional 200 ps dynamics simulation was carried out. However, the regular helix was maintained during the dynamics simulations. The steric interactions of the bulky side groups at the *para* position play an important role in maintaining a helical conformation. These results agreed well with the experimental ones; the copolymer of chiral **1** with phenylacetylene showed little induced CD, whereas the copolymers of **1** with **3** or **4** showed intense induced CD. The latter copolymers may have a stable helical structure induced by a small amount of chiral monomer units, and, therefore, they showed an induced CD in the UV−visible region.

The calculations of a conformation of cis−transoidal poly[(*R*)-**1**] may be particularly interesting, for there are two possible helical conformations with a right- or left-handed helix in the main chain, whose free energies may differ from one another because they are diastereomers. We anticipate that the chiral side groups could control a helical state to one-handedness in excess since poly[(*R*)-**1**] showed a very intense induced CD in the UV−visible region. Preliminary molecular mechanics calculations of a model polymer of (*R*)-**1** revealed that a stable structure of the model polymer was a helix as seen in the cases of model polymers of **3** and **4**. To presume a more stable helical state, more detailed molecular mechanics and molecular dynamics calculations of model polymers of **1** and **2** are now in progress.

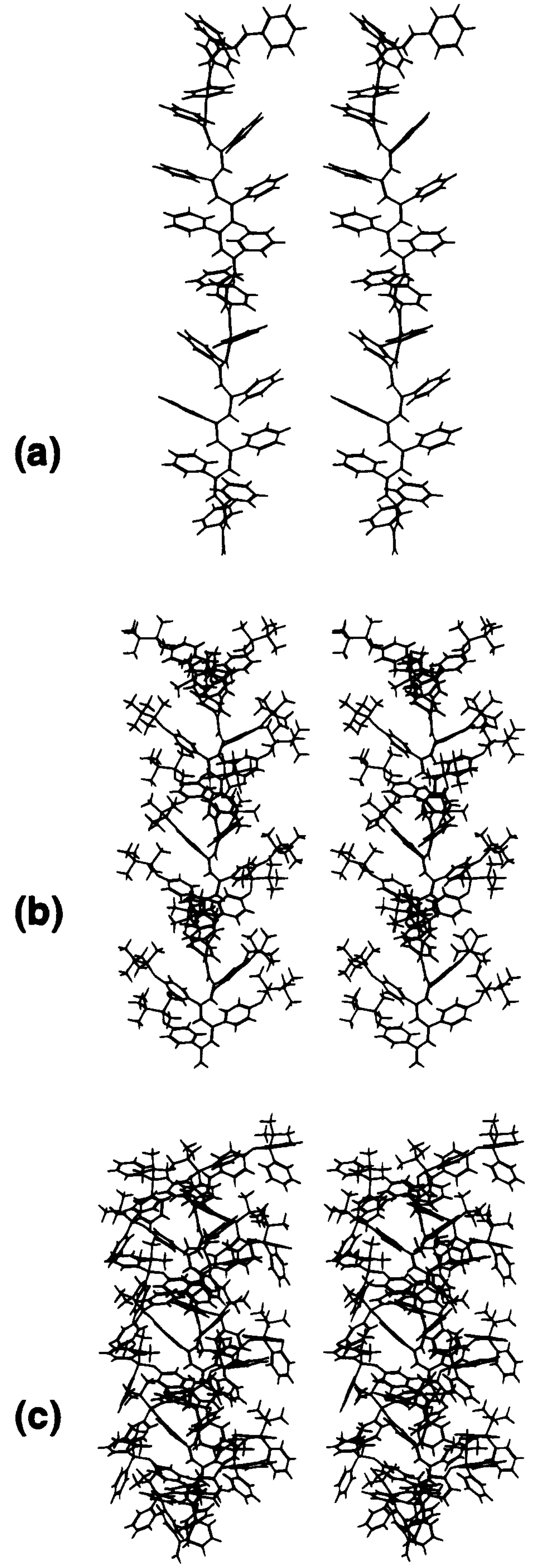


Figure 6. Stereoviews of the calculated structures of the model polymers (20-mer) of **7** (a), **3** (b), and **4** (c).

Experimental Section

Materials. Tetrahydrofuran (THF) was dried over sodium benzophenone ketyl and distilled onto $LiAlH_4$ under nitrogen. Triethylamine was distilled and dried over KOH pellets under a nitrogen atmosphere. These solvents were distilled under high vacuum just before use. Dimethylformamide (DMF) was dried over calcium hydride under nitrogen and distilled under reduced pressure. Toluene and benzene were distilled from sodium benzophenone ketyl under nitrogen. Pyridine was distilled and dried over KOH pellets under nitrogen.

3-Iodophenol, *tert*-butyldiphenylchlorosilane, bis(triphenylphosphine)palladium dichloride, (trimethylsilyl)acetylene, and bis[(norbornadiene)rhodium(I) chloride] {[Rh(NBD)Cl]$_2$} were purchased from Aldrich. *tert*-Butyldimethylchlorosilane, 2-methyl-3-butyn-2-ol, imidazole, tetrabutylammonium fluoride (1.0 M in THF), (*R*)-(-)-(1-naphthyl)ethyl isocyanate, 4-bromobiphenyl, and 2-bromonaphthalene were obtained from Tokyo Kasei (Japan). 4-Iodophenol was purchased from Nacarai Tesque (Kyoto, Japan), and triphenylphosphine and copper(I) iodide were from Kishida (Osaka, Japan). (*R*)-(+)-1-Phenylethyl isocyanate was prepared from (*R*)-1-phenylethylamine (Tokyo Kasei) by the conventional method using triphosgene.[24]

Phenylacetylene (**7**) was purchased from Aldrich, dried using calcium hydride, and distilled two times under nitrogen.

Phenylacetylene derivatives (**1**–**6**, **8** and **9**) were prepared according to Schemes 1 and 2.

4-(*tert*-Butyldimethylsiloxy)iodobenzene. A solution of 4-iodophenol (34.1 g, 0.155 mol) and *tert*-butyldimethylchlorosilane (26.5 g, 0.176 mol) in 70 mL of dry DMF containing imidazole (31.7 g, 0.466 mol) was stirred under nitrogen at room temperature for 10 h. After evaporation of the solvent under reduced pressure, the residue was diluted with ether and washed three times with water, and then the ethereal layer was dried over $MgSO_4$. After filtration, the filtrate was evaporated, quantitatively yielding a clear oil. This was used for the next reaction without further purification. ^1H NMR ($CDCl_3$): δ 0.15 (s, $SiCH_3$, 6H), 0.94 (s, *t*-Bu, 9H), 6.58 (d, aromatic, 2H), 7.47 (d, aromatic, 2H).

4-(4′-(*tert*-Butyldimethylsiloxy)phenyl)-2-methyl-3-butyn-2-ol. To a mixture of 4-(*tert*-butyldimethylsiloxy)iodobenzene (18.2 g, 54.5 mmol), bis(triphenylphosphine)palladium dichloride (0.147 g, 0.2 mmol), triphenylphosphine (0.226 g, 0.9 mmol), and copper(I) chloride (0.229 g, 1.2 mmol) in triethylamine (120 mL) was added 2-methyl-3-butyn-2-ol (5.45 g, 64.8 mmol). The reaction mixture was stirred under nitrogen at room temperature for 14 h before the solvent was removed under reduced pressure. The residue was diluted with ether and the solution was filtered, washed with 1% HCl aqueous solution and two times with water, and then dried over $MgSO_4$. After evaporating the solvent, the crude product was purified by column chromatography on silica gel using hexane–ether (2/1) as the eluent, yielding a colorless oil weighing 14.3 g (91%). ^1H NMR ($CDCl_3$): δ 0.19 (s, $SiCH_3$, 6H), 0.97 (s, *t*-Bu, 9H), 1.60 (s, $CH(CH_3)_2$, 6H), 2.30 (s, $(CH_3)_2CH$, 1H), 6.76 (d, aromatic, 2H), 7.29 (d, aromatic, 2H).

4-(*tert*-Butyldimethylsiloxy)phenylacetylene (3). To a solution of the butyne derivative prepared above (14.3 g, 49.2 mmol) in dry toluene (60 mL) was added sodium hydride (4.9 g, 0.20 mol). The dispersion solution was refluxed for 8 h and stirred for 36 h at room temperature under nitrogen. After water was added, the solution was neutralized with 1% HCl aqueous solution, extracted with ether, and dried over $MgSO_4$. After evaporating the solvent, the residue was distilled under reduced pressure (bp 88 °C/0.35 mmHg) to give 4-(*tert*-butyldimethylsiloxy)phenylacetylene (5.6 g, 50%). ^1H NMR ($CDCl_3$): δ 0.20 (s, $SiCH_3$, 6H), 0.98 (s, *t*-Bu, 9H), 2.99 (s, $\equiv$CH, 1H), 6.78 (d, aromatic, 2H), 7.37 (d, aromatic, 2H).

(*R*)-(+)-4-(((1-Phenylethyl)carbamoyl)oxy)phenylacetylene (1). To a solution of **3** (3.9 g, 16.8 mmol) in THF (10 mL) was added tetrabutylammonium fluoride (54 mL) in THF (1.0 M). The solution was stirred under nitrogen at room temperature for 7 h before evaporating the solvent. The crude product was diluted with ether, washed with 1% aqueous HCl and water, and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was chromatographed on silica gel with hexane, followed by ether as the eluent. After evaporating the solvent, a slight yellow oil, 4-hydroxyphenylacetylene was obtained; this was allowed to react with (*R*)-(+)-1-phenylethyl isocyanate (2.79 g, 19 mmol) in the presence of a catalytic amount of dry pyridine (0.3 mL). The crude product was purified by silica gel chromatography with chloroform as the eluent and then recrystallized with ether–hexane (2/1) to give white crystals (2.4 g, 50%), mp 123.5–124.5 °C; $[\alpha]_D^{25}$ +134° (THF, c = 0.94 g dL^{-1}). The enantiomeric excess of the product was determined to be nearly 100% by chromatographic enantioseparation on a chiral column packed with cellulose tris(3,5-dimethylphenylcarbamate)[25] which completely resolved the racemate **1** with a separation factor (α) = 1.11 in hexane-2-propanol (95/5) as the eluent. IR (KBr): 3386 (ν_{NH}), 3270 ($\nu_{\equiv CH}$), 1721 ($\nu_{C=O}$); ^1H NMR ($CDCl_3$): δ 1.58 (d, CH_3, 3H), 3.04 (s, $\equiv$CH, 1H), 4.92 (m, NHC*H*, 1H), 5.30 (d, NH, 1H), 7.10–7.50 (m, aromatic, 9H). Anal. Calcd for $C_{17}H_{15}O_2N$: C, 76.96; H, 5.70; N, 5.28. Found: C, 76.94; H, 5.84; N, 5.36.

3-(*tert*-Butyldimethylsiloxy)phenylacetylene (5). This compound was prepared from 3-iodophenol according to an analogous method for the synthesis of **3**; bp 63 °C (0.35 mmHg). ^1H NMR ($CDCl_3$): δ 0.20 (s, $SiCH_3$, 6H), 1.00 (s, *t*-Bu, 9H), 3.05 (s, $\equiv$CH, 1H), 6.8–7.3 (m, aromatic, 4H).

(*R*)-(+)-3-(((1-Phenylethyl)carbamoyl)oxy)phenylacetylene (6). 3-Hydroxyphenylacetylene, which had been prepared by desilylation of **5** with tetrabutylammonium fluoride (1.0 M in THF), was allowed to react with (*R*)-(+)-1-phenylethyl isocyanate in the presence of a catalytic amount of dry pyridine. The crude slight yellow solid was purified by chromatography on silica gel using chloroform as the eluent, followed by recrystallization from ether–hexane (3/1) to give white crystals in 19.4% yield, mp 93.0–94.0 °C; $[\alpha]_D^{25}$ +110.2° (THF, c = 0.98 g dL^{-1}). The enantiomeric excess of the product was determined to be nearly 100% by chromatographic enantioseparation using cellulose tris(3,5-dimethylphenylcarbamate)-coated silica gel as the chiral stationary phase, which almost completely resolved the racemate **6** with a separation factor (α) = 1.19 with hexane–2-propanol (90/10) as the eluent. IR (KBr): 3364 (ν_{NH}), 3284 ($\nu_{\equiv CH}$), 1702 ($\nu_{C=O}$); ^1H NMR ($CDCl_3$): δ 1.55 (d, CH_3, J = 8.5 Hz, 3H), 3.05 (s, $\equiv$CH, 1H), 4.90 (m, NHC*H*, 1H), 5.30 (d, NH, 1H), 7.1–7.4 (m, aromatic, 9H). Anal. Calcd for $C_{17}H_{15}O_2N$: C, 76.96; H, 5.70; N, 5.28. Found: C, 76.90; H, 5.76; N, 5.35.

(*R*)-(+)-4-[((1-(1-Naphthyl)ethyl)carbamoyl)oxy]phenylacetylene (2). This compound was prepared by the same method used for the synthesis of **1** from 4-hydroxyphenylacetylene with (*R*)-(-)-[(1-naphthyl)ethyl isocyanate] in dry benzene (2.0 mL) with dry pyridine (0.3 mL); a crude product was obtained as a slight yellow solid. Purification by silica gel chromatography using chloroform as the eluent followed by recrystallization from benzene–hexane (5/1) gave white crystals in 58% yield, mp 132.5–133.5 °C; $[\alpha]_D^{25}$ +69.1° (THF, c = 0.88 g dL^{-1}). The enantiomeric excess of the product was determined to be nearly 100% by chromatographic enantioseparation on a chiral column packed with cellulose tris(3,5-dimethylphenylcarbamate), which completely resolved the racemate **2** with a separation factor (α) = 1.11 with hexane–2-propanol (95/5) as the eluent. IR (KBr): 3326 (ν_{NH}), 3294 ($\nu_{\equiv CH}$), 1696 ($\nu_{C=O}$); ^1H NMR ($CDCl_3$): δ 1.74 (d, CH_3, 3H), 3.04 (s, $\equiv$CH, 1H), 5.36 (d, NH, 1H), 5.74 (m, CH_3CH, 1H), 7.09–8.18 (m, aromatic, 11H). Anal. Calcd for $C_{21}H_{17}O_2N$: C, 79.98; H, 5.43; N, 4.44. Found: C, 80.65; H, 5.18; N, 4.49.

4-(*tert*-Butyldiphenylsiloxy)phenylacetylene (4). To a solution of 4-iodophenol (7.0 g, 31.8 mmol), bis(triphenylphosphine)palladium dichloride (0.092 g, 0.13 mmol), triphenylphosphine (0.123 g, 0.47 mmol), and copper(I) chloride (0.137 g, 0.72 mmol) in triethylamine (48 mL) was added (trimethylsilyl)acetylene (3.4 g, 34.6 mmol). The reaction mixture was stirred under nitrogen at room temperature overnight. After the solvent was removed under reduced pressure, the residue was dissolved in THF (10 mL), and tetrabutylammonium fluoride (54 mL) in THF (1.0 M) was added to the solution. The solution was stirred under nitrogen at room temperature for 7 h before evaporating the solvent. The crude product was diluted with ether and washed with 5% aqueous HCl and water, and the ether layer was dried over Na_2SO_4. The solvent was removed by evaporation and the residue was chromatographed on silica gel with hexane, followed by ether as the eluent. The obtained 4-hydroxyphenylacetylene was allowed to react with *tert*-butyldiphenylchlorosilane (6.7 g, 24.5 mmol) in dry DMF (12 mL) in the presence of imidazole (4.9 g, 72 mmol) at room temperature overnight. The DMF was removed under reduced pressure, and the crude product was diluted with ether, washed with water, and then dried over Na_2SO_4. Purification by chromatography on silica gel with hexane and with hexane−ether (2/1) as the eluents followed by recrystallization from methanol gave 4.4 g of white crystals in 39% yield based on 4-iodophenol; mp 86.5−87.5 °C. IR (KBr): 3290 ($\nu_{\equiv CH}$); ^1H NMR ($CDCl_3$): δ 1.09 (s, *t*-Bu, 9H), 2.95 (s, ≡CH, 1H), 6.70 (d, aromatic, 2H), 7.22 (d, aromatic, 2H), 7.35−7.72 (m, aromatic, 10H). Anal. Calcd for $C_{24}H_{24}O$: C, 80.85; H, 6.78. Found: C, 80.81; H, 6.84.

4-Biphenylacetylene (8). To a mixture of 4-bromobiphenyl (11.0 g, 47.1 mmol) and palladium catalyst in dry triethylamine (60 mL) was added (trimethylsilyl)acetylene (5.56 g, 56.6 mmol), and the reaction mixture was stirred for 20 h at 90 °C to give 7.3 g (62%) of 4-[(trimethylsilyl)ethynyl]biphenyl after purification by column chromatography on silica gel with hexane−$CHCl_3$ (4/1) as the eluent and recrystallization from methanol; mp 56.5−60.5 °C. IR (KBr): 2164 ($\nu_{C\equiv C}$); ^1H NMR ($CDCl_3$): δ 0.25 (s, 9H), 7.35 (m, 1H), 7.45 (m, 2H), 7.5−7.6 (m, 6H). This compound (7.3 g) was allowed to react with tetrabutylammonium fluoride to give a slightly brown solid, which was purified by silica gel chromatography with hexane and hexane−ether (2/1) and sublimed at ~45 °C (0.015 mmHg) to give white crystals in 31% yield (1.6 g), mp 85.0−86.5 °C. IR (KBr): 3276 ($\nu_{\equiv CH}$): ^1H NMR ($CDCl_3$): δ 3.15 (s, ≡CH, 1H), 7.40 (m, aromatic, 1H), 7.45 (m, aromatic, 2H), 7.55−7.60 (m, aromatic, 6H).

2-Naphthylacetylene (9). To a mixture of 2-bromonaphthalene (4.92 g, 23.8 mmol) and palladium catalyst in dry triethylamine (90 mL) was added (trimethylsilyl)acetylene (4.93 g, 50.2 mmol). The solution was stirred for 7 h at 90 °C. After filtration, the filtrate was evaporated under reduced pressure. The residue was chromatographed on silica gel with hexane. The recovered compound was recrystallized from methanol to yield 2.79 g (52%) of ((trimethylsilyl)ethynyl)naphthalene; mp 47.0−48.0 °C. IR (KBr): 2156 ($\nu_{C\equiv C}$); ^1H NMR ($CDCl_3$): δ 0.30 (s, 9H), 7.45−7.50 (m, 3H), 7.75−7.80 (m, 3H), 8.00 (s, 1H). Desilylation of this compound (2.8 g, 12.4 mmol) with tetrabutylammonium fluoride (38 mL) in THF (1.0 M) gave a slightly yellow solid, which was sublimed at ~24 °C (0.015 mmHg) to give white crystals in 80% yield (1.51 g), mp 43.0−44.0 °C. IR (KBr): 3284 ($\nu_{\equiv CH}$); ^1H NMR ($CDCl_3$): δ 3.25 (s, ≡CH, 1H), 7.45−7.50 (m, aromatic, 3H), 7.75−7.80 (m, aromatic, 3H), 8.00 (s, aromatic, 1H).

Polymerization. Polymerization was carried out in a dry glass ampule under a dry nitrogen atmosphere using $[RhCl(NBD)]_2$ or WCl_6−Ph_4Sn as catalysts. A typical polymerization procedure is described below.

Monomer **1** (0.10 g, 0.38 mmol) was placed in a dry ampule, which was then evacuated on a vacuum line and flushed with dry nitrogen. After this evacuation−flush procedure was repeated three times, a three-way stopcock was attached to the ampule, and THF was added with a syringe. To this was added a solution of a rhodium catalyst in THF at 30 °C. The concentrations of the monomer and the rhodium catalyst were 0.5 and 0.005 M, respectively. The color of the mixture changed from bright yellow to dark red within 1 h. After 1 h, the resulting polymer was precipitated into a large amount of methanol, collected by centrifugation, and dried in vacuo at 50 °C for 3 h (0.094 g, 94% yield). IR (KBr): 3326 (ν_{NH}), 1718 ($\nu_{C=O}$); ^1H NMR ($CDCl_3$): δ 1.40 (d, CH_3, 3H), 4.77 (m, CH, 1H), 5.67 (s, =CH, 1H), 5.80 (br, NH, 1H), 6.58−7.23 (m, aromatic, 9H). Anal. Calcd for $C_{17}H_{15}O_2N$: C, 76.96; H, 5.70; N, 5.28. Found: C, 76.91; H, 5.83; N, 5.31.

Polymerization of the same monomer (0.11 g, 0.41 mmol) with WCl_6−Ph_4Sn (0.016 mmol) was carried out in dry toluene at 30 °C for 3.5 h and 60 °C for 12 h.

Poly-**1** was also prepared by a different route; the monomer **3** (1.61 g, 6.93 mmol) was polymerized with WCl_6−Ph_4Sn (0.28 mmol) in dry toluene (12.3 mL) for 19.5 h. The resulting polymer was poured into methanol, collected by filtration, and dried in vacuo at 50 °C for 3 h to yield 1.03 g of poly-**3** (64%). This polymer was treated with tetrabutylammonium fluoride in THF, and the poly(4-hydroxyphenylacetylene) obtained was allowed to react with (*R*)-(+)-1-phenylethyl isocyanate in dry pyridine at 50 °C for 7 h to give poly[(*R*)-4-(((1-phenylethyl)carbamoyl)oxy)phenylacetylene]; $M_n = 2.5 \times 10^4$ by GPC. Anal. Calcd for $C_{17}H_{15}O_2N$: C, 76.96; H, 5.70; N, 5.28. Found: C, 75.04; H, 5.73; N, 5.73.

Measurements. Melting points were measured on a Büchi melting point apparatus and are uncorrected. NMR spectra were measured on a Varian VXR-500S (500 MHz for ^1H) spectrometer using TMS as the internal standard. IR spectra were recorded using a Jasco Fourier transform IR-7000 spectrophotometer with a Jasco PTL-396 data processor. UV spectra were measured in THF solutions using a Jasco Ubest-55 spectrophotometer. CD spectra were measured in THF solutions in a 0.01 or 0.05 cm quartz cell using a Jasco J-720 L spectropolarimeter. Gel permeation chromatography (GPC) was performed using a Jasco Trirotar-II liquid chromatograph equipped with UV−visible (254 nm; Jasco 875-UV) and polarimetric (780 nm; Shodex OR-1) detectors. GPC columns, Shodex KM-80M (30 cm) and A-80M (50 cm) and Tosoh TSK-G3000H (50 cm), were connected in series, and THF was used as the eluent at a flow rate of 1.0 mL/min. The molecular weight calibration curve was obtained with standard polystyrenes (Tosoh). The determination of the enantiomeric excess (ee) of the chiral monomers was carried out on a Jasco Trirotar-II liquid chromatograph equipped with UV−visible and polarimetric (Hg without filter; Jasco 181-C) detectors by using a chiral column packed with cellulse tris(3,5-dimethylphenylcarbamate)-coated macroporous silica gel[25] and hexane−2-propanol as the eluent.

Molecular Modeling and Calculations. Molecular mechanics and molecular dynamics calculations were performed with the Dreiding force field[22] (version 2.21) as implemented in CERIUS^2 software (version 1.5; Molecular Simulations Inc., Burlington, MA) running on an Indigo^2-Extreme graphics workstation (Silicon Graphics). The polymer models of 20-mer were built by Polymer Builder in CERIUS.^{2} The starting main chain conformation of a polymer model was defined as the double-bond geometry (cis or trans) and a conformation of a rotational single bond. The double-bond geometry was fixed to cis and the twist angles about a single bond were allowed to rotate from 180° (transoid) to 90° at 10° intervals. The constructed models were optimized by the conjugate gradient method. The minimization was terminated when the root mean square value reached below 0.1 kcal/mol. Molecular dynamics calculations were run for 20 ps with a step size of 1 fs at 300 K.

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