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A Novel Polyaddition of Bifunctional Acetylenes Containing Electron-Withdrawing Groups. 2. Synthesis of Polymers Having β-Alkylmercaptoenoate Moieties by the Reaction with Dithiols

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ABSTRACT: Tri-*n*-butylphosphine-catalyzed polyadditions of bifunctional acetylenes having ester groups [i.e., bis(propiolate)s (**1A–C**)] with dithiols (**2a–e**) are described. Although a gel was obtained by the polyaddition of a terminal bispropiolate (**1A**) with α,α'-xylene dithiol (**2a**) through the second addition of thiol moieties to the produced double bonds, the polyaddition of **1A** with 1,4-benzene dithiol (**2b**) in THF (0.3 M) using tri-*n*-butylphosphine (5 mol %) as a catalyst proceeded at room temperature within 1 h to obtain a soluble polymer (**3Ab**) having β-alkylmercaptoenoate moieties in the main chain in quantitative yield, whose M_n and M_w/M_n were estimated as 20 700 and 2.12, respectively. Further, polyadditions of **1B** having internal acetylene moieties with dithiols (**2a–e**) proceeded under mild conditions and the corresponding polymers were obtained in almost quantitative yield. For instance, the polyaddition of **1B** with **2a** in THF (0.5 M) proceeded at room temperature within 3 h and a polymer (**3Ba**) was obtained in 93% yield whose M_n and M_w/M_n were estimated as 25 200 and 2.16, respectively. The obtained polymer was colorless and stable in air. Furthermore, **3Ba** showed a good film-forming character by casting from a dichloromethane solution. On the other hand, the polyaddition of **1C** with **2a** gave a polymer (**3Ca**) that mainly contains regioisomeric units (i.e., α-alkylmercaptoenoate units) by means of a radical reaction in almost quantitative yield.

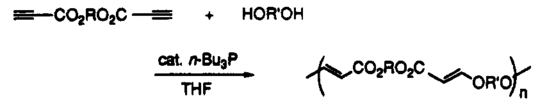
Introduction

A number of conjugate additions of heteronucleophiles to activated alkynes have been reported for the construction of heteroatom substituted olefins in organic synthesis.[1] The resulting olefins have both an electron-withdrawing group and an electron-donating group at each terminal (i.e., "push-pull" olefins) that serve as equivalents of vinyl cations in the following reactions. For instance, the addition reactions of organometallic reagents to these olefins are important synthetic processes where alkenic units retain their geometry.[2]

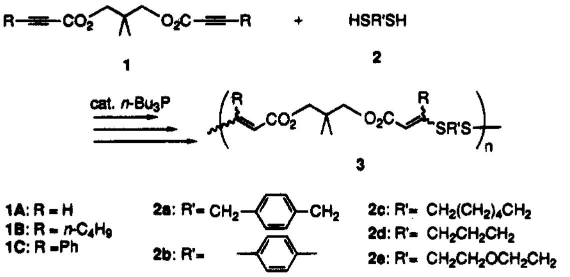
Recently, we have described a trialkylphosphine-catalyzed polyaddition of dipropiolates with diols, from which polymers having β-alkoxyenoate moieties (only the *E* isomer) in the main chain were obtained in almost quantitative yield (Scheme 1).[3] The obtained polymers may be expected to have unique characteristics (i.e., reactivity, degradability, etc.) originating from the β-alkoxyenoate moieties. By the replacement of the oxygen at the β-position to other heteroatoms, the reactivity as well as function of the polymers might be varied.

Divalent sulfur atoms (RSR′, RSH, and RS^-) are known as soft and strong nucleophiles toward the reaction with soft electrophiles such as conjugated triple bonds.[4] Furthermore, divalent sulfur atoms have unique characteristics,[5] such as a wide variability of oxidation numbers (sulfide–sulfoxide–sulfone) and facility of C–S bond cleavage by various reactions. In addition, the sulfur-containing polymers are paid much attention to as materials with high refractive indexes.[6] Thus, dithiols might be attractive monomers for the polyaddition by means of conjugate additions. The resulting polymers containing vinyl sulfide moieties in the main chain might show unique functions (reactivity, degradability, high refractive index, etc.). Although the radical polyaddition of diethynylbenzene with benzene dithiol has been reported to produce a polymer containing vinyl sulfide moieties in the main chain,[7] this method is limited in terms of diyne monomers that can stabilize intermediate vinyl radicals.

Scheme 1



Scheme 2



Trialkylphosphine-catalyzed conjugate addition of thiols to methyl propiolate has been reported to proceed smoothly under mild condition and to give β-alkylmercaptoenoate in quantitative yield.[8] Herein, we wish to report a novel phosphine-catalyzed polyaddition of bifunctional acetylenes (**1A–C**) with dithiols (**2a–e**, Scheme 2).

Experimental Section

Materials and Instruments. **1A** was prepared by the previously reported method.[3] Tetrahydrofuran (THF) was dried over sodium benzophenone ketyl and distilled under nitrogen. **2a–e**, benzyl mercaptan, and tri-*n*-butylphosphine were purified by distillation under reduced pressure.

Infrared (IR) spectra were obtained with a JASCO FT/IR 5300 infrared spectrometer. ^1H and ^{13}C NMR spectra were

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recorded on JNM-PMX60SI, EX90, or 400 spectrometers in $CDCl_3$ (tetramethylsilane as an internal standard). Gel permeation chromatographic analyses (GPC) were performed on a Tosoh HLC 8020 (TSK gel G5000HXL, G4000HXL, G3000-HXL, and G2500HXL, THF as eluent). Gas chromatographic analyses (GC) were conducted on a Shimazu GS chromatograph 4C PF equipped with a FID detector and silica gel SE30 column (1 m) using tetradecane as an internal standard. Gradient temperature (from 100 to 230 °C, 10 °C/min) was used at a constant flow rate of 0.1 kg/cm^2 (N_2 as carrier gas). X-ray analysis of **6** was made on a Rigaku AFC5R diffractometer with graphite monochromated Mo Kα radiation and 12 kW rotating anode generator. Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using the setting angles of 0 carefully centered reflections in the range $20.00 < 2\theta < 30.00°$ corresponded to a primitive cell with dimensions: $a = 9.655$ Å, $b = 12.388$ Å, $c = 5.899$ Å, $V = 685$ Å^3, $\alpha = 100.67$ °, $\beta = 98.55$ °, $\gamma = 87.43$ °. For $Z = 2$ and FW = 270.35, the calculated density is 1.31 g/cm^3. On the basis of a statistical analysis of intensity distribution and the successful solution and refinement of the structure, the space group was determined to be $P\bar{1}$ (No. 2). The data were collected at 23 °C using the ω scan technique to a maximum 2θ value of 50.0°, and the data were corrected for Lorentz–polarization effects. The structure was solved by direct methods. All of the atoms with the exception of hydrogen were refined anisotropically. The final cycle of full-matrix least-squares refinement was based on 2159 observed reflections ($I > 3.00\sigma(I)$) and 172 variable parameters. The calculation was performed using the teXsan crystallographic software package of Molecular Structure Corp.

Synthesis of Monomers and Model Compounds. *2,2-Dimethylpropylene-1,3-bis(2-heptynoate) (1B).* 1B was prepared from 2-heptynoic acid in two steps: 2-Heptynoic acid was obtained by modification of the method described in the literature.[9] To a solution of 1-heptyne (15.9 g, 0.194 mol) in THF (120 mL) at −50 °C was added *n*-butyllithium (1.70 M in hexane, 114 mL, 0.194 mol) under nitrogen. After 30 min, the temperature of the mixture was allowed to rise to −10 to 0 °C and carbon dioxide was introduced with vigorous stirring, which was kept between 0 and −10 °C by cooling with an ice–salt bath. The introduction was continued until the exothermic reaction ceased. The resulting solution was poured carefully into ice water. The aqueous layer was separated and the organic layer was extracted twice with a 25 mL portion of water. The aqueous extracts were combined with the first aqueous layer and was added concentrated hydrochloric acid to adjust pH to 1. The resulting mixture was extracted with a 25 mL portion of ether four times, and the combined extract was dried over magnesium sulfate. After the evaporation of the solvent, the residue was purified by distillation ($bp_{0.2}$ 96–97 °C) to give 20.8 g (0.165 mol, 83.2%) of 2-heptynoic acid. IR (neat) 3200, 2963, 2938, 2876, 2238, 1690, 1279 cm^{-1}; ^{1}H NMR (60 MHz, δ, ppm) 0.95 (br t, $J = 6$ Hz, 3 H, CH_3-), 0.2–2.0 (m, 4 H, $-CH_2-$), 2.35 (br t, $J = 6$ Hz, 2 H, $-CH_2C\equiv$), 9.90 (s, 1 H, $-CO_2H$).

To a solution of heptynoic acid (20.0 g, 159 mmol) in benzene (120 mL) were added neopentyl glycol (7.52 g, 72.3 mmol) and *p*-toluenesulfonic acid monohydrate (0.50 g, 2.63 mmol). The mixture was refluxed by using a Dean–Stark apparatus until the evolution of water ceased. The reaction mixture was poured into saturated aqueous sodium bicarbonate. The organic layer was collected, and the remaining materials were extracted with ethyl acetate three times. The combined extract was dried over magnesium sulfate. After the evaporation of the solvents, the residue was purified by column chromatography on silica gel (hexane/ethyl acetate = 20/1) to give 21.3 g (66.6 mmol, 92.2%) of **1B**. $R_f = 0.63$ on TLC (SiO_2, hexane/ethyl acetate = 4/1); IR (neat) 2961, 2874, 2238, 1713, 1246 cm^{-1}; ^{1}H NMR (90 MHz, δ, ppm) 0.93 (br t, $J = 7.47$ Hz, 3 H, CH_3CH_2-), 1.00 (s, 6 H, $-C(CH_3)_2-$), 0.2–1.9 (m, 8 H, $-CH_2-$), 2.34 (br t, $J = 6.57$ Hz, 4 H, $-CH_2C\equiv$), 3.98 (s, 4 H, $-CO_2CH_2-$); ^{13}C NMR (22.5 MHz, δ, ppm) 13.4, 18.4, 21.6, 21.9, 29.5, 34.7, 70.1, 72.9, 90.0, 153.8.

Similarly, 2,2-dimethylpropylene-1,3-bis(phenylpropiolate) (**1C**) was obtained in 77.3% yield (two steps): $R_f = 0.53$ on TLC (SiO_2, hexane/ethyl acetate = 4/1); mp 75–77 °C [recrystallized from hexane/ethyl acetate (5/1)]; IR (KBr) 3063, 2976, 2222, 1709, 1491, 1373, 1283 cm^{-1}; ^{1}H NMR (90 MHz, δ, ppm) 1.08 (s, 6 H, $-C(CH_3)_2-$), 4.12 (s, 4 H, $-CO_2CH_2-$), 7.1–7.8 (m, 10 H, C_6H_5-); ^{13}C NMR (100 MHz, δ, ppm) 21.7, 34.8, 70.4, 80.4, 86.7, 119.5, 128.5, 130.6, 133,0, 154.0.

Model Compound (6). **6** was obtained in three steps as follows: Methyl phenylpropiolate (**4**) was prepared by modification of the method reported previously[9]. To a solution of phenylacetylene (6.53 g, 64.0 mmol) in THF (50 mL) was added *n*-butyllithium (1.68 M in hexane, 38 mL, 64.0 mmol) at −30 °C. The reaction mixture was added slowly to a THF (20 mL) solution of methyl chloroformate (7.86 g, 83.2 mmol). During the addition, the temperature was kept between −20 and −35 °C. After stirring was continued for 30 min at that temperature, the cooling bath was removed and the temperature was allowed to rise to room temperature. The reaction mixture was then poured into a saturated aqueous solution of ammonium chloride with vigorous stirring. After the separation of the organic layer, the remaining aqueous layer was extracted three times with ether. The combined extract was dried over magnesium sulfate and was concentrated in vacuo. The residue was purified by column chromatography on silica gel (hexane/ethyl acetate = 30/1) to give 9.16 g (57.3 mmol, 89.5%) of **4**. $R_f = 0.56$ on TLC (hexane/ethyl acetate = 4/1); IR (neat) 2955, 2226, 1715, 1491, 1435, 1290 cm^{-1}; ^{1}H NMR (90 MHz, δ, ppm) 3.81 (s, 3 H, $-CO_2CH_3$), 7.10–7.80 (m, 5 H, C_6H_5-).

To a THF (1.3 mL) solution of **4** (200 mg, 1.25 mmol) and benzyl mercaptan (155 mg, 1.25 mmol) was added tri-*n*-butylphosphine (25 mg, 0.124 mmol) at room temperature. After stirring for 3 h, the reaction mixture was concentrated in vacuo. The residue was purified by column chromatography on silica gel (hexane/ethyl acetate = 50/1) to give 349 mg (1.23 mmol, 98.3%) of methyl 3-(benzylmercapto)cinnamate (**5**). $R_f = 0.49$ on TLC (hexane/ethyl acetate = 4/1); IR (neat) 3061, 3029, 2949, 1715, 1591, 1493, 1447, 1433, 1238 cm^{-1}; ^{1}H NMR (90 MHz, δ, ppm) 3.85 (s, 3 H, $-CO_2CH_3$), 4.01 (s, 2 H, $PhCH_2S-$), 7.19 (s, 5 H, $C_6H_5CH_2-$), 7.1–7.8 (m, 5 H, C_6H_5-$CH=$), 7.87 (s, 1 H, $PhCH=C(CO_2Me)S-$); ^{13}C NMR (100 MHz, δ, ppm) 38.6, 52.7, 126.2, 127.2, 128.1, 128.4, 129.0, 129.5, 130.8, 134.6, 137.3, 144.8, 166.7.

To a solution of **5** (210 mg, 0.739 mmol) in THF (1.2 mL) and water (0.6 mL) was added lithium hydroxide monohydrate (155 mg, 3.70 mmol), and the reaction mixture was stirred for 2 days at room temperature, to which aqueous 10% hydrochloric acid was added (~pH = 4). The mixture was extracted with ether three times, and the combined extract was dried over magnesium sulfate. The mixture was concentrated in vacuo to give 175 mg (0.648 mmol, 87.5%) of 3-(benzylmercapto)cinnamic acid (**6**) as white crystals: mp 122.0–123.5 °C [recrystallized from hexane/ethyl acetate (10/1)]; IR (KBr) 3063, 3026, 2946, 2804, 2611, 1674, 1587, 1446, 1263 cm^{-1}; ^{1}H NMR (400 MHz, δ, ppm) 4.08 (br s, 2 H, $PhCH_2S-$), 7.18 (s, 5 H, $C_6H_5CH_2S-$), 7.35 (s, 3 H, $C_6H_5CH=$), 7.72 (s, 2 H, $C_6H_5CH=$), 8.10 (s, 1 H, $C_6H_5CH=$), 10.90 (br, 1 H, $-CO_2H$); ^{13}C NMR (100 MHz, δ, ppm) 38.6, 124.9, 127.2, 128.2, 128.4, 128.8, 130.0, 130.8, 171.7.

Benzyl Propiolate. Benzyl propiolate was prepared from propiolic acid and benzyl alcohol using Dean–Stark apparatus, similarly to the case of **5B** and was purified by distillation ($bp_{3.5}$ 93–95 °C): yield 85.0%; IR (neat) 3277, 2122, 1717, 1223 cm^{-1}; ^{1}H NMR (90 MHz, δ, ppm) 2.87 (s, 1 H, $HC\equiv$), 5.21 (s, 2 H, $BnCH_2-$), 7.36 (s, 5 H, C_6H_5-); ^{13}C NMR (100 MHz, δ, ppm) 67.9, 74.5, 75.0, 128.5, 128.6, 134.5, 152.5.

Methyl 2-Nonynoate. Methyl 2-nonynoate was obtained from 1-octyne by modification of the method described in the literature[9] similarly to the case of methyl phenylpropiolate and was purified by distillation ($bp_{0.2}$ 47–52 °C): yield 72.3%; IR (neat) 2953, 2934, 2861, 2238, 1719, 1256 cm^{-1}; ^{1}H NMR (400 MHz, δ, ppm) 0.89 (t, $J = 7.60$ Hz, 3 H, CH_3CH_2-), 1.2–1.4 (6 H, $-CH_2-$), 1.58 (m, $J = 7.20$ Hz, 2 H, $-CH_2CH_2CH_2C\equiv$), 1.58 (m, $J = 7.20$ Hz, 2 H, $-CH_2CH_2C\equiv$), 2.33 (t, $J = 7.20$ Hz, 2 H, $-CH_2C\equiv$), 3.76 (s, 3H, $-CO_2CH_3$) ^{13}C NMR (100 MHz, δ, ppm) 14.0, 18.6, 22.4, 27.5, 28.5, 31.2, 52.5, 72.8, 89.9, 154.3.

Polyadditions. *Typical Procedure.* A polyaddition of 2,2-dimethylpropylene-1,3-bis(2-heptynoate) (**1B**) with *p*-xylene-α,α′-dithiol (**2a**) was carried out as follows: To a THF (1.3 mL) solution of **1B** (200 mg, 0.625 mmol) and **2a** (106 mg, 0.625 mmol) was added tri-*n*-butylphosphine (29 mg, 0.124 mmol) at ambient temperature. After stirring for 4 h, the reaction mixture was diluted with THF (3.7 mL) and was poured into hexane (100 mL). The precipitate was filtered and was dried under vacuum. **3Ba**: 285 mg (93%); IR (neat) 2959, 2932, 2872, 1589, 1167 cm^{-1}; ^1H NMR (90 MHz, δ, ppm) 0.91 (br t, $J = 5.94$ Hz, 6 H, $C\mathit{H}_3CH_2-$), 0.99 (s, 6 H, $-CH_2C(C\mathit{H}_3)_2-$), 1.10−2.00 (8 H, $CH_3C\mathit{H}_2C\mathit{H}_2-$), 2.45 (br t, $J = 8.01$ Hz, *E*-$C\mathit{H}_2$-CH=), 2.80 (br t, $J = 8.01$ Hz, *Z*-$C\mathit{H}_2$CH=), 3.93 (s, 4 H, $-OC\mathit{H}_2CMe_2-$), 3.98 (s, *E*-$C\mathit{H}_2$S(Bu)C=), 4.04 (s, *Z*-$C\mathit{H}_2$S-(Bu)C=), 5.55 (s, *E*-C=$C\mathit{H}CO_2-$), 5.79 (s, *Z*-C=$C\mathit{H}CO_2-$), 7.32 (s, 4 H, $-C_6\mathit{H}_4-$); ^{13}C NMR (100 MHz, δ, ppm) 13.8, 21.8, 22.2, 22.6, 29.7, 31.6, 32.0, 33.8, 34.6, 34.7, 34.8, 36.2, 36.4, 68.7, 108.0, 111.6, 129.2, 129.3, 129,4, 133.9, 134.3, 135.7, 136.1, 162.0, 164.4, 164.6, 166.1. From the ^1H NMR spectrum, the *E*:*Z* ratio in **3Ba** was determined to be 70:30.

Similarly, other polymers (**3**) were prepared as follows:

3Ab (from **1A** and **2b**): yield 100%; IR (neat) 3051, 3018, 2967, 2888, 1701, 1578, 1578, 1478 1159 cm^{-1}; ^1H NMR (90 MHz, δ, ppm) 0.97−1.05 (m, $-CH_2C(C\mathit{H}_3)_2-$) 3.99−4.07 (m, 4 H, $-OC\mathit{H}_2CMe_2-$), 5.74 (d, $J = 15.3$ Hz, *E*-=$C\mathit{H}S-$), 5.97 (d, $J = 10.2$ Hz, *Z*-=$C\mathit{H}S-$), 7.24 (d, $J = 10.2$ Hz, *Z*-=$C\mathit{H}CO_2-$), 7.48 (s, $-C_6\mathit{H}_4-$), 7.76 (d, $J = 15.2$ Hz, *E*-=$C\mathit{H}CO_2-$), *E*:*Z* = 21:79; ^{13}C NMR (100 MHz, δ, ppm) 21.9, 34.8, 53.4, 69.3, 69.3, 113.9, 114.1, 116.0, 130.8, 131.5, 131.7, 133.1, 133.3, 136.4, 137.5, 145.6, 146.1, 148.2, 148.6, 164.9, 166.3.

3Bb (from **1B** and **2b**): yield 94%; IR (neat) 2959, 2934, 2872, 1703, 1586, 1471, 1169 cm^{-1}; ^1H NMR (90 MHz, δ, ppm) 0.50−1.90 (20 H, $C\mathit{H}_3CH_2-$, $-CH_2C(C\mathit{H}_3)_2-$, $CH_3C\mathit{H}_2C\mathit{H}_2-$) 2.14 (br t, $J = 8.01$ Hz, *Z*-$C\mathit{H}_2$C=), 2.83 (br t, $J = 7.74$ Hz, *E*-$C\mathit{H}_2$C=), 3.99−4.03 (m, 4 H, $-OC\mathit{H}_2CMe_2-$), 5.36 (s, *E*-=$C\mathit{H}S-$), 5.92 (s, *Z*-=$C\mathit{H}S-$), 7.53 (s, $-C_6\mathit{H}_4-$), *E*:*Z* = 25:75; ^{13}C NMR (100 MHz, δ, ppm) 13.6, 13.8, 21.9, 22.6, 31.2, 31.8, 33.0, 34.6, 36.4, 68.7, 69.0, 111.3, 112.3, 112.4, 112.6, 131.5, 131.9, 132.6, 133.1, 135.5, 136.0, 136.6, 160.7, 164.3, 164.7, 165.9, 166.0.

3Bc (from **1B** and **2c**) yield 62%; IR (neat) 2959, 2932, 2872, 1709, 1591, 1466, 1167 cm^{-1}; ^1H NMR (90 MHz, δ, ppm) 0.92 (br, 6 H, $C\mathit{H}_3CH_2-$), 0.99 (s, 6 H, $-CH_2C(C\mathit{H}_3)_2-$), 1.10−2.00 (8 H, $CH_3C\mathit{H}_2C\mathit{H}_2-$) 2.20−3.20 (8 H, $-C\mathit{H}_2C=$, $-SC\mathit{H}_2-$), 3.93 (s, 4 H, $-OC\mathit{H}_2CMe_2-$), 5.45 (s, *E*-=$C\mathit{H}S-$), 5.82 (s, *Z*-=$C\mathit{H}S-$), *E*:*Z* = 72:28; ^{13}C NMR (100 MHz, δ, ppm) 13.8, 21.8, 22.2, 22.6, 25.4, 27.1, 28.9, 30.1, 31.7, 32.1, 34.0, 34.7, 36.1, 68.7, 107.9, 112.0, 164.1, 164.6, 166.2.

5Bd (from **3B** and **4d**) yield 58%; IR (neat) 2957, 2932, 2861, 1711, 1591, 1462, 1165 cm^{-1}; ^1H NMR (90 MHz, δ, ppm) 0.92 (br, 6 H, $C\mathit{H}_3CH_2-$), 0.99 (s, 6 H, $-CH_2C(C\mathit{H}_3)_2-$), 1.10−2.00 (16 H, $CH_3C\mathit{H}_2C\mathit{H}_2-$, $-SCH_2(C\mathit{H}_2)_4-$) 2.20−3.20 (8 H, $-C\mathit{H}_2C=$, $-SC\mathit{H}_2-$), 3.93 (s, 4 H, $-OC\mathit{H}_2CMe_2-$), 5.42 (s, *E*-=$C\mathit{H}S-$), 5.79 (s, *Z*-=$C\mathit{H}S-$), *E*:*Z* = 89:11; ^{13}C NMR (100 MHz, δ, ppm) 13.8, 21.9, 22.7, 27.2, 28.5, 31.3, 32.2, 34.1, 34.7, 68.6, 107.4, 164.7, 165.1.

3Be (from **1B** and **2e**): yield 49%; IR (neat) 2959, 2932, 2872, 1709, 1591, 1466, 1167 cm^{-1}; ^1H NMR (90 MHz, δ, ppm) 0.89 (br, 6 H, $C\mathit{H}_3CH_2-$), 0.97 (s, 6 H, $-CH_2C(C\mathit{H}_3)_2-$), 1.10−2.00 (8 H, $CH_3C\mathit{H}_2C\mathit{H}_2-$) 2.20−3.20 (8 H, $-C\mathit{H}_2C=$, $-SC\mathit{H}_2-$), 3.68 (m, 4 H, $-OC\mathit{H}_2CH_2S-$), 3.91 (s, 4 H, $-OC\mathit{H}_2CMe_2-$), 5.46 (s, *E*-=$C\mathit{H}S-$), 5.81 (s, *Z*-=$C\mathit{H}S-$), *E*:*Z* = 75:25; ^{13}C NMR (100 MHz, δ, ppm) 13.8, 21.9, 22.2, 22.6, 24.3, 29.6, 31.2, 31.6, 32.1, 34.1, 34.7, 36.1, 68.0, 68.2, 68.7, 70.0, 70.1, 107.6, 112.2, 161.2, 164.1, 164.5, 166.1.

3Ca (from **1C** and **2a**): yield 95%; IR (neat) 3057, 2963, 2876, 1703, 1574, 1475, 1161 cm^{-1}; ^1H NMR (90 MHz, δ, ppm) 0.8−1.5 (m, 6 H, $-CH_2C(C\mathit{H}_3)_2-$), 3.91 (br s, 4 H, $-OC\mathit{H}_2$-CMe_2-), 4.15 (br s, 4 H, $-C_6H_4C\mathit{H}_2S-$), 5.88 (m, $-C\mathit{H}$=C-(Ph)S−), 7.01 (s, 4 H, $-C_6\mathit{H}_4-$), 6.7−7.8 (m, 10 H, C_6H_5-), 7.84 (s, PhC*H*=C(S−)CO_2-), ^{13}C NMR (22.5 MHz, δ, ppm) 22.0, 35.2, 38.0, 70.5, 126.2, 128.0, 128.3, 128.9, 129.4, 130.6, 134.3, 136.1, 144.7, 165.8. From the ^1H NMR spectrum, the structure of **3Ca** was constituted of 9% of conjugate addition units (β-mercaptoenoate) and the 91% of the regioisomeric unit (α-mercaptoenoate).

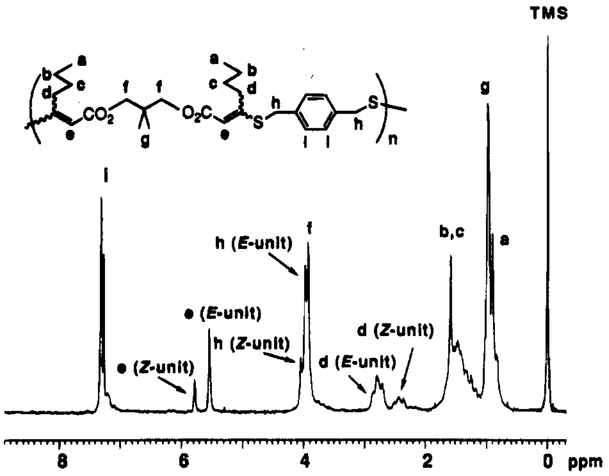
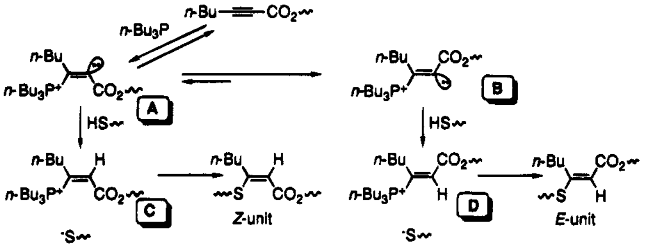


Figure 1. ^1H NMR spectrum of **3Ba**.

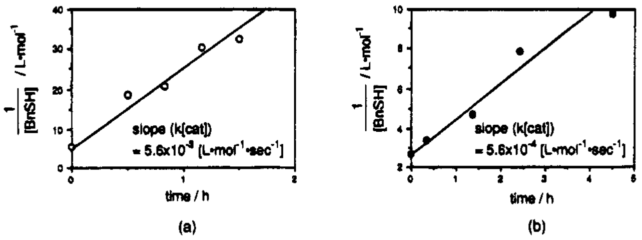
Scheme 3



Results and Discussion

A polyaddition of **1B** and **2a** was carried out at room temperature in THF (0.5 M) for 4 h in the presence of tri-*n*-butylphosphine (20 mol %) to obtain a polymer (**3Ba**) having β-alkylmercaptoenoate moieties in the main chain in almost quantitative yield.[10] The number average molecular weight (M_n) and the molecular distribution (M_w/M_n) of **3Ba** were estimated as 25 200 and 2.16, respectively (GPC, PSt).

The structure of the obtained polymer (**3**) was confirmed by ^1H and ^{13}C NMR and IR analyses. From the ^1H NMR spectrum (Figure 1), signals of olefinic protons in the main chain of the polymer were observed at 5.55 and 5.79 ppm (*E* and *Z* units, respectively, *E*/*Z* = 70/30).[11] The double bond was detected quantitatively from the integrated ratio between these peaks and other protons, indicating that side reactions such as a second attack toward the produced double bonds are negligible. The geometric selectivity in the present system (*E*/*Z* = 70/30) was rather lower in comparison with the previously reported results in case of diols as monomers (*E*/*Z* = 100/0).[3] The lower selectivity might be explained by the difference in acidity between dithiols and diols. As shown in Scheme 3, the present reaction may proceed by initial attack of phosphine catalyst toward acetylenes. The produced zwitterionic intermediate (**A**) may isomerize to the thermodynamically much more stable *E* form (**B**) by the equilibration. In the case of diol monomers, the slow protonation may enhance this equilibration. On the other hand, thiol groups have higher acidity than the hydroxyl groups, thus the rate of protonation by the thiol group is faster than that by alcohols. Therefore, the *Z* unit might be obtained through the protonation of zwitterionic intermediate (**A**) before the completion of the equilibration between **A** and **B**.[12] As a result, *Z* units would also be produced in the



(a) (b)

Figure 2. Plot between 1/[BnSH] and time for the reaction of benzyl propiolate with benzyl mercaptan (a) and for the reaction of benzyl nonynoate with benzyl mercaptane (b).

polyaddition of **1B** with **2b** having higher acidity (vide infra).

Rate of Polyaddition. The rate of the present polyaddition was estimated by the model reaction of benzyl mercaptane with methyl 2-nonynoate or methyl propiolate. Regardless of the position of the rate determining step, the exact kinetic expression should become too complicated to solve on the basis of the proposed mechanism. However, the kinetics of the reaction was found to be best fitted by proposing an eq 1, similar to the addition reaction of alcohols.[13] Because

$$-\mathrm{d}[\mathrm{BnSH}]/\mathrm{d}t = k[\mathrm{propiolates}][\mathrm{BnSH}][n\text{-}\mathrm{Bu}_3\mathrm{P}] \quad (1)$$

$$-\mathrm{d}[\mathrm{BnSH}]/\mathrm{d}t = k[n\text{-}\mathrm{Bu}_3\mathrm{P}][\mathrm{BnSH}]^2 \quad (2)$$

$$1/[\mathrm{BnSH}] = k[n\text{-}\mathrm{Bu}_3\mathrm{P}]t + 1/[\mathrm{BnSH}]_0 \quad (3)$$

the desired adduct was obtained almost quantitatively and there were no undesirable side reactions, we may assume equivalent concentration throughout the reaction (i.e., [propiolates] = [BnSH]). Thus, eq 1 can be reduced to eqs 2 and 3. When the reaction of benzyl mercaptan with stoichiometric benzyl propiolate in THF (0.182 M) was carried out at 20 °C in the presence of tri-*n*-butylphosphine (2.77×10^{-3} M), a linear relationship between time and 1/[BnSH] was obtained (Figure 2). From the slope of this plot, the kinetic coefficient was estimated as 2.0 [$\mathrm{L}^2\ \mathrm{mol}^{-2}\ \mathrm{s}^{-1}$]. Similarly, the kinetic coefficient for the reaction of methyl 2-nonynoate with benzyl mercaptane was estimated as 1.6×10^{-2} [$\mathrm{L}^2\ \mathrm{mol}^{-2}\ \mathrm{s}^{-1}$] on the basis of the result shown in Figure 2. Thus, the introduction of alkyl group at the β-position in propiolate moieties was found to decrease the rate of the reaction by 1.2×10^2 times. In the case of the addition reaction with benzyl alcohol toward benzyl propiolate and methyl 2-heptynoate, the kinetic coefficients were estimated as 0.91 and 1.1×10^{-2} [$\mathrm{L}^2\ \mathrm{mol}^{-2}\ \mathrm{s}^{-1}$], respectively.[13] Therefore, the addition of thiols may proceed faster than that of alcohols in accordance with the increase of the acidity as well as nucleophilicity.

The polyaddition of **1B** with **2a** was carried out in THF (0.5 M) by using tri-*n*-butylphosphine (20 mol %) and the consumption of monomers (i.e., **1B** and **2a**) and the molecular weight of the resulting polymer were monitored by GPC after the designated reaction time (Figure 3). Both monomers were consumed completely within 30 min, and the molecular weight of the polymer gradually increased throughout the reaction for 4 h.

Effect of the Concentration of the Catalyst. The polyaddition of **1B** with **2a** was examined at ambient temperature in THF by varying the concentration of the catalyst ranging from 1 to 20 mol % (Table 1). When 1 mol % of the catalyst was used, oligomers were obtained (run 1) as a soluble part in hexane. This might be due to some side reactions[14] that deactivated the phosphine catalyst, as already suggested in the case of the polyaddition with diol monomers.[3] On the other hand, the polyaddition using the catalyst ranging from 5 to 20 mol % proceeded smoothly, and polymers having higher molecular weights were obtained in good to excellent yields (runs 2–4). These results show that the higher concentration of the catalyst is suitable for obtaining the polymer with a higher molecular weight in a higher yield.[15]

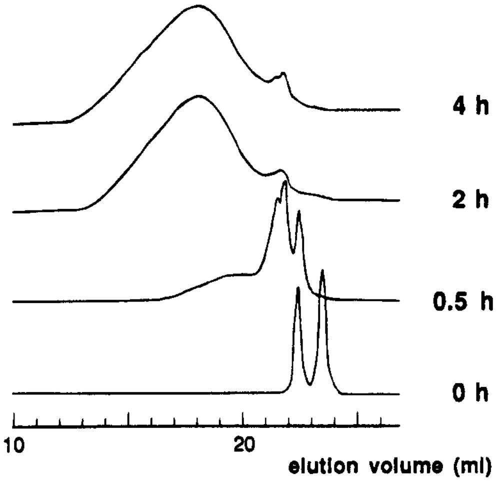


Figure 3. GPC traces for the polymerization of **1B** with **2a** after designated reaction time.

Table 1. Effect of Catalyst Concentration[a]

run	n-Bu$_3$P (mol %)	yield[b]/%	M_n (M_w/M_n)[c]
1	1	0	
2	5	75	12 200 (1.30)
3	10	80	14 800 (1.53)
4	20	93	25 200 (2.16)

[a] Polyaddition was carried out at room temperature in THF (0.5 M) for 4 h using n-Bu$_3$P as a catalyst under nitrogen. [b] Isolated yield after precipitation with hexane. [c] Estimated by GPC (PSt, THF as an eluent).

Table 2. Effect of Monomer Concentration[a]

run	concn (M)	yield[b]/%	M_n (M_w/M_n)[c]
1	0.1	7	6 000 (1.42)
2	0.2	74	11 600 (1.25)
3	0.3	87	22 900 (1.90)
4	0.5	93	25 200 (2.16)

[a] Polyaddition was carried out at room temperature in THF for 4 h using n-Bu$_3$P (20 mol %) as a catalyst under nitrogen. [b] Isolated yield after precipitation with hexane. [c] Estimated by GPC (PSt, THF as an eluent).

Effect of Monomer Concentration. The polyaddition of **1B** with **2a** was performed under various concentrations of two monomers keeping the stoichiometric conditions (Table 2). As expected, the molecular weights and yields of the obtained polymers increased by increasing the concentrations of the two monomers.[15]

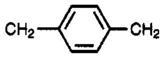
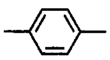
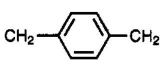
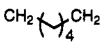
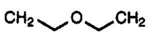
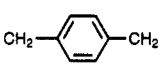
The polyaddition of **1B** with **2a** was also carried out under the varied feed ratios of two monomers (Table 3). The stoichiometric conditions were suitable for obtaining a polymer with higher molecular weight (run 4). In the presence of an excess amount of either **1B** or **2a**, it might be expected to produce a polymer having propiolate or thiol moieties as end group, respectively. In these cases, gelations might take place either by the phosphine-initiated anionic polymerization of the end-propiolate moieties or the second attack of the thiol group toward double bonds in the main chain. However,

Table 3. Effect of Monomer Feed Ratio[a]

run	feed ratio **1B**:**2a**	yield[b]/%	M_n (M_w/M_n)[c]
1	1.0:1.5	34	7 500 (1.27)
2	1.0:1.2	68	8 900 (1.23)
3	1.0:1.1	90	15 200 (1.67)
4	1.0:1.0	93	25 200 (2.16)
5	1.1:1.0	93	15 600 (1.55)
6	1.2:1.0	86	7 700 (1.31)
7	1.5:1.0	33	7 200 (1.21)

[a] The polymerization was carried out at room temperature in THF (0.5 M) for 4 h with n-Bu$_3$P (20 mol %) under nitrogen. [b] Isolated yield after precipitation with hexane. [c] Estimated by GPC (PSt, THF as an eluent).

Table 4. Polyaddition of Dipropiolates with Dithiols[a]

run	R in **1**	R′ in **2**	yield[b]/ %	M_n (M_w/M_n)[c]	$E/Z/$ other[d]
1	H (**1A**)		*e*		
2[f]	H (**1A**)		100	20 700 (2.12)[g]	21/79/0
3	n-C$_4$H$_9$ (**1B**)		93	25 200 (2.16)	70/30/0
4[h]	n-C$_4$H$_9$ (**1B**)		75	11 300 (1.26)	
5	n-C$_4$H$_9$ (**1B**)		94	11 600 (1.57)	25/75/0
6[i]	n-C$_4$H$_9$ (**1B**)		100	13 700 (1.65)	
7	n-C$_4$H$_9$ (**1B**)		62	9 900 (1.22)	72/28/0
8	n-C$_4$H$_9$ (**1B**)		58	20 100 (1.31)	89/11/0
9	n-C$_4$H$_9$ (**1B**)		49	10 600 (1.26)	75/25/0
10	Ph (**1C**)		95[j]	5 300 (1.19)	9/0/91

[a] Polyaddition was carried out at room temperature in THF (0.5 M) for 4 h using n-Bu$_3$P (20 mol %) as a catalyst under nitrogen. [b] Isolated yield after precipitation with hexane. [c] Estimated by GPC (PSt, THF as an eluent). [d] Determined by ^{1}H NMR. [e] Gel was obtained. [f] Polyaddition was carried out at room temperature in THF (0.3 M) for 4 h using n-Bu$_3$P (5 mol %) as a catalyst under nitrogen. [g] Estimated by GPC (PSt, CHCl$_3$ as an eluent). [h] In the presence of water (20 mol %). [i] In the presence of water (30 mol %).

soluble polymers were obtained in all the examined feed ratios of two monomers in the polyaddition of **1B** with **2a**.[16] The molecular weights and yields of the obtained polymers decreased by slipping off the stoichiometry of two monomers as is usual for polyaddition reactions. These results can be taken to mean that such side reactions were negligible in the present system. When the reaction of methyl 2-heptynoate with 2 equiv of benzyl mercaptane was carried out under similar conditions, a monoadduct was obtained in high yield. Furthermore, **1B** did not undertake any side reactions in the presence of tri-n-butylphosphine.

Polyaddition of Various Monomers. Polyadditions were carried out by using various acetylene monomers (**1A**–**C**) and dithiols (**2a**–**e**, Table 4). In the case of bifunctional terminal propiolate (**1A**) and **2a**, a cross-linked polymer was obtained under similar reaction conditions (run 1). The gelation might be due to a second addition of thiol moieties toward the produced double bonds, as shown in Scheme 4. In fact, methyl β,β-bis(benzylmercapto)propiolate was obtained when the model reaction of methyl propiolate with benzyl mercaptan (2 equiv) was examined in the presence of tri-n-butylphosphine in high yield.[17] In the case of the polyaddition of **1A** with a dithiol monomer with lower nucleophilicity and higher acidity such as **2b**, a soluble polymer (**3Ab**) with the expected structure was obtained quantitatively (run 2).

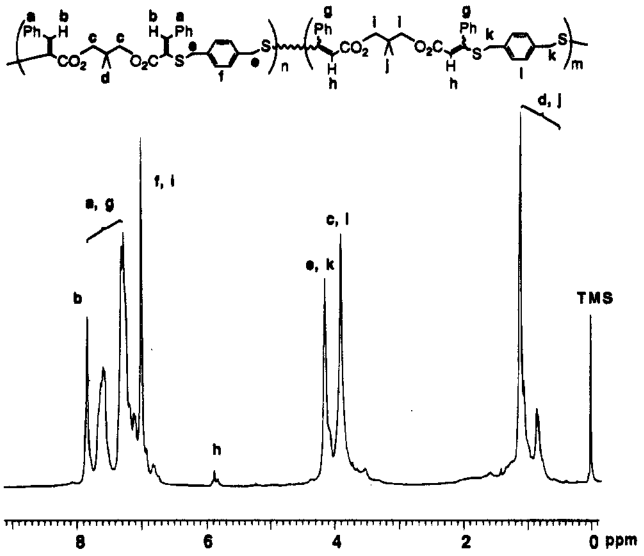
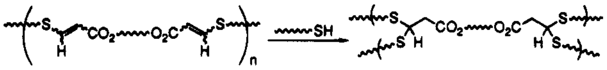
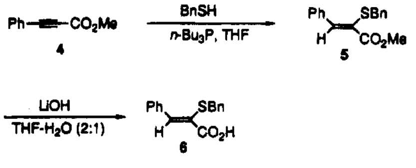


Figure 4. ^{1}H NMR spectrum of **3Ca**.

Scheme 4



Scheme 5



The side reaction caused by the second attack of thiol group could also be inhibited by the introduction of alkyl groups at the β-position of propiolate. Regardless to the dithiol monomers, the polyaddition of **1B** having internal acetylene moieties gave the corresponding polymers (**3Ba**–**3Be**) without any side reactions in good to excellent yields (runs 3–9). Although polyadditions of **1B** with **2a**, **2c**, **2d**, or **2e** gave polymers containing mainly E units, a polymer containing predominantly Z units was obtained in the case of **2b** (runs 3 and 5 vs 7–9). The geometrical selectivity may be explained by the difference of acidity of dithiols, as mentioned above.

In the case of the polyaddition of **1A** with diols, the reaction was interrupted by the addition of water. Interestingly, water did not have any influence on the polyaddition of **1B** with **2b**, while the polyaddition of **1B** with **2a** was effected by water (runs 3 vs 4 and 5 vs 6). The acidity of aromatic thiols are known to be considerably higher (p$K_a \approx 8$) compared with that of water (p$K_a \approx 16$), while benzyl mercaptan has lower acidity (p$K_a \approx 11$) compared with aromatic one. Thus, the protonation of zwitterionic intermediates might not be interfered by water in the case of **2b**. The decrease of the molecular weight in the presence of water in the polyaddition of **1B** with **2a** might be due to the competitive nucleophilic attack of the phosphonium intermediate between thiolate and hydroxide.

When the polyaddition of **1C** with **2a** was carried out, a soluble polymer (M_n = 5300, M_w/M_n = 1.19) was obtained in almost quantitative yield by precipitation with hexane. The structure of the obtained polymer was, however, different from that expected. In the ^{1}H

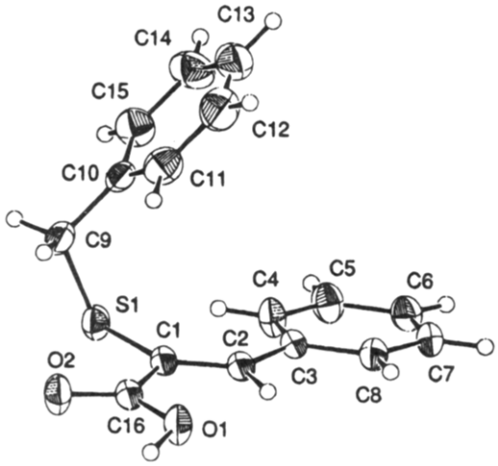
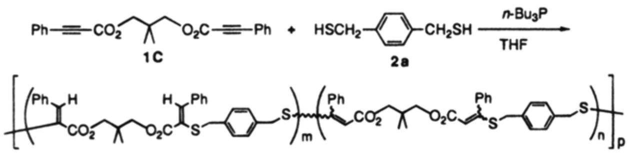


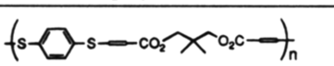
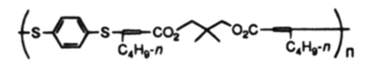
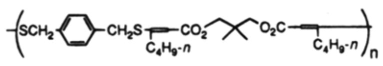
Figure 5. ORTEP view of **6**.

Scheme 6



3Ca

Table 5. Refractive Indexes of the Obtained Polymers

polymers	$M_n(M_w/M_n)^a$	$n_D^{20\,b}$
 (3Ab)	20 700 (2.12)	1.66
 (3Ba)	13 800 (1.65)	1.67
 (3Bb)	26 400 (2.60)	1.67

^{a} Estimated by GPC (PSt, THF as an eluent). ^{b} Determined by Abbe refractometer.

NMR spectrum, olefinic protons in the main chain were mainly observed at 7.8 ppm accompanied by a small peak at 5.9 ppm (Figure 4).

To identify its structure, a model reaction of methyl phenylpropiolate (**4**) and benzyl mercaptan was carried out at room temperature in THF (1 M) for 3 h with tri-*n*-butylphosphine (10 mol %) under nitrogen (Scheme 5). As a result, a main product (**5**) was obtained that showed its olefinic protons at 7.87 ppm. **5** was hydrolyzed to obtain the corresponding carboxylic acid (**6**) as white crystals, which could be assigned as (*Z*)-2-benzylmercaptocinnamic acid from the X-ray analysis (Figure 5).

On the basis of these results, the polymer (**3Ca**) was found to contain 91% of the regioisomeric unit (Scheme 6). It has been reported that aryl mercaptans react with methyl phenylpropiolate at α-positions in the case of a radical chain reaction.[18] When the model reaction was carried out in the presence of water, the formation of the conjugate addition product was inhibited, while that of the regioisomer was not effected at all. These results strongly suggest the presence of a radical path for the production of the α-mercapto units. That is, the polyaddition of **1C** with **2a** may mainly proceed by the radical chain mechanism. The reaction of methyl phenylpropiolate with mercaptans did not proceed in the absence of tri-*n*-butylphosphine, indicating that the catalyst is also concerned with the radical mechanism. In the case of propiolates without aromatic substituents, the reaction with mercaptans did not occur even in the presence of radical initiator (AIBN) to recover the starting materials.[10]

The obtained polymers (**3Ab**, **3Ba**, and **3Bb**) showed a good film forming character by casting from dichloromethane solution. Noteworthly, the films were found to have high refractive indexes (Table 5).

As the polymers obtained by the present polyaddition have novel β-alkylmercaptoenoate moieties in the main chain, unique reactivities and degradabilities may be expected that are currently investigated.

References and Notes

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(4) For example: Kobayashi, S.; Mukaiyama, T. *Chem. Lett.* **1974**, 705. Mori, K.; Mori, H. *Tetrahedron* **1987**, *43*, 4097. Huang, H.; Chen, B. *Synthesis* **1987**, 480. Hanessian, S.; Bedeschi, A.; Battistini, C.; Mogelli, N. *J. Am. Chem. Soc.* **1985**, *107*, 1438.
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(8) Inanaga, J.; Baba, Y.; Hanamoto, T. *Chem. Lett.* **1993**, 1113.
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(10) Although a polyaddition of **3B** with **4a** in the presence of a radical initiator (azobisisobutyronitrile, AIBN, 3.8 mol %) at 60 °C in THF (0.5 M) for 29 h in a sealed tube was carried out, no polymer was obtained and the monomers used were recovered quantitatively.
(11) Although it has been reported that only the *E* isomer can be obtained from the reaction of methyl propiolate with benzyl mercaptane in ref 8, the reaction of methyl propiolate or methyl 2-heptynoate with benzyl mercaptane gave products as a geometric mixture (*E*:*Z* = 50:50 or 60:40, respectively).
(12) The conjugate addition of amines to methyl propiolate has been reported to produce the adduct with fairly higher stereoselectivity. In the case of secondary amines, *E* isomers were produced as a major product. On the other hand, *Z* isomers were mainly obtained in the cases of primary amines. The distinct geometric change may be explained by the difference of the rate of isomerization from *Z* to *E* zwitterionic intermediates as a result of the internal hydrogen bonding. See, Huisgen, R.; Herbig, K.; Siegel, A.; Huber, H. *Chem. Ber.* **1966**, *99*, 2526.
(13) Kuroda, H.; Tomita, I.; Endo, T., unpublished results.
(14) The oxidation reaction of phosphine catalyst and/or hydrolysis of zwitterionic intermediate by water might be considerable for the deactivation of the catalyst as mentioned ref 3.
(15) It might be expected that the polyaddition under higher concentrations of the catalyst as well as monomers gave the polymer having higher molecular weight in higher yield. The polymer obtained under such conditions were, however, less soluble in organic solvents. The decrease of solubility might be due to the higher molecular weight of polymer.
(16) In the case the polyaddition of a terminal propiolate (**3A**), a gelation took place in the presence of an excess amount of either **3A** or dithiol monomers.
(17) The reaction of benzylmercaptane (2 equiv) with methyl propiolate was carried out at room temperature in THF (1 M) for 24 h by using tri-*n*-butylphosphine (20 mol %) under nitrogen. As a result, methyl 3,3-bis(benzylmercapto)propanoate and methyl 3-benzylmercaptopropenoate were obtained in 80 and 20% yields, respectively.
(18) Wadsworth, D. H.; Detty, M. R. *J. Org. Chem.* **1980**, *45*, 4611.

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