

Synthesis and Helical Structure of Poly(1-methylpropargyl ester)s with Various Side Chains

Yuji Suzuki, Masashi Shiotsuki, Fumio Sanda,* and Toshio Masuda*[a]

Abstract: Optically active 1-methylpropargyl esters bearing various substituents were polymerized with $[(\text{nbd})\text{Rh}]^+[\eta^6\text{-C}_6\text{H}_5\text{B}(\text{C}_6\text{H}_5)_3]^-$ (nbd = norbornadiene) as a catalyst to afford the corresponding poly(1-methylpropargyl ester)s with moderate molecular weights in good yields. The polymers have a *cis*-stereoregular structure, which was determined by $^1\text{H NMR}$

spectroscopy. Large optical rotations and clear CD signals demonstrated that all these polymers take on a helical structure with a predominantly one-handed screw sense. The polymers ex-

Keywords: chirality · helical structures · polyacetylenes · polymers · rhodium

hibited large viscosity indices in the range 1.14–1.75. Chiral amplification was observed in *R/S* copolymerization. Conformational analysis revealed that the polymers form a tightly twisted helical structure with a dihedral angle of 70° at the single bond of the main chain.

Introduction

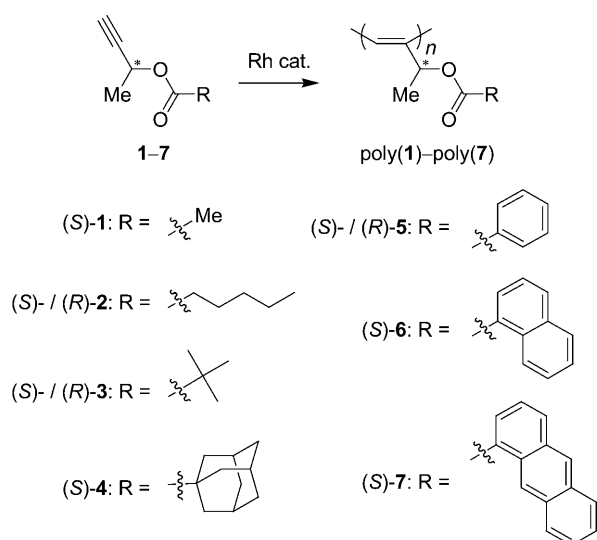
The helix is the most common higher-order structure of synthetic polymers as well as biomacromolecules such as nucleic acids^[1] and proteins.^[2] Helices are molecularly asymmetric; therefore, polymers that take on a predominantly one-handed helical structure are optically active. Helical polymers exhibit interesting functions such as chirality sensing and asymmetric catalysis. Hence, well-ordered synthetic helical polymers have been extensively studied, dating back to the discovery of isotactic polypropylene by Natta et al.^[3] Nowadays, advances in precisely controlled organic synthesis have allowed us to design monomers and catalysts with sophisticated functions. As a result, various optically active helical polymers have been synthesized,^[4] which include polymethacrylates, polyisocyanates, polyisocyanides, polysilanes, and polyacetylenes.

Substituted polyacetylenes show unique properties such as photo- and electroluminescence based on the conjugated double bonds in the main chain.^[5] They also show high gas

permeability and form helices owing to the rigid backbone. The introduction of appropriately bulky chiral substituents onto the side chains leads them to take on a predominantly one-handed helical structure,^[5,6] especially in the case of *cis*-stereoregular substituted polyacetylenes. (*S*)-3-Methylpentyn-1-yn-3-ol undergoes polymerization with an iron catalyst to give a polyacetylene with stereogenic centers adjacent to the main chain, which forms a predominantly one-handed helical structure in solution.^[7] In recent years, rhodium complexes have been commonly used as catalysts for the stereospecific polymerization of monosubstituted acetylenes owing to their high tolerance toward polar functional groups, which enables the synthesis of a wide variety of helical polyacetylenes.^[8]

We recently reported that a chiral 1-methylpropargyl alcohol undergoes rhodium-catalyzed polymerization to afford the corresponding polyacetylene, which forms a predominantly one-handed helical structure.^[9] It is notable that such a simple chiral monomer can produce a helical polymer. Moreover, as this chiral alcohol can be easily converted into ester derivatives, it is possible to synthesize helical polymers with diverse side-chain functionalities. In the present study, we synthesized poly(1-methylpropargyl ester)s with bulky aliphatic groups (Scheme 1) and investigated the substituent effect on the helical structure. We also introduced aromatic groups onto the side chain not only to stabilize the helix further by steric effect but also to confirm the helical arrangement of the side chains. Finally, we examined chiral amplification by *R/S* copolymerization, the conformation of the

[a] Y. Suzuki, Dr. M. Shiotsuki, Prof. Dr. F. Sanda, Prof. Dr. T. Masuda
Department of Polymer Chemistry
Graduate School of Engineering, Kyoto University
Katsura Campus, Kyoto 615-8510 (Japan)
Fax: (+81) 75-383-2592
E-mail: sanda@adv.polym.kyoto-u.ac.jp
masuda@adv.polym.kyoto-u.ac.jp



Scheme 1. Polymerization of 1-methylpropargyl esters 1–7.

polymers by molecular mechanics calculations, and their thermal stability.

Results and Discussion

Polymerization

As described in the Introduction, the polymerization of monosubstituted acetylenes with rhodium catalysts gives the corresponding polyacetylenes with highly *cis*-stereoregular main chains.^[10] Thus, the polymerization of (S)-1–(S)-7 was carried out with [(nbd)Rh]⁺[η^6 -C₆H₅B(C₆H₅)₃]⁻ (nbd = norbornadiene) as a catalyst in the present study. As summarized in Table 1, poly[(S)-1]–poly[(S)-7], which have moderate molecular weights, were obtained in good yields, which implies that the ester substituents hardly affect the polymerizability. All the polymers exhibited a ¹H NMR signal based on the *cis*-olefinic protons of the main chain, and the integration ratio of the signals confirmed that the *cis* contents of the polymers were quantitative.

Table 1. Polymerization of (S)-1–(S)-7.^[a]

Monomer	Yield ^[c] [%]	M_n ^[e]	M_w/M_n ^[e]	α ^[f]
(S)-1	65 ^[d]	36 400	3.09	1.14
(S)-2	88	34 400	3.38	1.36
(S)-3	98	58 100	2.61	1.24
(S)-4	86	81 000	2.21	— ^[e]
(S)-5	88	24 300	2.10	1.75
(S)-6	90	33 200	2.57	1.69
(S)-7 ^[b]	91	48 200	2.85	— ^[e]

[a] Polymerized with [(nbd)Rh]⁺[η^6 -C₆H₅B(C₆H₅)₃]⁻ in THF at 30 °C for 24 h. [monomer]₀ = 1.0 M, [monomer]₀/[Rh] = 100. [b] [monomer]₀ = 0.33 M. [c] Methanol-insoluble part. [d] Hexane-insoluble part. [e] Estimated by GPC eluted with CHCl₃ calibrated by polystyrene standards. [f] Determined by GPC equipped with a viscometer detector eluted with THF. [g] Not determined owing to insolubility of the polymers in THF.

Secondary Structure

All the polymers obtained were soluble in organic solvents and displayed extremely large optical rotations that were opposite in sign to those of the corresponding monomers, irrespective of the solvent used (Table 2). Furthermore,

Table 2. Optical rotations of (S)-1–(S)-7 and the polymers.

Monomer	$[\alpha]_D^{[a]}$ [°]	Polymer $[\alpha]_D^{[b]}$ [°]			
		Toluene	THF	CHCl ₃	DMF
(S)-1	-139	+1109	+1166	+1108	+1050
(S)-2	-97	+840	+600	+766	— ^[c]
(S)-3	-92	+965	+1055	+863	— ^[c]
(S)-4	-38	+752	— ^[c]	+773	— ^[c]
(S)-5	-31	+1067	+695	+888	+896
(S)-6	-77	+555	+646	+638	+523
(S)-7	-125	— ^[c]	— ^[c]	+520	— ^[c]

[a] Measured in CHCl₃, $c = 0.10$ g dL⁻¹. [b] $c = 0.06$ – 0.60 g dL⁻¹. [c] Not measured owing to insolubility of the polymer. DMF = *N,N*-dimethylformamide.

poly[(S)-1]–poly[(S)-6] showed intense CD signals in the absorption region of the main-chain chromophore in CHCl₃ (Figure 1). The large optical rotations and CD signals can be attributed to the helical structure of the polyacetylene main chain with a predominantly one-handed screw sense, which is presumably stabilized by steric repulsion between the methyl branches adjacent to the main chain. The CD signals of the polymers were hardly affected by the type of solvent.^[9] The UV/Vis absorption maxima and CD signals were located in the longer-wavelength region in the case of polymers with bulky substituents; the absorption maxima of poly[(S)-1] and poly[(S)-6] were 310 and 330 nm, respectively. When the polyacetylene main chain is twisted, the conju-

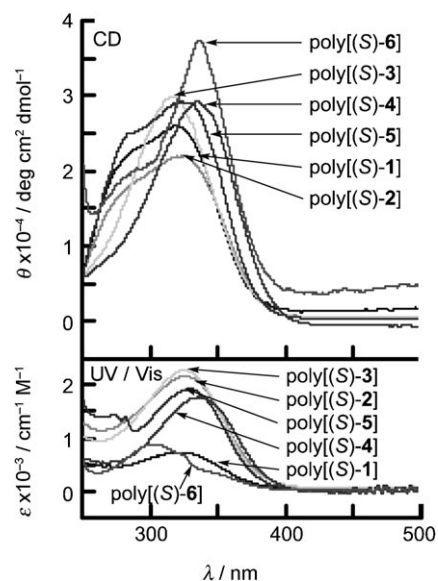


Figure 1. CD and UV/Vis spectra of poly[(S)-1]–poly[(S)-6] recorded in CHCl₃ at 20 °C ($c = 0.09$ – 0.55 mM).

gation length shortens to shift the absorption maximum toward the shorter-wavelength region.^[11] Therefore, it is concluded that the present polymers with bulky substituents have longer conjugation than those with less bulky substituents, and so form a loosely twisted helix.

The polymers with phenyl and naphthyl groups, poly[(S)-5] and poly[(S)-6], displayed CD signals accompanied by a shoulder, which are presumably derived from the helically aligned aromatic substituents as well as the helical polyacetylene backbone. Anthracene-carrying poly[(S)-7] showed CD signals that originate from plural chromophores (Figure 2), that is, the Cotton effects at around 330 and 260 nm are assignable to the main and side chains, respectively. It is considered that the latter Cotton effect is caused

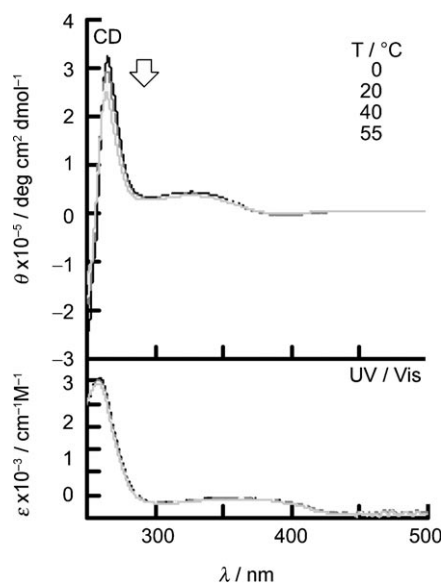


Figure 2. CD and UV/Vis spectra of poly[(S)-7] recorded in CHCl_3 at various temperatures ($c=0.057$ mM).

by the exciton chirality of helically arranged anthracene strands in the side chain,^[12] and the sense is right-handed, because the Davydov splitting showed positive 1st and negative 2nd Cotton effects at 270 and 250 nm.^[13] The CD signal intensity was hardly changed by raising the temperature to 55°C, which indicates that the helical structure is thermally stable in this temperature range.

We further examined the thermal stability of the helical conformation of the polymers. Figure 3 plots the CD signal intensity at the wavelength of the absorption maximum versus temperature measured in toluene. Poly[(S)-1]–poly[(S)-6] apparently exhibited intense Cotton effects even at 100°C. It is concluded that the helical structure of these polymers is thermally stable compared to those of the other polyacetylenes reported so far; for example, poly[(S)-N-propargyl-4-methylhexanamide] changes its conformation randomly even at 50°C.^[8e] The helical structure of poly[(S)-1], which has less bulky side chains, is the most stable among the present polymers.

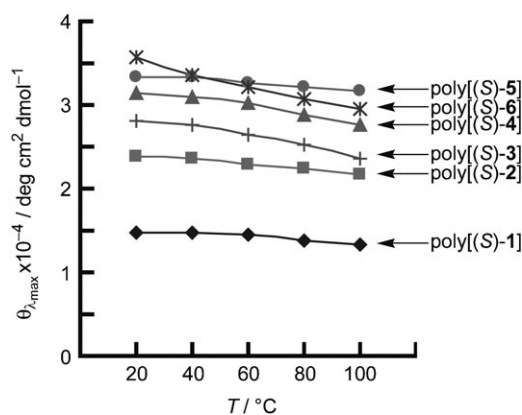


Figure 3. Plots of $\theta_{\lambda_{\text{max}}}$ of poly[(S)-1]–poly[(S)-6] versus temperature measured in toluene ($c=0.09\text{--}0.94$ mM).

To elucidate the heat response of the Cotton effects, we determined the Kuhn dissymmetry factor ($g = \Delta\epsilon/\epsilon$, in which $\Delta\epsilon = \theta/3298$) of the polymers. The g value gives quantitative information associated with the degree of preferential screw sense when the CD signal shows a profile similar to that of the UV/Vis absorption band.^[14] Table 3 summarizes the g values of poly[(S)-1]–poly[(S)-7] at the wavelength of the absorption maxima based on the main-chain chromophore

Table 3. Values of g for poly[(S)-1]–poly[(S)-7].

Polymer	$g^{[a]} \times 10^3$	Relative ee of helix ^[b] [%]
poly[(S)-1]	2.21	7.9
poly[(S)-2]	3.10	11.2
poly[(S)-3]	4.33	15.6
poly[(S)-4]	4.94	17.8
poly[(S)-5]	4.61	16.6
poly[(S)-6]	27.8	100.0
poly[(S)-7]	5.71	20.5

[a] Calculated by the equation $g = \Delta\epsilon/\epsilon$, measured in CHCl_3 at 20°C.

[b] The enantiomeric excess of poly[(S)-6] was assumed to be 100%.

in CHCl_3 . All the polymers exhibited g values of the order of 10^{-3} . The polymers with bulky side chains tended to show large g values, which leads to the conclusion that the screw sense of such helical polymers is relatively biased owing to steric hindrance by the bulky side chains. Poly[(S)-6], which bears a naphthyl group, showed the largest g value among the present polymers. With the assumption that poly[(S)-6] forms a completely one-handed helical structure (100% ee), it is estimated that the enantiomeric excesses of screw sense of the polymers are 7.9–20.5% ee (Table 3). However, it may not be reasonable to consider that poly[(S)-6] forms a perfect one-handed helical structure on account of the nature of helical polyacetylenes. Therefore, the preferences of screw sense of poly[(S)-1]–poly[(S)-7] seem to be lower than those estimated. All the polymers gradually decreased the intensities of the Cotton effects with increasing temperature (Figure 3), but they hardly changed the g values (Figure 4). This is caused by a decrease in UV absorbance in

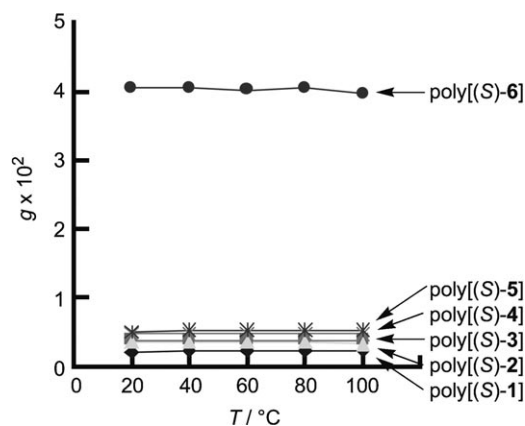


Figure 4. Plots of the g values of poly[(S)-1]–poly[(S)-6] versus temperature measured in toluene ($c=0.09$ – 0.94 mM).

accordance with the decrease in Cotton effect. This result indicates that the polymers maintain their preference of screw sense in this temperature region.

In general, helical polymers take on a rigid rodlike main chain at least by part, which leads to some unique solution properties. In fact, the polymers in this study displayed extremely high viscosity indices (α) in the Mark–Houwink–Sakurada plot, $\eta = kM^\alpha$, in which η and M are the intrinsic viscosity and absolute molecular weight, respectively, and k is a constant. For example, poly(*sec*-octylisocyanide) displays a large α value (1.75),^[15a] and so does poly(butylisocyanate) (1.83),^[15b] owing to its rigid helical conformation. Some substituted helical polyacetylenes also display large α values owing to the conjugated main chain, including poly(*N*-propargyl-*n*-hexanamide) (0.98),^[16] poly(*n*-hexylpropiolate) (1.2),^[17] and poly(*p*-phenoxy carbonylphenylacetylene) (0.97).^[18] As summarized in Table 1, the large α values of the present polymers (1.14–1.75, in THF at 40°C) verify the presence of a stiff main chain, whereas that of nonhelical poly(propargyl hexanoate), which does not have a branch adjacent to the main chain (0.63),^[16] is close to the value for glassy polystyrene (0.68). In particular, poly[(S)-5], which bears phenyl side chains, showed the largest α value among substituted polyacetylenes reported so far.

Chiral Amplification

Some dynamic helical polymers that consist of *R/S*-monomer units bias the helical sense only to a small degree when the persistence length is long enough. The one-handedness is maintained by a slight excess of enantiomeric monomer units. This is called the “majority rule”.^[19] We carried out the *R/S* copolymerization of **2**, **3**, and **5** with various enantiomeric excesses (Table 4). All the copolymers obtained had moderate molecular weights irrespective of the enantiomeric excess. As depicted in Figure 5, the $[\alpha]_D$ and θ_{\max} of the copolymers decreased upon lowering the enantiomeric excess, wherein chiral amplification was observed. The degree of amplification of poly[(*R*)-3-*co*-(*S*)-3] was larger than that of

Table 4. *R/S* copolymerization of **2**, **3**, and **5**.^[a]

Monomer	<i>ee</i> (<i>S/R</i>) [%]	Yield ^[b] [%]	M_n ^[c]	M_w/M_n ^[c]	$[\alpha]_D$ ^[d] [°]
2	70	73	45 000	2.28	+602
2	50	65	46 000	2.45	+469
2	20	65	62 000	2.50	+298
2	10	74	89 000	2.22	+66
3	70	50	62 000	2.22	+777
3	50	57	65 000	2.08	+660
3	20	53	66 000	2.20	+350
3	10	36	72 000	1.92	+192
3	0	52	79 000	1.84	+4
5	70	91	27 000	2.24	+782
5	50	96	33 000	2.41	+624
5	40	90	37 000	2.59	+498
5	30	93	33 000	3.19	+346
5	20	98	38 000	3.11	+259
5	10	93	59 000	2.61	+103
5	0	95	45 000	3.27	+5

[a] Polymerized with [(nbd)Rh]⁺[η⁶-C₆H₅B(C₆H₅)₃]⁻ in THF at 30°C for 24 h. [monomer]₀ = 1.0 M, [monomer]₀/[Rh] = 100. [b] Methanol-insoluble part. [c] Estimated by GPC eluted with CHCl₃ calibrated by polystyrene standards. [d] Measured by polarimetry in CHCl₃ at room temperature, $c=0.04$ – 0.21 g dL⁻¹.

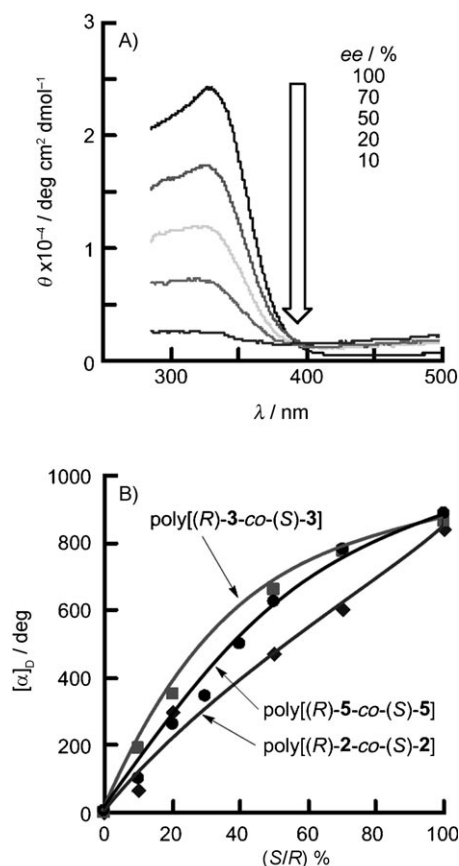


Figure 5. A) CD spectra of poly[(*R*)-2-*co*-(*S*)-2] recorded in CHCl₃ at 20°C ($c=0.19$ – 0.55 mM). B) Plots of $[\alpha]_D$ versus enantiomeric excess of poly[(*R*)-2-*co*-(*S*)-2], poly[(*R*)-3-*co*-(*S*)-3], and poly[(*R*)-5-*co*-(*S*)-5].

poly[(*R*)-2-*co*-(*S*)-2], which indicates that the bulky *tert*-butyl group is favorable for inducing the helical structure in

a manner similar to those in the previous reports.^[20] The α value of poly[(*S*)-**5**] was the largest among the present polymers (Table 1), but the chiral amplification observed in poly[(*R*)-**5-co-(S)**-**5**] was smaller than that in poly[(*R*)-**3-co-(S)**-**3**]. Hence, it is concluded that the rigidity of the main chain is not straightforwardly related to the chiral amplification. Compared to the case of other helical polymers such as polyisocyanates^[19] and polyacetylenes^[17,20a] that obey the majority rule, the persistence length of poly(1-methylpropargyl ester)s seems not to be very long.^[21]

Conformation

As described above, it is considered that the chiral poly(1-methylpropargyl ester)s take on a helical structure with a predominantly one-handed screw sense. We therefore attempted the molecular mechanics calculation (MMFF94^[22]) of poly(1-methylpropargyl ester)s to gain knowledge on the helical structure. We first constructed an 18-mer sequence of (*S*)-**1** terminated with hydrogen as the initial model, and varied the dihedral angle at the single bonds in the main chain from -130 to -50° (left-handed helix) and from 50 to 130° (right-handed helix) with an increment/decrement of 10° . Otherwise, all the geometries were optimized. As shown in Figure 6, the computationally estimated dihedral

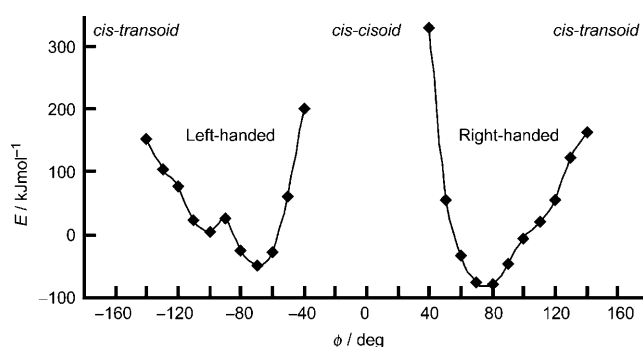


Figure 6. Relationship between the dihedral angle ϕ at the single bond in the main chain of the 18-mer sequence of (*S*)-**1** and the energy calculated by MMFF94.

angle of the most stable 18-mer sequence was 70° , which means that the helical structure of poly(1-methylpropargyl ester)s is tighter than those of previously reported helical polyacetylenes, including poly(phenylacetylene)s (147 – 155°)^[23] and poly(*N*-propargylamide)s ($\approx 130^\circ$).^[24] The global energy minimum shows that the right-handed helix is preferred to the left-handed by 1.5 kJ mol^{-1} per monomer unit. Thus, it is concluded that a poly[(*S*)-1-methylpropargyl ester] that exhibits a positive CD signal at 330 nm has a right-handed tight helical structure with *cis*-cisoidal main-chain geometry.

Thermal Stability

The thermal stability of the polymers was examined by thermogravimetric analysis (TGA) in air. Table 5 summarizes the onset temperatures of weight loss (T_0) of poly[(*S*)-**1**–

Table 5. Thermal stability of poly[(*S*)-**1**]–poly[(*S*)-**7**] determined by TGA.

Polymer	T_0 ^[a] [°C]
poly[(<i>S</i>)- 1]	210
poly[(<i>S</i>)- 2]	182
poly[(<i>S</i>)- 3]	218
poly[(<i>S</i>)- 4]	259
poly[(<i>S</i>)- 5]	216
poly[(<i>S</i>)- 6]	229
poly[(<i>S</i>)- 7]	246

[a] T_0 = onset temperature of weight loss in TGA, measured at a heating rate of $10^\circ\text{C min}^{-1}$ in air.

poly[(*S*)-**7**]. All the polymers showed two-stage weight loss as depicted in Figure 7, in which the TGA curve of poly[(*S*)-**1**] is illustrated as a representative. The T_0 value of the polymers depended on the bulk of the side chains in the range

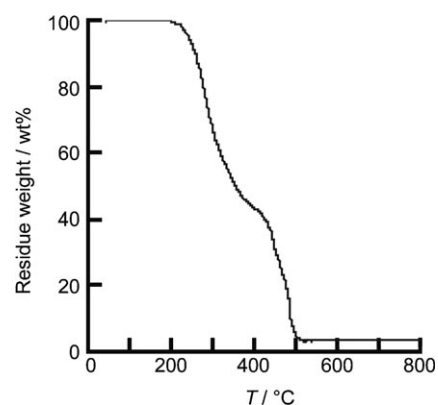


Figure 7. TGA curve of poly[(*S*)-**1**].

182 – 259°C . As the polymers were stable up to 180°C , it was proved that the polymers did not decompose during the variable-temperature CD measurement described above. No glass-transition or melting temperatures were detected by differential scanning calorimetry from room temperature to T_0 in every case.

Conclusions

We have demonstrated that (*S*)-1-methylpropargyl esters successfully undergo polymerization with a rhodium catalyst to give the corresponding polymers, which have a helically twisted polyacetylene backbone with a predominantly one-handed screw sense in solution. It is considered that the methyl branch adjacent to the main chain plays an impor-

tant role for the polymers to take on a helical structure, which is presumably stabilized by steric repulsion between the side chains. The side chains also form helically aligned strands, which was confirmed by the intense Cotton effect at the absorption region of the anthracene moiety of poly[(*S*-7)]. The polymers exhibited extremely large viscosity indices in the range 1.14–1.75, thus indicating the rigidity of the main chain. Conformational analysis revealed that poly[(*S*-1-methylpropargyl ester)s] that exhibit a positive Cotton effect at around 330 nm form a right-handed helical structure, with a dihedral angle at the single bonds in the main chain of 70°.

Experimental Section

Measurements

Melting points (m.p.) were measured with a Yanako micromelting-point apparatus. Specific rotations ($[\alpha]_D$) were measured with a JASCO DIP-1000 digital polarimeter. IR spectra were obtained with a JASCO FTIR-4100 spectrophotometer. NMR (^1H : 400 MHz; ^{13}C : 100 MHz) spectra were recorded on a JEOL EX-400 spectrometer. Elemental analysis was conducted at the Microanalytical Center of Kyoto University. TGA was conducted in air with a Shimadzu TGA-50 apparatus. Number-average molecular weights (M_n) and molecular-weight distributions (M_w/M_n) of the polymers were estimated by GPC (Shodex columns K803, K804, K805) eluted with CHCl_3 calibrated by polystyrene standards. Viscosity indices were determined by GPC equipped with a viscometer and right-angle laser light-scattering detectors (Viscotek T60A) eluted with THF at 40°C. CD and UV/Vis spectra were recorded on a JASCO J-820 spectropolarimeter.

Materials

Unless otherwise stated, reagents were used as received, including (*S*)-(–)-3-butyn-2-ol (Aldrich), (*R*)-(+)-3-butyn-2-ol (Aldrich), (\pm)-3-butyn-2-ol (Wako), acetic acid (Wako), trimethylacetyl chloride (Wako), 1-adamantanecarboxylic acid (Aldrich), benzoyl chloride (Wako), 1-naphthoyl chloride (Wako), and 1-anthracenecarboxylic acid (TCI). Monomers (*S*-2 and (*R*)-2^[9]) and $[(\text{nbD})\text{Rh}]^+[\eta^6\text{-C}_6\text{H}_5\text{B}(\text{C}_6\text{H}_5)_3]^-$ ^[25] were prepared according to the literature. THF used for polymerization was distilled prior to use.

Monomer Synthesis

Monomers (*S*-1), (*S*-4), and (*S*-7) were synthesized from (*S*)-(–)-3-butyn-2-ol and the corresponding carboxylic acids in a manner similar to the previously reported method.^[9] Monomer (*S*-5) was prepared as follows: (*S*)-(–)-3-butyn-2-ol (1.0 g, 14.3 mmol) and Et_3N (5 mL, 68 mmol) were added dropwise to a solution of benzoyl chloride (2.0 g, 14.3 mmol) in CH_2Cl_2 (100 mL) at 0°C, and the reaction mixture was kept stirring at room temperature overnight. The mixture was washed with 2 M HCl and saturated aqueous NaHCO_3 and NaCl, dried over MgSO_4 , and concentrated on a rotary evaporator. The residual mass was purified by recrystallization from methanol/water (10:1 v/v) to afford (*S*-5) as colorless crystals. Monomers (*S*-3) and (*S*-6) were synthesized in a similar way.

(*S*-1): Yield: 21%. $[\alpha]_D = -139^\circ$ ($c = 0.19 \text{ g dL}^{-1}$ in CHCl_3); IR (neat): $\tilde{\nu} = 3252, 2905, 2880, 2121, 1722, 1449, 1234, 1072, 1030, 735 \text{ cm}^{-1}$; $^1\text{H NMR}$ (CDCl_3): $\delta = 1.50$ (d, $J = 6.8 \text{ Hz}$, 3H, CHCH_3), 2.08 (s, 3H, COCH_3), 2.48 (d, $J = 2.0 \text{ Hz}$, 1H, $\text{C}\equiv\text{CH}$), 5.43 ppm (qd, $J = 6.8 \text{ Hz}$, $J = 2.0 \text{ Hz}$, 1H, CHCH_3); $^{13}\text{C NMR}$ (CDCl_3): $\delta = 21.0, 59.8, 72.7, 82.0, 169.6 \text{ ppm}$; elemental analysis: calcd for $\text{C}_6\text{H}_8\text{O}_2$: C 64.27, H 7.19; found: C 63.55, H 7.02.

(*S*-3): Yield: 41%. $[\alpha]_D = -92.1^\circ$ ($c = 0.10 \text{ g dL}^{-1}$ in CHCl_3); IR (neat): $\tilde{\nu} = 3298, 2978, 2939, 2360, 1736, 1481, 1279, 1154, 1036, 669 \text{ cm}^{-1}$; $^1\text{H NMR}$ (CDCl_3): $\delta = 1.21$ (s, 9H, $\text{C}(\text{CH}_3)_3$), 1.49 (d, $J = 6.8 \text{ Hz}$, 3H, CHCH_3), 2.42 (d, $J = 2.4 \text{ Hz}$, 1H, $\text{C}\equiv\text{CH}$), 5.40 ppm (qd, $J = 6.8 \text{ Hz}$, $J = 2.0 \text{ Hz}$, 1H,

CHCH_3); $^{13}\text{C NMR}$ (CDCl_3): $\delta = 21.0, 26.9, 38.6, 59.8, 72.5, 82.3, 177.3 \text{ ppm}$; elemental analysis: calcd for $\text{C}_9\text{H}_{14}\text{O}_2$: C 70.10, H 9.15; found: C 70.14, H 9.08.

(*S*-4): Yield: 25%. M.p.: 83.5–84.5°C; $[\alpha]_D = -37.5^\circ$ ($c = 0.11 \text{ g dL}^{-1}$ in CHCl_3); IR (KBr): $\tilde{\nu} = 3259, 2912, 2854, 2113, 1724, 1450, 1234, 1072, 1030, 713, 528 \text{ cm}^{-1}$; $^1\text{H NMR}$ (CDCl_3): $\delta = 1.48$ (d, $J = 7.2 \text{ Hz}$, 3H, CH_3), 1.72 (br, 6H, adamantyl), 1.86–1.93 (m, 3H, adamantyl), 2.12–2.22 (m, 6H, adamantyl), 2.42 (s, 1H, $\text{C}\equiv\text{CH}$), 5.41 ppm (qd, $J = 6.8 \text{ Hz}$, $J = 2.0 \text{ Hz}$, 1H, CHCH_3); $^{13}\text{C NMR}$ (CDCl_3): $\delta = 21.0, 27.8, 30.9, 36.4, 38.5, 59.4, 72.3, 82.4, 176.3 \text{ ppm}$; elemental analysis: calcd for $\text{C}_{15}\text{H}_{20}\text{O}_2$: C 77.55, H 8.68; found: C 77.26, H 8.52.

(*S*-5): Yield: 64%. M.p.: 69.8–70.5°C; $[\alpha]_D = -31.3^\circ$ ($c = 0.10 \text{ g dL}^{-1}$ in CHCl_3); IR (KBr): $\tilde{\nu} = 3251, 2985, 2939, 2117, 1712, 1273, 1107, 1030, 706 \text{ cm}^{-1}$; $^1\text{H NMR}$ (CDCl_3): $\delta = 1.64$ (d, $J = 6.4 \text{ Hz}$, 3H, CHCH_3), 2.49 (s, 1H, $\text{C}\equiv\text{CH}$), 5.69 (q, $J = 6.8 \text{ Hz}$, 1H, CHCH_3), 7.43–7.47 (m, 2H, Ph), 7.55–7.59 (m, 1H, Ph), 8.06–8.08 ppm (m, 2H, Ph); $^{13}\text{C NMR}$ (CDCl_3): $\delta = 21.3, 60.6, 82.2, 128.4, 129.8, 133.2, 165.4 \text{ ppm}$; elemental analysis: calcd for $\text{C}_{11}\text{H}_{10}\text{O}_2$: C 75.84, H 5.79; found: C 75.70, H 6.02.

(*S*-6): Yield: 41%. M.p.: 94.5–95.0°C; $[\alpha]_D = -76.5^\circ$ ($c = 0.10 \text{ g dL}^{-1}$ in CHCl_3); IR (KBr): $\tilde{\nu} = 3255, 3051, 2981, 2935, 2114, 1709, 1238, 1134, 1088, 783, 690 \text{ cm}^{-1}$; $^1\text{H NMR}$ (CDCl_3): $\delta = 1.69$ (d, $J = 4.4 \text{ Hz}$, 3H, CHCH_3), 2.51 (s, 1H, $\text{C}\equiv\text{CH}$), 5.78 (q, $J = 4.4 \text{ Hz}$, 1H, CHCH_3), 7.45–7.56 (m, 2H, Ar), 7.58–7.64 (m, 1H, Ar), 7.84–7.89 (m, 1H, Ar), 7.99–8.04 (m, 1H, Ar), 8.14–8.24 (m, 1H, Ar), 8.90–8.95 ppm (m, 1H, Ar); $^{13}\text{C NMR}$ (CDCl_3): $\delta = 21.3, 60.6, 73.1, 82.2, 124.4, 125.7, 126.2, 126.5, 127.9, 128.5, 130.5, 131.4, 133.7, 133.8, 166.3 \text{ ppm}$; elemental analysis: calcd for $\text{C}_{15}\text{H}_{12}\text{O}_2$: C 80.34, H 5.39; found: C 80.50, H 5.67.

(*S*-7): Yield: 53%. M.p.: 172.0–173.0°C; $[\alpha]_D = -124.8^\circ$ ($c = 0.10 \text{ g dL}^{-1}$ in CHCl_3); IR (KBr): $\tilde{\nu} = 3259, 3055, 2981, 2935, 2113, 1705, 1254, 1219, 1111, 741 \text{ cm}^{-1}$; $^1\text{H NMR}$ (CDCl_3): $\delta = 1.75$ (d, $J = 6.8 \text{ Hz}$, 3H, CHCH_3), 2.56 (s, 1H, $\text{C}\equiv\text{CH}$), 5.84 (q, $J = 6.6 \text{ Hz}$, 1H, CHCH_3), 7.46–7.50 (m, 3H, Ar), 7.99 (s, 1H, Ar), 8.08 (s, 1H, Ar), 8.20 (d, $J = 8.5 \text{ Hz}$, 1H, Ar), 8.30 (d, $J = 7.1 \text{ Hz}$, 1H, Ar), 8.47 (s, 1H, Ar), 9.62 ppm (s, 1H, Ar); $^{13}\text{C NMR}$ (CDCl_3): $\delta = 21.4, 50.8, 60.6, 73.1, 82.3, 123.6, 125.2, 126.0, 126.1, 127.1, 127.8, 128.6, 129.1, 131.2, 131.4, 131.8, 132.8, 134.4, 166.2 \text{ ppm}$; elemental analysis: calcd for $\text{C}_{10}\text{H}_{14}\text{O}_2$: C 72.49, H 9.95; found: C 72.00, H 9.70.

Polymerization

A solution of $[(\text{nbD})\text{Rh}]^+[\eta^6\text{-C}_6\text{H}_5\text{B}(\text{C}_6\text{H}_5)_3]^-$ (5.1 mg, 10 μmol) in distilled THF (0.5 mL) was added to a solution of the monomer (1.0 mmol) in distilled THF (0.5 mL) under dry nitrogen, and the resulting solution was kept at 30°C for 24 h. The resulting mixture was poured into a large amount of methanol to precipitate the polymer, which was separated by filtration and dried under reduced pressure.

Poly[(*S*-1)]: IR (KBr): $\tilde{\nu} = 2985, 2935, 1739, 1373, 1242, 1072, 1041 \text{ cm}^{-1}$; $^1\text{H NMR}$ (CDCl_3): $\delta = 1.24$ (br, 3H, CHCH_3), 2.03 (br, 3H, COCH_3), 5.63 (br, 1H, $\text{C}\equiv\text{CH}$), 6.41 ppm (br, 1H, $\text{C}\equiv\text{CH}$).

Poly[(*S*-3)]: IR (KBr): $\tilde{\nu} = 2975, 2934, 1726, 1481, 1282, 1158, 1073 \text{ cm}^{-1}$; $^1\text{H NMR}$ (CDCl_3): $\delta = 1.19$ (br, 9H, $\text{CH}(\text{CH}_3)_3$), 1.48 (br, 3H, CHCH_3), 5.70 (br, 1H, $\text{C}\equiv\text{CH}$), 6.45 ppm (br, 1H, $\text{C}\equiv\text{CH}$).

Poly[(*S*-4)]: IR (KBr): $\tilde{\nu} = 2908, 2854, 1724, 1454, 1234, 1072 \text{ cm}^{-1}$; $^1\text{H NMR}$ (CDCl_3): $\delta = 1.48$ (br, 3H, CHCH_3), 1.64–2.13 (m, 15H, adamantyl), 3.55 (br, 1H, $\text{C}\equiv\text{CH}$), 6.16 ppm (br, 1H, $\text{C}\equiv\text{CH}$).

Poly[(*S*-5)]: IR (KBr): $\tilde{\nu} = 2981, 2935, 1720, 1601, 1269, 1107, 710 \text{ cm}^{-1}$; $^1\text{H NMR}$ (CDCl_3): $\delta = 1.14$ (br, 3H, CHCH_3), 5.95 (br, 1H, $\text{C}\equiv\text{CH}$), 6.67 (br, 1H, $\text{C}\equiv\text{CH}$), 7.19–7.22 (m, 2H, Ph), 7.30–7.34 (m, 1H, Ph), 8.03–8.05 ppm (m, 2H, Ph).

Poly[(*S*-6)]: IR (KBr): $\tilde{\nu} = 3051, 2978, 1712, 1593, 1242, 1134, 779 \text{ cm}^{-1}$; $^1\text{H NMR}$ (CDCl_3): $\delta = 1.22$ (br, 3H, CHCH_3), 6.06 (br, 1H, $\text{C}\equiv\text{CH}$), 6.84 (br, 1H, $\text{C}\equiv\text{CH}$), 7.07 (br, 1H, Ar), 7.30 (br, 2H, Ar), 7.53 (br, 1H, Ar), 7.61 (br, 1H, Ar), 8.37 (br, 1H, Ar), 8.96 ppm (br, 1H, Ar).

Poly[(*S*-7)]: IR (KBr): $\tilde{\nu} = 3051, 2978, 2931, 1709, 1616, 1257, 1219, 1111, 879, 733 \text{ cm}^{-1}$; $^1\text{H NMR}$ (CDCl_3): $\delta = 1.38$ (br, 3H, CHCH_3), 6.22 (br, 1H, $\text{C}\equiv\text{CH}$), 6.96 (br, 1H, $\text{C}\equiv\text{CH}$), 7.05–7.09 (br, 3H, Ar), 7.47–7.54 (m, 3H, Ar), 8.47 (br, 1H, Ar), 9.45 ppm (br, 1H, Ar).

Acknowledgements

This research was partly supported by a Grant-in-Aid for Science Research in a Priority Area "Super-Hierarchical Structures" (No. 446) from the Ministry of Education, Culture, Sports, Science, and Technology, Japan. We thank Prof. Michiya Fujiki at the Nara Institute of Science and Technology, Japan for his helpful suggestion on g values.

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Received: March 27, 2008

Revised: July 10, 2008

Published online: September 4, 2008