Synthesis and Characterization of Poly(*N*-propargylsulfamides)

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ABSTRACT: A variety of novel *N*-propargylsulfamide monomers ($HC{\equiv}CCH_2NHSO_2R$) with alkyl (**1**−**4**) or aryl groups (**5**−**10**) were polymerized with a Rh catalyst, $(nbd)Rh^+B^-(C_6H_5)_4$ (nbd = 2,5-norbornadiene), to provide polymers with moderate molecular weights (3000−15 000) in good yields (above 80%). Polymerization of monomer **4** (R = $-(CH_2)_7CH_3$) at −15 °C yielded a stereoregular polymer whose cis content was nearly 100%, while the cis content remained 79% at 30 °C. Thus, the stereoregularity of the polymer largely depended on polymerization temperature. On the other hand, polymerization solvents hardly affected stereoregularity. Copolymerization of monomer **4** and *N*-propargylamide monomer **11** afforded copolymers with various compositions in high yields (above 87%), and the cis contents of the resultant copolymers were located between those of the corresponding homopolymers. The presence of intramolecular hydrogen bonding between the neighboring sulfamide groups was confirmed by IR spectroscopy measured in chloroform, suggesting that these types of polymers with appropriate substitutents also have the potential to form helices under suitable conditions like poly(*N*-propargylamides).

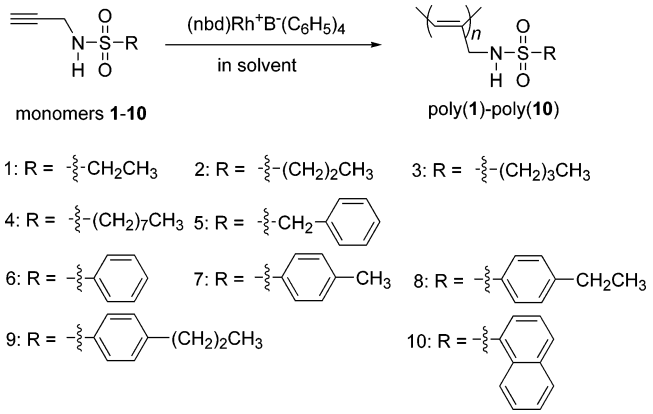
Introduction

High-quality polyacetylene film which exhibits high electrical conductivity upon doping became available with the advent of the Shirakawa method.[1] Since then, conjugated polymers including substituted polyacetylene,[2] polythiophene,[3] polyaniline,[4] polypyrrole,[5] poly-*p*-phenylene,[6] and polyfluorene[7] have received a great deal of attention mainly because of their excellent electronic and optical properties and, in turn, their potential in electronic and photonic applications.[8] Studies on σ-conjugated materials like polysilanes have also been performed.[9] Further, it has been found that incorporation of transition-metal complexes into conjugated polymer backbones can lead to interesting and promising materials showing magnetic, electronic, and optical properties and unique catalytic and sensory characteristics as well.[10] In addition, the use of conjugated polymers as responsive materials also draws growing attention. It has been pointed out and experimentally clarified that conjugated polymers are advantageous in collecting response over small conterparts.[11] For instance, cationic conjugated polymers have been proven useful for strand-specific DNA detection, which gathers intense current interest.[12]

Meanwhile, self-assembly systems through noncovalent interactions, such as hydrogen bonds, ionic bonds, and hydrophobic and van der Waals interactions, also draw growing attention.[13] Among these noncovalent interactions, hydrogen bonds occupy significant positions in developing self-assembly systems.[14] In some self-assemblies consisting of sulfamide groups, hydrogen bonds are formed practically and effectively.[15] Several helical polyacetylenes containing amino acids also form self-assemblies.[16]

We have investigated two types of helical polyacetylenes: poly(*N*-propargylamides)[17] and poly(propiolic esters).[18] If these polymers possess appropriate substituents, they can form stable helices, owing to the formation of intramolecular hydrogen bonding in the former polymers[17] or steric repulsion between the bulky pendent groups in the latter.[18] Therefore, the incorporation of sulfamide groups as side chains onto conjugated polymer main chains in principle will lead to novel interesting polymers, since the resultant polymers simultaneously bear the conjugated backbone and functional side groups which are able to form hydrogen bonds, like poly(*N*-propargylamides).[17,18]

Scheme 1



On the basis of the above-stated background, the present research deals with the synthesis of a new type of polyacetylene, poly(*N*-propargylsulfamides), as shown in Scheme 1. Among the polymers, poly(**1**)−poly(**4**) contain alkyl pendent groups; poly(**5**)−poly(**10**) have aryl groups in their side chains. When polymerized at −15 °C, monomer **4** gave polymers with high stereoregularity; i.e., the cis content was quantitative. In addition, poly(*N*-propargylsulfamides) bearing either alkyl or aryl groups in side chains can form intramolecular hydrogen bonding between neighboring sulfamide groups. These results essentially suggest that

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poly(*N*-propargylsulfamides) with appropriate pendent groups have the potential to form stable helical structure under certain conditions.

Experimental Section

Measurements. Melting points (mp) were measured by a Yanaco micro-melting point apparatus. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL EX−400 spectrometer. IR spectra were recorded with a Shimadzu FTIR-8100 spectrophotometer. Elemental analysis was carried out at the Kyoto University Elemental Analysis Center. Molecular weights and molecular weight distributions of the polymers were determined by GPC (Shodex KF-850 column) calibrated by using polystyrenes as standards and THF as an eluent. UV−vis spectra were recorded on a JASCO J-820 spectropolarimeter.

Materials. Solvents were distilled by the standard methods. Propargylamine, ethanesulfonyl chloride, 1-propanesulfonyl chloride, 1-butanesulfonyl chloride, 1-octanesulfonyl chloride, α-toluenesulfonyl chloride, benzenesulfonyl chloride, *p*-toluenesulfonyl chloride, 4-ethylbenzenesulfonyl chloride, 4-*n*-propylbenzenesulfonyl chloride, and 1-naphthalenesulfonyl chloride were used as received from TCI without further purification. (nbd)Rh$^+$B$^-$(C_6H_5)$_4$ was prepared as reported.[19]

Monomer Synthesis. All of the *N*-propargylsulfamide monomers (**1**−**10**) were synthesized for the first time. *N*-Propargylamide **11** was synthesized according to the method reported earlier.[20a] Synthesis of monomer **1**: Pyridine (6.3 mL, 78.0 mmol), propargylamine (5.3 mL, 78.0 mmol), and ethanesulfonyl chloride (3.7 mL, 39.0 mmol) were added to diethyl ether (150 mL) sequentially. The solution was stirred overnight at 0 °C. Then, a white precipitate which formed during the reaction was filtered off. The filtrate was collected and washed with 2 N hydrochloric acid three times and with saturated aqueous $NaHCO_3$ solution to neutralize the solution. Then, the solution was dried over anhydrous $MgSO_4$, filtered, and concentrated to give the target monomer. The crude monomer was further purified by flash column chromatography on silica gel (hexane/AcOEt = 2/1, v/v). Monomers **2**−**10** were prepared in a similar way to monomer **1** using the corresponding sulfonyl chlorides. The data of the newly synthesized monomers are as follows: Monomer **1**: yield 43%, colorless liquid, bp 99−101 °C (distilled at 760 mmHg). IR (KBr): 3300 (H−N), 2360 (H−C≡), 1320, 1150 cm^{-1} (S=O). ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): δ 1.30−1.40 (CH_3CH_2), 2.35−2.41 (C≡CH), 3.10−3.20 (CH_3CH_2), 3.89−3.95 (C≡C−CH_2), 4.90−5.10 (*NH*). ^{13}C NMR ($CDCl_3$, 400 MHz, 25 °C): δ 8.12, 32.39, 47.67, 72.75, 78.97. Anal. Calcd for $C_5H_9NO_2S$: C, 40.80; H, 6.16; N, 9.52. Found: C, 40.67; H, 6.14; N, 9.38. Monomer **2**: yield 52%, colorless crystal, mp 19−21 °C. IR (KBr): 3300 (H−N), 2290 (H−C≡), 1320, 1143 cm^{-1} (S=O). ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): δ 0.90−1.90 ($CH_3CH_2CH_2$), 2.35−2.40 (C≡CH), 3.00−3.10 ($CH_3CH_2CH_2$), 3.80−4.00 (C≡C−CH_2), 4.50−4.60 (*NH*). ^{13}C NMR ($CDCl_3$, 400 MHz, 25 °C): δ 12.91, 17.37, 32.58, 55.17, 72.91, 79.00. Anal. Calcd for $C_6H_{11}NO_2S$: C, 44.70; H, 6.88; N, 8.69. Found: C, 44.45; H, 6.62; N, 8.56. Monomer **3**: yield 61%, colorless crystal, mp 22−23 °C. IR (KBr): 3300 (H−N), 2200 (H−C≡), 1321, 1145 cm^{-1} (S=O). ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): δ 0.88−2.10 ($CH_3CH_2CH_2$), 2.18−2.20 (*CH*≡C), 3.18−3.20 ($CH_2C_3H_7$), 3.90−4.10 (CH≡CCH_2), 4.40−4.50 (*NH*). ^{13}C NMR ($CDCl_3$, 400 MHz, 25 °C): δ 13.51, 21.41, 25.42, 32.41, 53.12, 72.74, 79.07. Anal. Calcd for $C_7H_{13}NO_2S$: C, 47.97; H, 7.48; N, 7.99. Found: C, 47.77; H, 7.55; N, 7.72. Monomer **4**: yield 52%, colorless crystal, mp 42−44 °C. IR (KBr): 3280 (H−N), 2347 (H−C≡), 1319, 1136 cm^{-1} (S=O). ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): δ 0.80−2.10 ($CH_3CH_2CH_2$), 2.30−2.40 (*CH*≡C), 3.10−3.20 ($CH_2C_7H_{15}$), 3.90−4.10 (CH≡CCH_2), 5.30−5.40 (*NH*). ^{13}C NMR ($CDCl_3$, 400 MHz, 25 °C): δ 14.08, 22.61, 23.60, 28.25, 28.96, 29.05, 31.71, 32.61, 53.56, 72.91, 77.31. Anal. Calcd for $C_{11}H_{21}NO_2S$: C, 57.11; H, 9.15; N, 6.05. Found: C, 56.88; H, 9.39; N, 6.09. Monomer **5**: yield 51%, colorless crystal, mp 77−78 °C. IR (KBr): 3289 (H−N), 2300 (H−C≡), 1311, 1143 (S=O), 1491, 800, 705 cm^{-1} (phenyl group). ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): δ 2.40−2.48 (*CH*≡C), 3.80−3.90 (CH≡CCH_2), 4.35−4.40 (Ph−CH_2), 4.50−4.65 (*NH*), 7.35−7.50 (Ph−*H*). ^{13}C NMR ($CDCl_3$, 400 MHz, 25 °C): δ 33.91, 60.48, 74.32, 129.73, 129.80, 131.77. Anal. Calcd for $C_{10}H_{11}NO_2S$: C, 57.39; H, 5.30; N, 6.69. Found: C, 57.70; H, 5.33; N, 6.68. Monomer **6**: yield 57%, colorless crystal, mp 48−50 °C. IR (KBr): 3289 (H−N), 2200 (H−C≡), 1325, 1157 (S=O), 1508, 756, 721 cm^{-1} (phenyl group). ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): δ 1.90−2.00 (*CH*≡C), 3.80−3.90 (CH≡CCH_2), 4.60−4.75 (*NH*), 7.60−7.95 (*Ph*−*H*). ^{13}C NMR ($CDCl_3$, 400 MHz, 25 °C): δ 32.90, 73.03, 77.32, 127.31, 129.06, 132.96. Anal. Calcd for $C_9H_9NO_2S$: C, 55.37; H, 4.65; N, 7.17. Found: C, 55.39; H, 4.69; N, 7.11. Monomer **7**: yield 45%, colorless crystal, mp 57−59 °C. IR (KBr): 3290 (H−N), 2118 (H−C≡), 1330, 1160 (S=O), 1495, 810, 733 cm^{-1} (phenyl group). ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): δ 2.10−2.20 (Ph−CH_3), 2.40−2.45 (*CH*≡C), 3.80−3.90 (CH≡CCH_2), 4.50−4.60 (*NH*), 7.70−7.80 (Ph−*H*). ^{13}C NMR ($CDCl_3$, 400 MHz, 25 °C): δ 21.56, 32.85, 72.96, 127.34, 129.64, 136.42, 143.78. Anal. Calcd for $C_{10}H_{11}NO_2S$: C, 57.39; H, 5.30; N, 6.69. Found: C, 57.46; H, 5.24; N, 6.61. Monomer **8**: yield 48%, colorless crystal, mp 40−42 °C. IR (KBr): 3288 (H−N), 2395 (H−C≡), 1329, 1157 (S=O), 1508, 833, 657 cm^{-1} (phenyl group). ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): δ 0.94−1.70 (Ph−CH_2−CH_3), 2.08−2.10 (*CH*≡C), 2.66−2.72 (Ph−CH_2−CH_3), 3.83−3.87 (CH≡CCH_2), 4.60−4.65 (*NH*), 7.78−7.82 (Ph−*H*). ^{13}C NMR ($CDCl_3$, 400 MHz, 25 °C): δ 13.70, 28.48, 32.53, 72.57, 76.96, 127.09, 128.16. Anal. Calcd for $C_{11}H_{13}NO_2S$: C, 59.17; H, 5.87; N, 6.27. Found: C, 59.24; H, 5.79; N, 6.19. Monomer **9**: yield 46%, colorless crystal, mp 42−43 °C. IR (KBr): 3287 (H−N), 2391 (H−C≡), 1329, 1150 (S=O), 1431, 790, 696 cm^{-1} (phenyl group). ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): δ 0.92−1.69 (Ph−CH_2−C_2H_5), 2.08−2.09 (*CH*≡C), 2.64−2.68 (Ph−CH_2−C_2H_5), 3.83−3.85 (CH≡CCH_2), 4.60−4.63 (*NH*), 7.78−7.80 (Ph−*H*). ^{13}C NMR ($CDCl_3$, 400 MHz, 25 °C): δ 13.67, 24.23, 32.92, 37.86, 72.95, 77.32, 127.36, 129.12. Anal. Calcd for $C_{12}H_{15}NO_2S$: C, 60.73; H, 6.37; N, 5.90. Found: C, 60.57; H, 6.44; N, 5.87. Monomer **10**: yield 59%, colorless crystal, mp 100−102 °C. IR (KBr): 3283 (H−N), 2135 (H−C≡), 1320, 1130 (S=O), 1470, 800, 679 cm^{-1} (phenyl group). ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): δ 1.87−1.88 (*CH*≡C), 3.78−3.80 (CH≡CCH_2), 4.90−5.00 (*NH*), 7.53−8.63 (Ar−*H*). ^{13}C NMR ($CDCl_3$, 400 MHz, 25 °C): δ 32.96, 72.69, 77.63, 124.11, 124.13, 126.87, 128.27, 128.48, 129.10, 129.94, 134.20, 134.56. Anal. Calcd for $C_{13}H_{11}NO_2S$: C, 63.67; H, 4.49; N, 5.71. Found: C, 63.49; H, 4.49; N, 5.67.

Polymerization. Polymerizations were carried out with (nbd)Rh$^+$B$^-$(C_6H_5)$_4$ as the catalyst in a dry solvent at −15, 15, or 30 °C for a given time under nitrogen, [monomer]$_0$ = 1.0 M, [catalyst] = 10 mM. After polymerization, the resultant solution was poured into a large amount of hexane to precipitate the formed polymer. It was filtered and then dried under reduced pressure. The spectroscopic data of the polymers are as follows: Poly(**1**): IR (KBr): 3270 (H−N), 2347 (H−C=), 1317, 1140 (S=O), 1049 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz, 50 °C[21]): δ 0.90−1.80 (CH_3CH_2), 3.05−3.20 (CH_3CH_2), 3.65−3.90 (C=C−CH_2), 5.45−5.55 (*NH*), 6.30−6.40 (*HC*=C). Poly(**2**): IR (KBr): 3270 (H−N), 2347 (H−C=), 1319, 1140 (S=O), 1064 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz, 50 °C): δ 0.80−1.90 ($CH_3CH_2CH_2$), 2.90−3.20 ($CH_3CH_2CH_2$), 3.70−3.90 (C=C−CH_2), 5.45−5.55 (*NH*), 6.30−6.40 (*HC*=C). Poly(**3**): IR (KBr): 3270 (H−N), 2347 (H−C=), 1321, 1140 cm^{-1} (S=O), 1076 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz, 50 °C): δ 0.70−1.80 (CH_3CH_2-CH_2CH_2), 3.00−3.10 ($CH_3CH_2CH_2CH_2$), 3.70−3.80 (CH_3CH_2-CH_2CH_2, CH=CCH_2), 5.60−5.65 (*NH*), 6.30−6.40 (*CH*=C). Poly(**4**): IR (Figure S1 in Supporting Information as a representative) (KBr): 3265 (H−N), 2347 (H−C=), 1319, 1140 (S=O), 1070 cm^{-1}. ^{1}H NMR (Figure S2 in Supporting Information as a representative; $CDCl_3$, 400 MHz, 50 °C): δ 0.85−0.90 ($CH_3C_7H_{14}$), 1.30−1.80 ($CH_3C_6H_{12}CH_2$), 2.95−3.10 ($CH_3C_6H_{12}CH_2$), 3.75−3.85 (CH=CCH_2), 5.45−5.50 (*NH*), 6.30−6.35 (*CH*=C). Poly(**5**): IR (KBr): 3270 (H−N), 2347 (H−C=), 1319, 1124 (S=O), 1496, 781, 698 cm^{-1} (phenyl group). ^{1}H NMR ($CDCl_3$, 400 MHz, 50 °C): δ 1.45−1.55 (Ph−CH_2), 4.05−4.15 (CH=CCH_2), 5.40−5.45 (*NH*), 6.05−6.10 (*CH*=C), 7.25−7.40 (Ph−*H*). Poly(**6**): IR (KBr): 3265 (H−N), 2347 (H−C=), 1325, 1155 (S=O), 1508, 754, 721 cm^{-1} (phenyl group). ^{1}H

Table 1. Polymerization of *N*-Propargylsulfamides[a]

monomer	yield[b] (%)	M_n[c]	M_w/M_n[c]	cis content[d] (%)
1	89	5700	1.29	70
2	100	9300	2.41	75
3	100	9400	2.35	78
4	83	9000	2.36	79
5	100	6000	2.42	60
6	80	3000	1.33	n.d.[e]
7	100	10500	2.45	n.d.[e]
8	100	15000	2.00	n.d.[e]
9	93	10000	2.05	n.d.[e]
10	89	4500	1.58	n.d.[e]

[a] With (nbd)$Rh^+B^-(C_6H_5)_4$ catalyst in THF at 30 °C for 1 h; $[M]_0$ = 1.0 M; $[M]_0/[Rh]$ = 100. [b] Hexane-insoluble product. [c] Measured by GPC (polystyrenes as standards; THF as eluent). [d] Determined by ^1H NMR in $CDCl_3$ at 50 °C. [e] Could not be determined because the signal due to the olefinic proton was broad.

NMR ($CDCl_3$, 400 MHz, 50 °C): δ 3.30−3.90 (CH═CCH_2), 5.80−5.90 (*NH*), 6.00−6.20 (*CH*═C), 7.20−7.95 (*Ph*−*H*). Poly(**7**): IR (KBr): 3265 (H−N), 2347 (H−C═), 1321, 1155 (S═O), 1494, 812, 706 cm^{-1} (phenyl group). ^1H NMR ($CDCl_3$, 400 MHz, 50 °C): δ 1.50−2.50 (Ph−CH_3), 3.70−3.75 (CH═CCH_2), 5.90−6.20 (*CH*═C, *NH*), 7.20−7.70 (Ph−*H*). Poly(**8**): IR (KBr): 3275 (H−N), 2345 (H−C═), 1330, 1157 (S═O), 1508, 843, 655 cm^{-1} (phenyl group). ^1H NMR ($CDCl_3$, 400 MHz, 50 °C): δ 0.84−1.50 (Ph−CH_2−CH_3), 2.50−2.70 (Ph−CH_2−CH_3), 3.26−3.70 (CH═CCH_2), 5.83−6.27 (*CH*═C, *NH*), 7.28−7.82 (Ph−*H*). Poly(**9**): IR (KBr): 3275 (H−N), 2365 (H−C═), 1338, 1157 (S═O), 1419, 790, 669 cm^{-1} (phenyl group). ^1H NMR ($CDCl_3$, 400 MHz, 50 °C): δ 0.72−1.70 (Ph−CH_2−C_2H_5), 2.48−2.69 (Ph−CH_2−C_2H_5), 3.40−3.55 (CH═CCH_2), 5.90−6.05 (*NH*), 6.05−6.20 (*CH*═C), 7.05−7.80 (Ph−*H*). Poly(**10**): IR (KBr): 3275 (H−N), 2345 (H−C═), 1319, 1132 (S═O), 1473, 804, 669 cm^{-1} (phenyl group). ^1H NMR ($CDCl_3$, 400 MHz, 50 °C): δ 3.75−3.80 (CH═CCH_2), 4.65−4.80 (*NH*, *CH*═C), 7.50−8.75 (Ph−*H*). Spectral data for poly(**4**-*co*-**11**)s (take poly($\mathbf{4}_{0.38}$-*co*-$\mathbf{11}_{0.62}$ for example): IR (KBr): 3260 (H−N), 2350 (H−C═), 1650 (C═O), 1320, 1140 (S═O), 1545 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz, 50 °C): δ 1.30−1.55, 1.70−2.50, 2.65−2.95, 3.45−3.70 (nC_8H_{17}, nC_6H_{13}), 4.25−4.75 (CH═CCH_2), 6.25−6.95 (*CH*═C), 7.70−7.90 (*NH*).

Results and Discussion

Polymer Synthesis. The monomers shown in Scheme 1 were polymerized with a Rh catalyst, (nbd)$Rh^+B^-(C_6H_5)_4$, whose results are presented in Table 1. It has been reported that the polymerization of *N*-propargylamides with Rh catalysts provides polymers with high stereoregularity, predominantly cis structure.[22] This unique performance of Rh catalysts makes them be widely employed in the polymerization of phenylacetylenes and other substituted acetylenes in order to investigate the helix-forming ability of the resultant polymers.[17,18,20,22,23]

All of the monomers **1**−**10** smoothly polymerized with (nbd)$Rh^+B^-(C_6H_5)_4$ as a catalyst to provide the corresponding polymers in high yields (>80%), while the molecular weights of the formed polymers appreciably differed although all the polymerizations were carried out under the same conditions. For example, monomer **6** gave a polymer with a fairly low molecular weight (M_n = 3000), while monomer **8** provided a polymer having a relatively high M_n (15 000). Generally speaking, the molecular weights of these polymers were not very high. The polydispersity index (M_w/M_n) ranged from 1.29 to 2.45.

In the ^1H NMR spectra of the resulting polymers recorded in chloroform-*d* at 50 °C, the signal of cis-olefinic proton in the main chain (−C═C*H*−) appeared around 6.5 ppm. By comparing the intensity of this signal (6.5 ppm) with the integrated intensities of the protons in the alkyl group, the contents of cis structure were evaluated as summarized in Table 1. The cis contents of these poly(*N*-propargylsulfamides) were less than 80% and obviously lower than those of poly(*N*-propargylamides), whose cis contents, in general, are approximately 100%.[20] Poly(**6**)−poly(**10**) showed so broad olefinic proton signals that the cis contents could not be determined. Thus, it is noteworthy that the stereoregularity of the present polymers is obviously lower than that of the poly(*N*-propargylamides), even though they have analogous structures.

Figure 1 depicts the polymer yield, M_n, M_w/M_n, and cis content as a function of time in the polymerization of monomer **4** as a representative of the monomers having alkanesulfonyl groups. In Figure 1, the same polymerization conditions were employed as those in

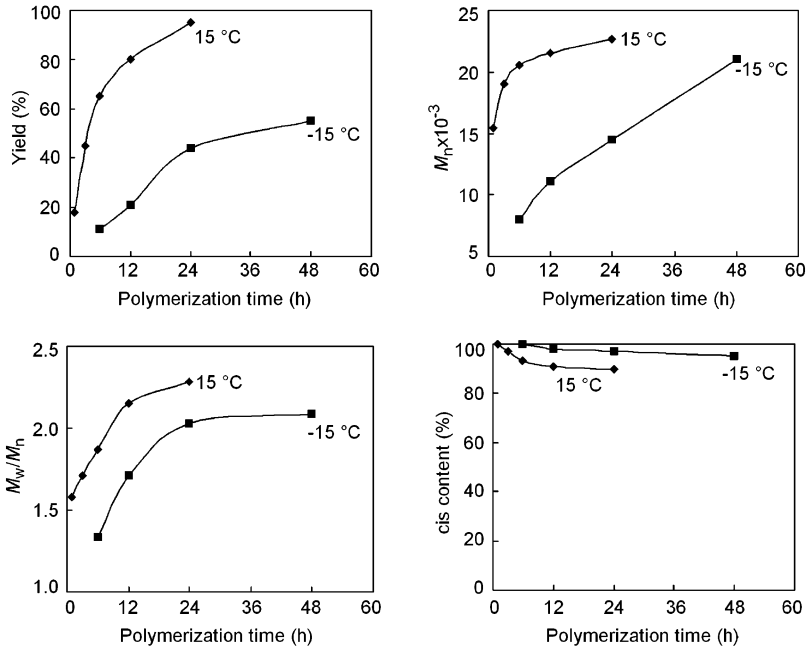


Figure 1. Time profiles of polymer yield, M_n, M_w/M_n, and cis content in the polymerization of monomer **4** at 15 and −15 °C with (nbd)$Rh^+B^-(C_6H_5)_4$ catalyst in THF for 1 h; $[M]_0$ = 1.0 M; $[M]_0/[Rh]$ = 100.

Table 2. Polymerization of Monomer 7 at −15 °C[a]

polymerization time (h)	yield[b] (%)	M_n[c]	M_w/M_n[c]
6	36	36 000	2.60
12	45	40 000	2.12
24	51	43 000	2.32
48	72	55 000	2.00

[a] With (nbd)$Rh^+B^-(C_6H_5)_4$ catalyst in THF; $[M]_0 = 1.0$ M; $[M]_0/[Rh] = 100$. [b] Hexane-insoluble product. [c] Measured by GPC (polystyrenes as standards; THF as eluent).

Table 3. Effect of Solvents on the Polymerization of Monomer 4[a]

solvent	yield[b] (%)	M_n[c]	M_w/M_n[c]	cis content[d] (%)
toluene	81	8400	2.00	50
THF	83	9000	2.36	79
$CHCl_3$	82	9200	2.02	70
CH_2Cl_2	80	8600	1.74	50
DMF	64	7500	1.76	70

[a] With (nbd)$Rh^+B^-(C_6H_5)_4$ catalyst at 30 °C for 1 h; $[M]_0 = 1.0$ M; $[M]_0/[Rh] = 100$. [b] Hexane-insoluble product. [c] Measured by GPC (polystyrenes as standards; THF as eluent). [d] Determined by ^1H NMR in $CDCl_3$ at 50 °C.

Table 4. Copolymerization of Monomers 4 and 11[a]

monomer feed (**4**/**11**)	yield[b] (wt %)	M_n[c]	M_w/M_n[c]	monomer **4** in copolymer[d] (mol %)	cis content[d] (%)
100/0	83	9 000	2.36	100	79
80/20	87	12 000	1.93	81	84
60/40	88	14 000	2.10	59	89
40/60	92	18 600	2.15	38	90
20/80	100	19 500	2.14	22	92
0/100	85	18 300	2.12	0	92

[a] With (nbd)$Rh^+B^-(C_6H_5)_4$ catalyst at 30 °C in THF for 1 h; $[M]_0 = 1.0$ M; $[M]_0/[Rh] = 100$. [b] Hexane-insoluble product. [c] Measured by GPC (polystyrenes as standards; THF as eluent). [d] Determined by ^1H NMR in $CDCl_3$ at 50 °C.[24]

Table 1, except for temperature and time. The polymer yield, M_n, and polydispersity index (M_w/M_n) increased with the polymerization time. When polymerization was carried out at 15 °C for 24 h, the polymer yield and M_n reached 95% and 23 000, respectively. On the other hand, the cis content of polymer gradually decreased with the polymerization time. The cis content of the formed polymer was quantitative when the monomer was polymerized at 15 °C for 1 h, while it decreased to 90% when the polymerization time was as long as 24 h. Therefore, it seems that isomerization took place during the polymerization process.

When polymerization was carried out at a lower temperature (−15 °C), it proceeded slower than at 15 °C. Even though the polymerization time was prolonged to 48 h, the product yield remained 55%. On the other hand, the M_n linearly increased with time to reach 21 000, almost the same as that at 15 °C (23 000). Particular attention should be paid to the cis contents of the polymers. Even though the polymerization time was extended to 48 h, the cis content changed only slightly compared to that in the polymerization for 6 h, where the cis content was nearly 100%. This result clearly manifests that the polymerization temperature is a key factor leading to low cis content of the polymers.

Monomer **7** which has an aromatic group was also subjected to polymerization at −15 °C, as summarized in Table 2. The polymerization proceeded smoothly even at this temperature. Both M_n and yield of polymer clearly increased along with elongation of the polymerization time. We could not determine the effect of temperature on the cis content of the polymer because the signals of the main chain olefinic proton were very broad in all cases.

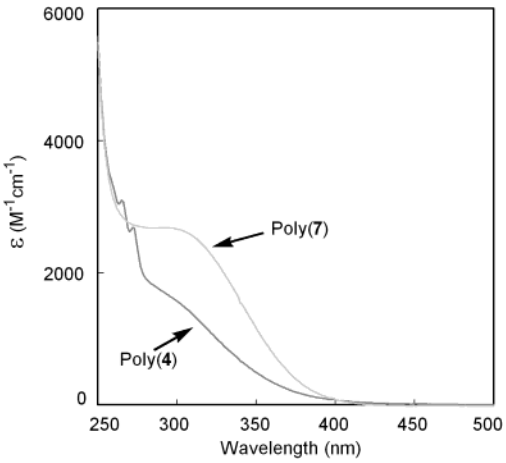
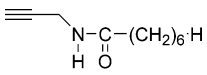


Figure 2. UV−vis spectra of poly(**4**) and poly(**7**) measured in chloroform ($c = 0.1$ mM; rt). Samples were obtained by the polymerization at −15 °C for 6 h.

Chart 1



monomer **11**

The influence of solvents on the polymerization of monomer **4** was examined, the results of which are shown in Table 3. All the solvents led to the formation of polymers in good yields whose M_n was in the range of 7500−9200. No remarkable solvent effects were observed with respect to product yield and M_w/M_n. Although THF afforded polymer having the highest cis content among the solvents, the value was not very high (79%). It is concluded that the polymerization temperature has a larger influence on the cis content than do solvents.

Copolymerization. *N*-Propargylamide monomer **11** in Chart 1 gives a polymer having high stereoregularity, whose cis content is 92%.[20] It seems interesting to examine the dependence of stereoregularity of copolymers obtained from **11** and *N*-propargylsulfamide monomer **4** on copolymer composition. The results are presented in Table 4.[24] All the copolymerizations gave the corresponding copolymers with moderate M_n in good yields. It can be concluded that the copolymerizations took place satisfactorily because the copolymers exhibited unimodal GPC traces and because the copolymer compositions practically agreed with the monomer feed ratios under conditions of high polymer yields. The cis contents of the copolymers could be determined by ^1H NMR spectroscopy, which ranged from 79 to 92%, between those of the homopolymers. Thus, it turns out that the cis content of the copolymer increases monotonically with increasing content of the unit of monomer **11**.

Solubility of the Polymers. The solubility of the polymers in various solvents was examined, and the results are summarized in Table 5. Nearly all the polymers were soluble in THF, chloroform, DMF, and DMSO but did not completely dissolve in other solvents examined. Poly(**7**)−poly(**9**) and poly(**4**)−poly(**7**) partly dissolved in toluene and methanol, respectively.

Table 5. Solubility of Poly(*N*-propargylsulfamides)[a]

solvent[b]	poly(**1**)	poly(**2**)	poly(**3**)	poly(**4**)	poly(**5**)	poly(**6**)	poly(**7**)	poly(**8**)	poly(**9**)	poly(**10**)
toluene	×	×	×	×	×	×	□	□	□	×
$CHCl_3$	○	○	○	○	○	○	○	○	○	□
THF	○	○	○	○	○	○	○	○	○	○
DMF	○	○	○	○	○	○	○	○	○	○
DMSO	○	○	○	○	○	○	○	○	○	○
AcOEt	×	×	×	×	×	×	×	×	×	×
acetone	×	×	×	×	×	×	×	×	×	×
MeOH	×	×	×	□	□	□	□	×	×	×
H_2O	×	×	×	×	×	×	×	×	×	×

[a] ○: soluble; □: partly soluble; ×: insoluble; at room temperature. [b] THF: tetrahydrofuran; DMF: *N*,*N*-dimethylformamide; DMSO: dimethyl sulfoxide; AcOEt: ethyl acetate; MeOH: methanol.

UV and IR Spectra of the Polymers. Figure 2 depicts the UV−vis spectra of poly(**4**) and poly(**7**) as representative samples of polymers with aliphatic and aromatic side chains, respectively. Both polymers showed a shoulder and a maximum, respectively, around 320 nm. As we have reported,[17,20] poly(*N*-propargylamides) in random coil and helical states show absorption at 320 and 390 nm, respectively. It is therefore suggested that both poly(**4**) and poly(**7**) exist in random coil conformation at room temperature. When the measuring temperature was lowered to −60 °C, the shape of the UV−vis spectra hardly changed. However, it seems still difficult to conclude that these polymers cannot form a helix, since we know that poly(*N*-propargylcarbamates) do not display a UV−vis absorption around 390 nm, but indeed they take a helical conformation.[25]

The IR spectra (measured in chloroform, $c = 50$ mmol/L, rt) of poly(**4**) (Figure S4 in Supporting Information as a representative) and poly(**7**) clearly displayed the peaks characteristic of sulfamide groups. The vibrational absorption peaks at 3267, 1320, and 1140 cm^{-1} in the IR spectrum of poly(**4**) can be assigned to ν_{NH}, ν_{a,SO_2}, and ν_{s,SO_2}, respectively.[26] When the IR peaks of poly(**4**) are compared to those of monomer **4** (3308, 1339, and 1146 cm^{-1}), shifts toward lower wavenumber are obviously seen. A similar phenomenon was observed between poly(**7**) (peaks at 3265, 1321, and 1161 cm^{-1}) and monomer **7** (3308, 1339, and 1161 cm^{-1}). In addition, only one broad strong peak of ν_{NH} appeared in a region of 3100−3400 cm^{-1} in the IR spectra of both poly(**4**) and poly(**7**). Changing the concentration of poly(**4**) in chloroform (25, 50, and 75 mmol/L) resulted in no change of wavenumber of the IR peaks. Consequently, it is reasonable to conclude that intramolecular hydrogen bonds exist between the sulfamide moieties of polymer side chains.

This resembles the previously reported case of poly(*N*-propargylamides) which take the helical structure stabilized by intramolecular hydrogen bonding between the amide moieties of polymer side chains.[17,20] As we have previously reported,[17b] two hydrogen-bond strands in an antiparallel way are likely to induce a helical structure in poly(*N*-propargylamides). Poly(*N*-propargylsulfamides) in the present study may also form intramolecular hydrogen bonds between the neighboring sulfamide groups in the side chains. The CD spectral information on poly(*N*-propargylsulfamides) having chiral pendent groups is required to conclude whether poly(*N*-propargylsulfamides) have the helix-forming ability, and the related research is now in progress.

Conclusion

The novel *N*-propargylsulfamides readily provided the corresponding polymers under the given polymerization conditions. The polymers obtained at 30 °C did not show high stereoregularity, which seems to be due to isomerization during the polymerization. Lowering the polymerization temperature was effective to improve the stereoregularity. Neither use of different solvents nor copolymerization could lead to (co)polymers with sufficiently high cis contents. IR spectra of the polymers measured in chloroform solution demonstrated the presence of intramolecular hydrogen bonding between the sulfamide groups of the side chains.

Supporting Information Available: IR and ^1H NMR spectra of poly(**4**) as a representative and the IR spectra of poly(**4**) measured in $CHCl_3$. This material is available free of charge via the Internet at http://pubs.acs.org.

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