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Synthesis and Characterization of Poly(chiral methylpropargyl ester)s Carrying Azobenzene Moieties

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Novel chiral methylpropargyl esters bearing azobenzene groups, namely, 4-[4'-(benzyloxy)phenylazophenyl]-carbonyl-(*S*)-1-methylpropargyl ester (**e**), 4-[4'-(*n*-butyloxy)phenylazophenyl]carbonyl-(*S*)-1-methylpropargyl ester (**f**), 4-[4'-(*n*-hexyloxy)phenylazophenyl]carbonyl-(*S*)-1-methylpropargyl ester (**g**), and 4-[4'-(*n*-octyloxy)phenylazophenyl]carbonyl-(*S*)-1-methylpropargyl ester (**h**) were synthesized and polymerized with $Rh^{+}(nbd)[\eta^{6}\text{-}C_6H_5B^{-}\text{-}(C_6H_5)_3]$ (nbd＝norbornadiene) catalyst to give the corresponding polymers with moderate molecular weights (M_n＝8.4×10^3—15.7×10^3) in good yields (76% — 91%). The structures of polymers were illustrated by IR and NMR spectroscopies. Polymers were soluble in comment organic solvents including toluene, $CHCl_3$ CH_2Cl_2, THF, and DMSO, while insoluble in diethyl ether, *n*-hexane and methanol. Large optical rotations of polymer solutions demonstrated that all the polymers take a helical structure with a predominantly one-handed screw sense in organic solvents.

Keywords 1-methylpropargyl ester, azobenzene, chirality, substituted polyacetylene, helical polymer

Introduction

Azobenzene is a well-known photoresponsive chromophore that undergoes photoinduced and thermal geometric isomerization.[1,2] Polymers carrying azobenzene moieties in main chain or side chain including polypeptides, polyisocyanates, polymethacrylates, polysilanes, polyisocyanides, and polyketones have attracted much attention because of their unique properties, which allow various photonic applications such as holographic and digital storage of information. There have been many reports concerning polymers carrying azobenzene moieties display photoresponsive, photoswitchable, optical memories and liquid crystalline properties.[3—7] On the other hand, substituted polyacetylenes possess alternating double bonds in the main chain, which endows them with unique properties such as semiconductivity, high gas permeability, nonlinear optical properties, and helix formation.[8] Helical polyacetylenes gather interest from not only fundamental viewpoints regarding synthesis and properties, but also practical applications, because they exhibit useful functions resulting from the regulated secondary structure, which include chiral discrimination and catalytic activity for asymmetric synthesis.[9] It is expected that azobenzene-containing helical polyacetylenes will combine these characteristics together and lead to the development of new functional materials.[10]

We have recently found that (*R*)- and (*S*)-1-methylpropargyl alcohols,[11] and the ester derivatives undergo polymerization to give stable helical polymers carrying carbazole, triphenylamine, cholesteryl and pyrene moieties.[12] They display electro-optical and liquid crystalline properties. Thus, (*R*)- and (*S*)-1-methylpropargyl alcohols are simple and powerful chiral sources for helical polyacetylenes. The present manuscript deals with the synthesis and polymerization of azobezene-based methylpropargyl esters (Scheme 1), and characterization of their structures.

Experimental

Measurements

^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra were recorded on a Bruker Avance/DMX 400-MHz NMR spectrometer with chloroform-*d* or dimethyl sulfoxide-d_6 (DMSO-d_6) as solvents. Tetramethylsilane, chloroform-*d*, or DMSO-d_6 was used as the internal reference. The FTIR spectra were recorded as KBr pellets on a Perkin-Elmer spectrum-2000 spectrophotometer. Melting points (m.p.) were measured on a Yanaco micromelting-point apparatus. Specific rotations ($[\alpha]_D^{25}$) were measured on a JASCO DIP-1000 digital polarimeter with a sodium lamp as a light source. Elemental analysis was carried out on an Elementar Vario EL-III instrument. The number- and weight-average molecular weights (M_n and M_w) of polymers were determined by gel permeation chromatography (GPC) on a JASCO

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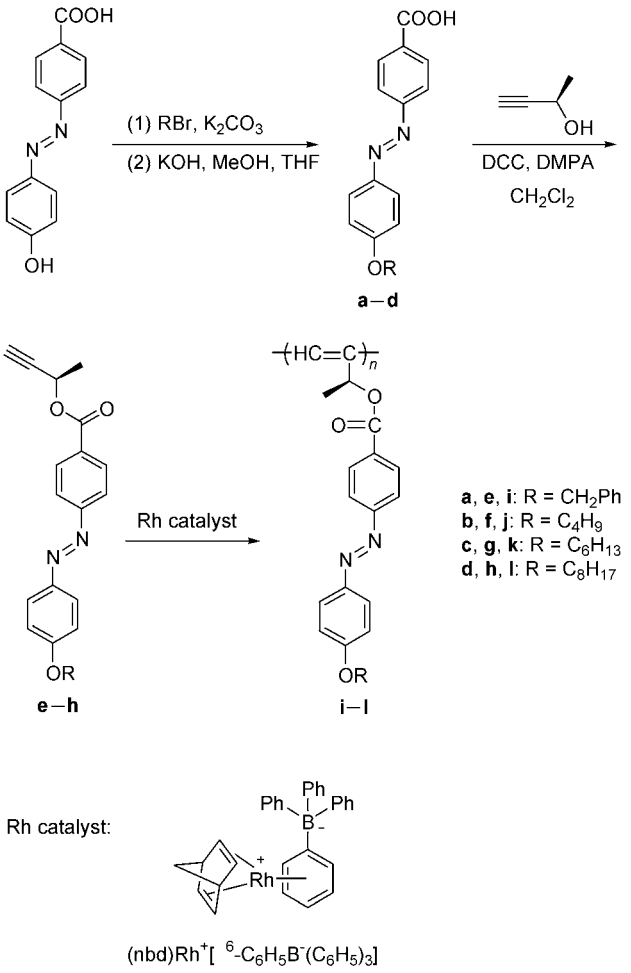
Scheme 1 Synthetic routes of the monomers and polymers



GULLIVER system (PU-980, CO-965, RI-930, and UV-1570) equipped with polystyrene gel columns (Shodex columns K804, K805, and J806) using tetrahydrofuran (THF) as an eluent at a flow rate of 1.0 mL/min, calibrated by polystyrene standards at 40 ℃.

Materials

(*S*)-(－)-1-Methylpropargyl alcohol (Aldrich), 4-aminobenzoic acid, phenol, 1-bromobutane, 1-bromoheptane and 1-bromododecane were purchased from Shanghai Chemical Reagent Co (Shanghai, China). *N*-(3-Dimethylaminopropyl)-*N'*-ethylcarbodiimide hydrochloride (EDC•HCl, Eiweiss) and 4-dimethylaminopyridine (DMAP, Aldrich) were purchased and used without further purification. All other reagents and solvents were purchased from Sinopharm Chemical Reagent Co., Ltd., and used as received. 4-Carboxy-4'-hydroxy-azobenzene and 4-carboxy-4'-(*n*-butylether)-azobenzene (**b**) were synthesized according to reference.[13] (nbd)$Rh^+[\eta^6$-$C_6H_5B^-(C_6H_5)_3]$ was synthesized according to the literature.[14]

Monomer synthesis

4-Carboxy-4'-hydroxy-azobenzene 2.5 g (0.01 mol) was dissolved in benzyl bromide 3.7 g (0.027 mol) solution with cyclohexanone (25 g) and K_2CO_3 (10 g) as a catalyst under stirring, and reacted under nitrogen atmosphere at 80 ℃ for 4 h, and at 120 ℃ for 4 h. Then K_2CO_3 was removed by filtration and the solvent was evaporated under vacuum. The yellowish solid intermediate product, 4-phenyoxycarbonyl-4'-phenyoxyazobenzene was obtained after recrystallization from acetone. 4-Phenyoxycarbonyl-4'-phenyoxyazobenzene was further hydrolyzed by KOH solution in a mixed solution of methanol and THF (V∶V=1∶1) under reflux condition for 5 h, and precipitated in HCl solution (pH=1—2) to give 4-[4-(benzyloxy)phenylazo]benzoic acid (**a**), yellow solid, yield 58%; ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 5.15 (s, 2H, >CH_2), 7.15 (d, J=2.0 Hz, 2H, ArH, *ortho* to O), 7.22—7.31 (m, 5H, ArH, next to >CH_2), 7.90—7.93 (m, 4H, ArH, *ortho* to N), 8.10 (d, J=2.4 Hz, 2H, ArH, *ortho* to COOH); ^{13}C NMR (DMSO-d_6, 100 MHz) δ: 73.2, 115.2, 125.0, 125.2, 127.5, 128.2, 128.7, 130.5, 132.1, 136.3, 146.0, 154.5, 161.9, 166.7.

c was synthesized in a manner similar to compound **a**. Yellow solid, yield 72%; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 0.89 (t, J=7.0 Hz, 3H, $CH_2C\mathbf{H}_3$), 1.31—1.33 [m, 4H, $CH_2(C\mathbf{H}_2)_2CH_2CH_3$], 1.45—1.47 (m, 2H, $C\mathbf{H}_2CH_3$), 1.80—1.82 (m, 2H, $OCH_2C\mathbf{H}_2$), 4.03 (t, J=12.4 Hz, 2H, $OC\mathbf{H}_2$), 6.99—7.02 [m, 2H, ArH, *ortho* to $O(CH_2)_7CH_3$], 7.92 (q, J=12.8 Hz, 4H, ArH, *ortho* to N=N), 8.16—8.23 (m, 2H, ArH, *ortho* to COOH); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 14.1, 22.7, 26.0, 29.2, 31.8, 68.5, 114.8, 122.4, 125.3, 130.8, 132.5, 146.9, 155.6, 162.4 , 165.0.

d was synthesized in a manner similar to compound **a**. Yellow solid, yield 75%; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 0.90 (t, J=7.2 Hz, 3H, CH_3), 1.31—1.33 (m, 8H, $CH_2(C\mathbf{H}_2)_4CH_2CH_3$), 1.45—1.47 (m, 2H, $C\mathbf{H}_2CH_3$), 1.80—1.82 (m, 2H, $OCH_2C\mathbf{H}_2$), 4.03 (t, J=6.5 Hz, 2H, $C\mathbf{H}_2(CH_2)_6CH_3$), 7.01 (t, J=8.89 Hz, 2H, ArH, *ortho* to $O(CH_2)_7CH_3$), 7.91—7.92 (m, 4H, ArH, *ortho* to N=N), 8.18 (d, J=8.39 Hz, ArH, 2H, *ortho* to COOH); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 14.1, 22.7, 26.0, 29.2, 29.3, 29.4, 31.8, 68.5, 114.8, 125.1, 125.2, 130.8, 132.5, 146.9, 155.6, 162.4, 166.7.

4-[4'-(Benzyloxy)phenylazophenyl]carbonyl-(*S*)-1-methylpropargyl ester (**e**): **a** (1.51 g, 5.08 mmol) was added to a solution of EDC•HCl (1.90 g, 9.0 mmol) and DMAP (0.1 g, 0.90 mmol) in CH_2Cl_2 (45 mL) at room temperature. (*S*)-(－)-1-Methylpropargyl alcohol (0.50 g, 7.1 mmol) was added to the solution, and the resulting mixture was stirred at room temperature overnight. The reaction mixture was washed with water (50 mL) three times, and the organic layer was dried over anhydrous $MgSO_4$. After filtration, the solvent was removed on a rotary evaporator to afford the crude product. It was purified by silica gel column chromatography eluted with hexane/ethyl acetate (V/V=20/1) as an eluent. Monomer **e** was obtained as yellow solid in 35% yield, m.p. 156—158 ℃; $[\alpha]_D^{25}$ −42.5 (c=0.1 g/dL, THF); ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.66 (s, 3H, $CHC\mathbf{H}_3C\equiv$CH), 2.51 (s, 1H, ≡CH), 5.15 (s, 2H, >CH_2),

5.69—5.72 (m, J=12.6 Hz, 1H, C**H**CH_3C≡CH), 7.08 (s, 2H, ArH, *ortho* to O), 7.10—7.46 (m, 5H, ArH, next to >CH_2), 7.89—7.96 (m, 4H, ArH, *ortho* to N), 8.18 (d, 2H, ArH, *ortho* to COOCHCH_3C≡CH); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 21.4, 60.9, 73.4, 73.2, 82.1, 115.2, 122.4, 125.6, 127.5, 128.2, 128.7, 130.8, 136.3, 147.1, 155.5, 161.9, 165.0; IR (KBr) v: 3288 (≡CH), 2933, 2853, 2119 (C≡C), 1717 (C=O), 1600, 1502, 1455, 842, 1142, 1092 (C—O—C) cm^{-1}. Anal. calcd for $C_{24}H_{20}N_2O_3$: C 74.98, H 5.24, N 7.29; found C 74.97, H 5.27, N 7.33.

f was synthesized from **b** and (*S*)-(−)-1-methylpropargyl alcohol in a manner similar to **e**. Yellow solid, yield 46%, m.p. 129—131 ℃; $[\alpha]_D^{25}$ −38 (c=0.1 g/dL, THF); ^{1}H NMR (400 MHz, DMSO-d_6) δ: 0.95 (t, J=7.4 Hz, 3H, CH_2C**H**$_3$), 1.44—1.46 (m, 2H, C**H**$_2$$CH_3$), 1.60 (d, J=2.0 Hz, 3H, CH≡CCHC**H**$_3$), 1.74—1.75 (m, 2H, C**H**$_2$$CH_2CH_3$), 3.61 (s, 1H, ≡CH), 4.10 [t, J=7.26 Hz, 2H, OC**H**$_2$$(CH_2)_2CH_3$], 5.64 (q, J=6.58 Hz, 1H, CH≡CC**H**CH_3), 7.15 [t, J=6.0 Hz, 2H, ArH, *ortho* to O$(CH_2)_3CH_3$], 7.92—7.95 (m, 4H, ArH, *ortho* to N=N), 8.15 (d, J=8.45 Hz, 2H, ArH, *ortho* to COOCH(CH_3)-C≡CH); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 14.1, 19.1, 21.6, 31.1, 61.3, 68.3, 72.7 (≡CH), 82.7 (CH≡C), 115.6, 122.9, 125.5, 130.9, 131.1, 146.6, 155.3, 162.8, 164.5; IR (KBr) v: 3287 (≡CH), 2951, 2871 (CH_3, CH_2), 2118 (C≡C), 1724 (C=O), 1597, 1504, 1463, 839 (Ar), 1142, 1093 (C—O—C) cm^{-1}. Anal. calcd for $C_{21}H_{22}N_2O_3$: C 71.98, H 6.33, N 7.99; found C 71.97, H 6.36, N 8.03.

g was synthesized from **c** and (*S*)-(−)-1-methylpropargyl alcohol in a manner similar to **e**. Yellow solid, yield 86%, m.p. 91—93 ℃; $[\alpha]_D^{25}$ −48 (c=0.1 g/dL, THF); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.92 (t, J=7.0 Hz, 3H, CH_2CH_3), 1.33—1.36 [m, 4H, (C**H**$_2$$)_2CH_2CH_3$], 1.47—1.49 (m, 2H, C**H**$_2$$CH_3$), 1.63—1.79 (m, 3H, CHC**H**$_3$C≡CH), 1.80—1.83 [m, 2H, OCH_2C**H**$_2$], 2.54 (s, 1H, ≡CH), 4.06 [t, J=6.57 Hz, 2H, OC**H**$_2$$(CH_2)_4$-$CH_3$], 5.71 (q, J=6.71 Hz, 1H, C**H**CH_3C≡CH), 6.99—7.02 [m, 2H, ArH, *ortho* to O$(CH_2)_5CH_3$], 7.89—7.95 (m, 4H, ArH, *ortho* to N=N), 8.15—8.20 (m, 2H, ArH, *ortho* to COOCHCH_3C≡CH); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.0, 21.4, 22.6, 25.7, 29.1, 31.6, 60.9, 68.5, 73.2 (≡CH), 82.1 (CH≡C), 114.8, 122.4, 125.2, 130.8, 132.5, 146.9, 155.6, 162.4, 165.0; IR (KBr) v: 3259 (≡CH), 2935, 2870 (CH_3, CH_2), 2115 (C≡C), 1714 (C=O), 1601, 1503, 1470, 838, 1109, 1091 (C—O—C) cm^{-1}. Anal. calcd for $C_{23}H_{26}N_2O_3$: C 72.99, H 6.92, N 7.40; found C 72.99, H 6.95, N 7.44.

h was synthesized from **d** and (*S*)-(−)-1-methylpropargyl alcohol in a manner similar to **e**. Yellow solid, yield 90%, m.p. 91—93 ℃; $[\alpha]_D^{25}$ −43 (c=0.1 g/dL, THF); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.89 (t, J=7.0 Hz, 3H, CH_2C**H**$_3$), 1.32—1.34 [m, 8H, CH_2(C**H**$_2$$)_4CH_2$-$CH_3$], 1.46—1.49 (m, 2H, C**H**$_2$$CH_3$), 1.66—1.69 [m, 3H, CH(C**H**$_3$)C≡CH], 1.80—1.83 [m, 2H, OCH_2C**H**$_2$-$(CH_2)_5CH_3$], 2.51 (s, 1H, ≡CH), 4.03 [t, J=8.42 Hz, 2H, OC**H**$_2$$(CH_2)_6CH_3$], 5.69 [q, J=6.73 Hz, 1H, C**H**(CH_3)C≡CH], 7.01 [d, J=8.88 Hz, 2H, ArH, *ortho* to O$(CH_2)_7CH_3$], 7.91—7.93 (m, 4H, ArH, *ortho* to N=N), 8.19 [d, J=8.39 Hz, 2H, ArH, *ortho* to COOCH-(CH_3)C≡CH]; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.1, 21.4, 22.7, 26.0, 29.2, 29.3, 29.4, 31.8, 60.9, 68.5, 73.2 (≡CH), 82.1 (CH≡C), 114.8, 122.4, 125.2, 130.8, 132.4, 146.9, 155.6, 162.4, 165.0; IR (KBr) v: 3258 (≡CH), 2927, 2858 (CH_3, CH_2), 2116 (C≡C), 1712 (C=O), 1593, 1496, 1464, 850, 1139, 1101 (C—O—C) cm^{-1}. Anal. calcd for $C_{25}H_{30}N_2O_3$: C 73.86, H 7.44, N 6.89; found C 73.85, H 7.48, N 6.92.

Polymerization

Typical procedure: All the polymerizations were carried out in a Schlenk tube equipped with a three-way stopcock under nitrogen. A THF solution of a monomer ($[M]_0$=0.2 mol•L^{-1}) was added to a THF solution of (nbd)Rh$^+$[η^6-$C_6H_5B^-(C_6H_5)_3$] ($[M]_0$/[cat] = 100) under dry nitrogen, and the solution was kept at 30 ℃ for 24 h. The polymerization mixture was poured into a large amount of MeOH to precipitate a polymer. It was separated from the supernatant by filtration and dried under reduced pressure.

Spectroscopic data of the polymers

i: ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.18—1.23 (br, 3H, CH(C**H**$_3$)C=), 4.79—4.80 (br, 2H, >CH_2), 4.89—4.93 (br, 1H, C**H**CH_3C=), 5.84—6.08 (br, 1H, >C=CH), 6.74—6.82 (br, 2H, ArH, *ortho* to O), 7.20—7.40 (br, 5H, ArH, next to >CH_2), 7.58—7.66 (br, 4H, ArH, *ortho* to N), 8.00—8.15 (br, 2H, ArH, *ortho* to COOCH(CH_3)C=); IR (KBr) v: 3440, 2924, 2866 (CH_3, CH_2), 1712 (C=O), 1592, 1496 (Ar), 1457, 1373, 1330, 1261, 1157, 1064, 1025, 871, 748, 721 cm^{-1}.

j: ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 0.90—0.94 (br, 3H, CH_2C**H**$_3$), 1.18—1.26 (br, 2H, C**H**$_2$$CH_3$), 1.43 (br, 3H, =CCHC**H**$_3$), 1.62—1.68 (br, 2H, C**H**$_2$$CH_2CH_3$), 3.81—3.82 (br, 2H, C**H**$_2$$(CH_2)_2CH_3$), 3.91—4.08 (br, 1H, =CC**H**CH_3), 5.81—6.01 (br, 1H, >C=CH), 6.66—6.82 [br, 2H, ArH, *ortho* to O$(CH_2)_3CH_3$], 7.65—7.68 (br, 4H, ArH, *ortho* to N), 8.11—8.12 (br, 2H, ArH, *meta* to N); IR (KBr) v: 3444, 2959, 2875 (CH_3, CH_2), 1717 (C=O), 1599, 1498 (Ar), 1319, 1268, 1172, 1099, 848, 755, 694 cm^{-1}.

k: ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 0.75—0.76 (br, 3H, CH_2CH_3), 1.29—1.37 [br, 9H, C**H**$_2$$(CH_2)_2CH_3$, C**H**$_2$$CH_2CH_2CH_3$, C**H**$_2$$CH_3$ and CH(C**H**$_3$)C=], 1.70—1.75 [br, 2H, C**H**$_2$$(CH_2)_3CH_3$], 3.80—3.84 [br, 2H, $CH_2(CH_2)_4CH_3$], 3.95—4.05 (br, 1H, C**H**(CH_3)C=), 5.87—6.01 (br, 1H, >C=CH), 6.60—8.13 (br, 8H, Ar); IR (KBr) v: 3444, 2930, 2862 (CH_3, CH_2), 1715 (C=O), 1596, 1496 (Ar), 1319, 1268, 1172, 1099, 848, 755, 694 cm^{-1}.

l: ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 0.85—0.88 (br, 3H, CH_2C**H**$_3$), 0.98—1.04 [br, 13H, C**H**$_2$$(CH_2)_4CH_3$, C**H**$_2$-$(CH_2)_3CH_3$, C**H**$_2$$(CH_2)_2CH_3$, C**H**$_2$$CH_2CH_3$, C**H**$_2$$CH_3$ and CH(C**H**$_3$)C=], 1.68—1.73 [br, 2H, C**H**$_2$$(CH_2)_5CH_3$], 3.80—3.85 [br, 2H, C**H**$_2$$(CH_2)_6CH_3$], 3.97—4.05 [br, 1H, C**H**(CH_3)C=], 5.92—5.94 (br, 1H, >C=CH),

6.77—8.13 (br, 8H, Ar); IR (KBr) *v*: 3444, 2926, 2858 (CH_3, CH_2), 1716 (C=O), 1596, 1496 (Ar), 1319, 1268, 1172, 1099, 848, 755, 694 cm^{-1}.

Results and discussion

Monomer synthesis

Scheme 1 illustrates the synthetic routes for the azobenzene containing **e**—**h**. 4-(Alkoxycarbonyl)-4'-alkoxyazobenzenes were synthesized by the reaction of 4-carboxy-4'-hydroxyazobenzene with the corresponding alkyl bromides using K_2CO_3 as a catalyst, and purified by recrystallization from acetone in 50%—78% yield. These intermediate products were hydrolyzed by KOH solution in methanol and THF (V∶V=1∶1) at reflux temperature for 5 h, precipitated in HCl solution to afford yellow powder **a**—**d** in good yields (58%—75%). Monomers **e**—**h** were synthesized by the condensation of the **a**—**d** with (*S*)-(−)-1-methylpropargyl alcohol using EDC•HCl and DMAP as condensation agents, and the desirable monomers were yielded in 35%—90% yields after purification by column chromatography and recrystallization. All azobenzene-containing chiral methylpropargyl esters were obtained as orange red solids, showing good solubility in common solvents including toluene, $CHCl_3$, CH_2Cl_2, THF, MeOH, and DMSO.

The structures of **e**—**h** were examined by IR and NMR spectroscopies. The monomers exhibited IR absorption peaks around 3300 and 2120 cm^{-1} associated with the ≡C—H and C≡C stretching vibrations, respectively. The absorption peaks around 1600, 1490 and 850 cm^{-1} attributed to phenyl group stretching vibrations. Accordingly, monomers **e**—**h** displayed ^{1}H NMR signal at δ 2—3 assignable to an ethynyl proton (Figure 1). In the ^{13}C NMR spectra, the monomers displayed signals assignable to ethynyl carbons around δ 73 and 82. The structures of the monomers **e**—**h** were also confirmed by elemental analysis. The monomers **e**—**h** displayed optical rotations ($[\alpha]_D^{25}$ −38——−48) in THF. These results clearly indicate that azobenzene-containing chiral methylpropargyl esters were obtained.

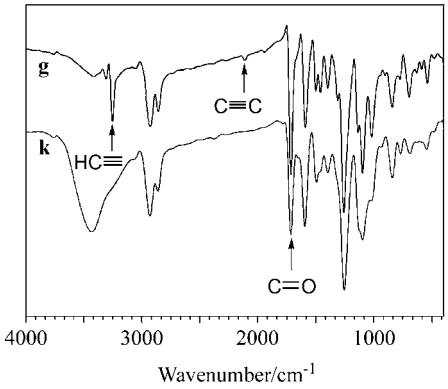


Figure 1 IR spectra of **g** and **k**.

Polymerization

Table 1 summarizes the conditions and results of the polymerization of monomers **e**—**h** catalyzed by (nbd)$Rh^+[\eta^6$-$C_6H_5B^-(C_6H_5)_3]$ catalysts. During the polymerization process, the yellow polymerization mixtures became black brown within 3 min, and gradually turned black with increasing the viscosity. After 24 h, the polymerization mixtures were poured into a large amount of MeOH to precipitate red-brown powdery polymers **i**—**l** with moderate molecular weights (M_n: 8.4×10^3—15.7×10^3) in good yields (76%—91%). The polymers were completely soluble in CH_2Cl_2, $CHCl_3$, toluene and THF, and insoluble in acetone, MeOH, diethyl ether, and *n*-hexane.

Table 1 Polymerizations of **e**—**h**[a]

Monomer	Yield[b]/%	$M_n\times10^{-3}$ [c]	M_w/M_n [c]	$[\alpha]_D^{25}$ [d]
e	86	13.0	2.03	+408
f	76	12.9	2.31	+375
g	84	8.4	2.18	+389
h	91	15.7	2.36	+412

[a] $[M]_0$=0.20 mol•L^{-1}, [Rh]=2 mmol•L^{-1}, 30 ℃, polymerized in THF for 24 h; [b] MeOH-insoluble part; [c] Determined by GPC eluted with THF on the basis of polystyrene calibration; [d] measured by polarimetry (c=0.1 g/dL, THF).

Polymer structures

The polymer structures were examined by IR and ^{1}H NMR spectroscopies. The monomers exhibited IR absorption bands around 3300 and 2120 cm^{-1} associated with the ≡C—H and C≡C stretching vibrations, respectively, while the polymers did not exhibit these peaks (Figure 1). Accordingly, the polymers displayed no ^{1}H NMR signal around δ 2.51 assignable to an acetylenic proton as shown in Figure 2. In the ^{13}C NMR spectra, the polymers displayed no signals assignable to ethynyl carbons around δ 73 and 81—83 (^{13}C NMR of polymers were not shown). All these results clearly indicate that the acetylene polymerization took place to form polymers composed of alternating single and double bonds. The *cis* contents of the main chain of **i**—**l** were 86%, 88%, 90%, and 95%, respectively, which were determined by the integration ratio of *cis* vinyl proton and the other proton signals.

Secondary structure of the polymers

The secondary structures of the polymers were examined by polarimetry. Table 1 lists the $[\alpha]_D^{25}$ values of **i**—**l** measured in THF. In contrast to **e** ($[\alpha]_D^{25}$ −43.5, c=0.100 g/dL in THF at room temperature), **i** displays large plus optical rotations, which suggests that it took a helical structure with a predominantly one handed screw sense. Similarly, **j**—**l** also seemed to form a helix with an excess of one-handedness in THF on the basis of the large $[\alpha]_D^{25}$ compared to those of monomers ($[\alpha]_D^{25}$ −38, −48, and −43, respectively; c=0.100 g/dL in THF at room temperature). We also examined the $[\alpha]_D^{25}$

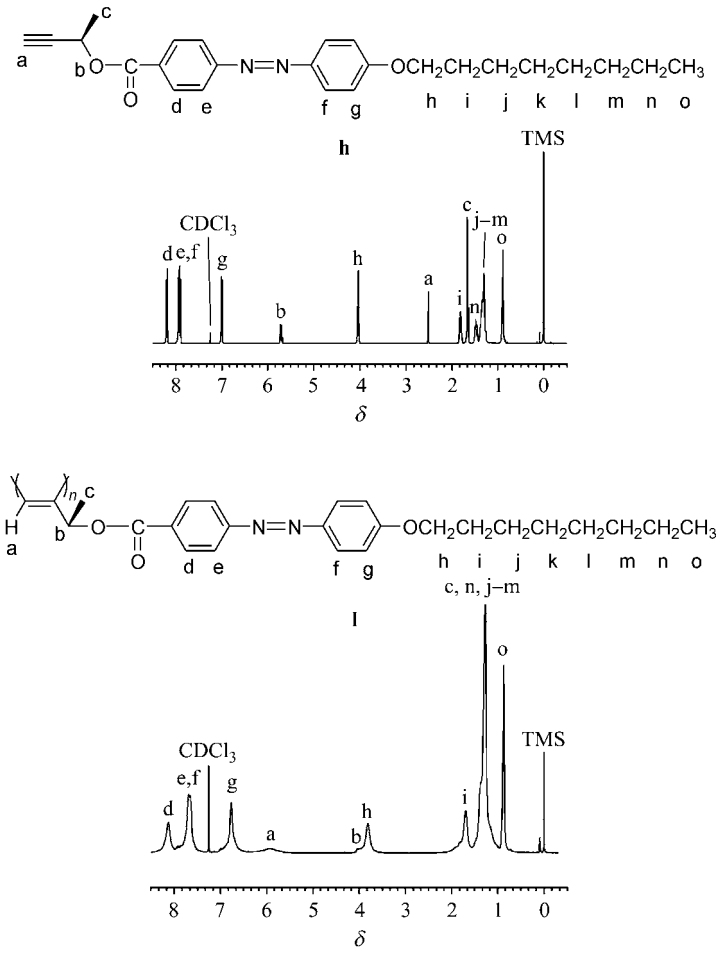


Figure 2 ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **h** and **l**.

of **i**—**l** in toluene and CH_2Cl_2 to find that the $[\alpha]_D^{25}$ slightly changed with solvents.

In conclusion, we have synthesized azobenzene-based novel chiral methyl methylpropargyl esters. Their structures were identified by IR, ^{1}H NMR, ^{13}C NMR and element analysis. Monomers **e**—**h** were polymerized with $Rh^+(nbd)[\eta^6\text{-}C_6H_5B^-(C_6H_5)_3]$ catalyst to give the corresponding polymers with moderate molecular weights ($M_n = 8.4\times10^3$—15.7×10^3) in good yields (76%—91%). The structures of polymers were testified by IR and NMR. Polymers were soluble in common organic solvents including toluene, $CHCl_3$ CH_2Cl_2, THF and DMSO, while insoluble in diethyl ether, *n*-hexane and methanol. The polymer solutions took predominantly one-handed helical structure in organic solvents such as THF. These polymers carrying azobenzene moieties in side chains can be a potential alternative nonlinear optical, helical polymer, and liquid crystalline materials.

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