

# A novel phosphine-catalysed polyaddition of terminal acetylenes bearing electron-withdrawing groups with dithiols. Synthesis of polymers having dithioacetal moieties in the main chain

Hirofumi Kuroda, Ikuyoshi Tomita and Takeshi Endo\*

Research Laboratory of Resources Utilization, Tokyo Institute of Technology, Nagatsuta-cho 4259, Midori-ku, Yokohama 226, Japan  
 (Received 9 January 1997)

A novel polyaddition of terminal acetylenes bearing electron-withdrawing groups with dithiols, via a phosphine-catalysed double conjugate addition, is described. From the model reaction of methyl propiolate (1) with benzylmercaptan in the presence of tri-*n*-butylphosphine catalyst, the corresponding dithioacetal was obtained in high yield when the reaction was carried out under higher concentrations of the catalyst and the reactants. By using aliphatic dithiols having a rigid spacer [i.e. *p*-xylene- $\alpha,\alpha'$ -dithiol (5)], the polyaddition of 1 took place smoothly to yield a polymer (6) bearing dithioacetal moieties in the main chain in 84% yield, whose  $M_n$  and  $M_w/M_n$  were estimated to be 8100 and 1.29, respectively. Further, the polymer (8) having dithioacetal moieties was also obtained quantitatively by the polyaddition of an ynone (7) with 5.  
 © 1997 Elsevier Science Ltd

(Keywords: polyaddition; phosphine-catalyst; terminal acetylenes)

## INTRODUCTION

Dithioacetals are well known as one of the protected forms of formyl groups and are important intermediates in organic synthesis. Further, carbanions generated at the  $\alpha$ -position by the treatment of dithioacetals with a base such as *n*-butyllithium serve as synthetic equivalents of acyl carbanions<sup>1</sup>. Although several methods for the preparation of dithioacetals have been reported (*Scheme 1*)<sup>2</sup>, synthetic methods starting from alkynes have been limited so far<sup>3,4</sup>.

Previously, we have described the polyaddition of bispropiolates with dithiols to obtain polymers having  $\beta$ -alkylmercaptoenoate moieties in the main chain<sup>5</sup>. In the reaction of terminal bispropiolate with aliphatic dithiols, insoluble polymers were obtained, presumably by the partial formation of dithioacetal moieties by the second addition of thiol moieties to the double bonds produced (*Scheme 2*). If this double conjugate addition takes place more effectively, dithioacetals might be directly obtained from substituted alkynes and thiols. By the application of this facile reaction to polymer synthesis, it may be expected to produce the polymers having dithioacetal skeletons in the main chain. Since dithioacetals are known to be cleft to the corresponding aldehydes by oxidative hydrolysis, the polymers having dithioacetal moieties in the backbone may reveal unique degradability.

Moreover, polymers having dithioacetal moieties may be regarded as reactive polymers that can generate

reactive carbanions by treatment with a base as mentioned above. Consequently, functional groups may be introduced by the reaction with appropriate electrophiles. In addition, sulfur-containing polymers are interesting optical materials due to their high refractive indices<sup>6</sup>. Herein, we wish to describe a facile synthetic method for dithioacetals via phosphine-catalysed double conjugate additions and its application to a novel polyaddition of terminal acetylenes bearing electron-withdrawing groups with dithiols (*Scheme 3*).

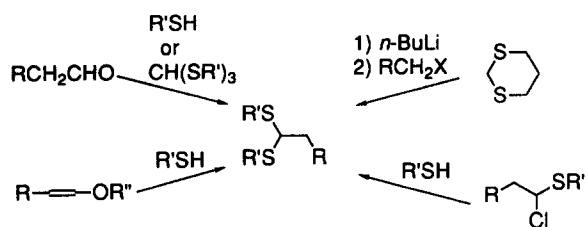
## EXPERIMENTAL

### Materials and instruments

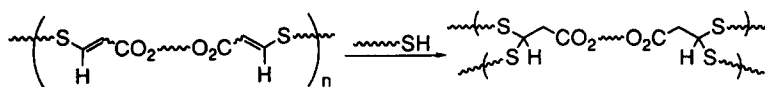
Tetrahydrofuran (THF) was dried over sodium benzophenone ketyl and distilled under nitrogen. Compounds 1, 2a, 2b, 2c, 5 and tri-*n*-butylphosphine were purified by distillation *in vacuo*.

Infra-red (i.r.) spectra were obtained with a Jasco Fourier transform i.r. 5300 spectrometer. <sup>1</sup>H and <sup>13</sup>C nuclear magnetic resonance (n.m.r.) spectra were recorded on JNM-EX90 or 400 spectrometers in CDCl<sub>3</sub> (tetramethylsilane as internal standard). Gel permeation chromatographic (g.p.c.) analyses were performed on a Tosoh HLC 8020 (TSK gels G5000HXL, G4000HXL, G3000HXL and G2500HXL; THF as eluent). Gas chromatographic analyses were conducted on a Shimadzu GS Chromatograph 4C PF equipped with a flame ionization detector and a silica gel SE30 column (1 m) using tetradecane as an internal standard. Gradient temperature (from 100 to 230°C, 10°C min<sup>-1</sup>) was used

\* To whom correspondence should be addressed



Scheme 1



Scheme 2

at a constant flow rate of  $0.1 \text{ kg cm}^{-2}$  ( $\text{N}_2$  as a carrier gas).

#### Synthesis of monomer

Ethynyl phenyl ketone (**7**) was prepared in two steps by modification of the method described in the literature<sup>7</sup>. To a solution (127 mmol) of ethynylmagnesium bromide<sup>8</sup> in THF (150 ml) was added slowly a solution of benzaldehyde (13.5 g, 127 mmol) in THF (30 ml). After 30 min, the reaction mixture was poured into a saturated aqueous solution of ammonium chloride containing crushed ice. The organic layer was separated and the aqueous layer was extracted twice with a 25 ml portion of diethyl ether. The organic extracts were combined with the first organic layer, and the combined extract was dried over magnesium sulfate. After evaporation of the solvent, the residue was purified by distillation (b.p.<sub>0.45</sub> 58–62°C) to obtain 10.2 g (77.3 mmol, 61%) of 1-phenylpropargyl alcohol. I.r. (neat) 3356, 3291, 2118, 1493, 1454  $\text{cm}^{-1}$ ;  $^1\text{H}$  n.m.r. (90 MHz,  $\delta$ , ppm) 2.56 (*bd*,  $J = 3.8 \text{ Hz}$ , 1 H,  $-\text{OH}$ ), 2.64 (*d*,  $J = 2.4 \text{ Hz}$ , 1 H,  $\text{HC}\equiv\text{C}$ ), 5.42 (*bd*,  $J = 3.8 \text{ Hz}$ , 1 H,  $-\text{CH}(\text{OH})-$ ), 7.1–7.7 (5 H,  $\text{C}_6\text{H}_5-$ ).

To a mixture of acetone (80 ml), water (25 ml) and concentrated sulfuric acid (8.75 g) was added 1-phenylpropargyl alcohol (10.0 g, 75.8 mmol) at 10°C. A solution of chromium(vi) oxide (5.57 g, 55.7 mmol) in water (20 ml) was added dropwise over 40 min, maintaining the temperature between 10 and 15°C. After an additional 2 h at 20°C, the solution was poured into ice-water and the mixture was extracted four times with a 25 ml portion of diethyl ether. The combined organic layer was washed with saturated aqueous ammonium chloride and dried over magnesium sulfate. The crude products remained after the removal of the solvent under reduced pressure was dissolved in refluxing pentane. The clear upper layer was decanted and kept in a refrigerator. Ethynyl phenyl ketone (**7**) was obtained as white crystals in 82% yield (8.20 g, 63.1 mmol) (m.p. 44–47°C). I.r. (KBr) 3235, 2095, 1644, 1597, 1580  $\text{cm}^{-1}$ ;  $^1\text{H}$  n.m.r. (90 MHz,  $\delta$ , ppm) 3.50 (*s*, 1 H,  $\text{HC}\equiv\text{C}$ ), 7.3–8.3 (5 H,  $\text{C}_6\text{H}_5-$ );  $^{13}\text{C}$  n.m.r. (22.5 MHz,  $\delta$ , ppm) 80.1, 80.9, 128.5, 129.5, 134.4, 136.0, 177.2.

#### Model reactions: typical procedure

To a solution of methyl propiolate (**1**) (102 mg, 1.21 mmol) and **2a** (301 mg, 2.43 mmol) in THF (0.3 ml) was added tri-*n*-butylphosphine (120 mg, 0.594 mmol) at

room temperature. After stirring for 24 h, the reaction mixture was concentrated under vacuum. The residue was purified by column chromatography on silica gel (hexane/ethyl acetate = 50/1) to give 366 mg (1.10 mmol, 91%) of methyl 3,3-bis(benzylmercapto)propanoate (**3a**);  $R_f = 0.53$  on thin layer chromatography (t.l.c.) (silica gel, hexane/ethyl acetate = 4/1); i.r. (neat) 3061, 3029, 2951, 2920, 1740, 1495, 1454  $\text{cm}^{-1}$ ;  $^1\text{H}$  n.m.r. (400 MHz,  $\delta$ , ppm) 2.73 (*d*,  $J = 7.60 \text{ Hz}$ , 2 H,  $-\text{CH}_2\text{CO}_2\text{Me}$ ), 3.62 (*s*, 3 H,

$-\text{CO}_2\text{CH}_3$ ), 3.77 (*d*,  $J = 13.2 \text{ Hz}$ , 2 H,  $\text{PhCH}_2-$ ), 3.84 (*d*,  $J = 13.2 \text{ Hz}$ , 2 H,  $\text{PhCH}_2-$ ), 4.00 (*t*,  $J = 7.60 \text{ Hz}$ , 1 H,  $(\text{BnS})_2\text{CH}-$ ), 7.27 (*m*, 10 H,  $\text{C}_6\text{H}_5\text{S}-$ );  $^{13}\text{C}$  n.m.r. (100 MHz,  $\delta$ , ppm) 35.0, 41.3, 46.3, 51.9, 127.1, 128.5, 129.0, 137.6, 170.2.

Similarly, other dithioacetals (**3b** and **3c**) were prepared as follows.

#### Methyl 3,3-bis(phenylmercapto)propanoate (**3b**).

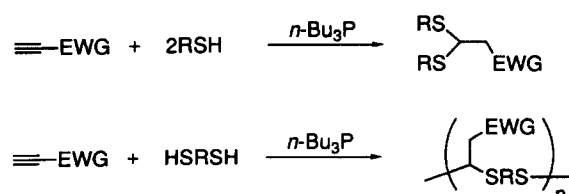
Yield 80%;  $R_f = 0.58$  on t.l.c. (silica gel, hexane/ethyl acetate = 4/1); i.r. (neat) 3059, 2951, 1738, 1582, 1478, 1439  $\text{cm}^{-1}$ ;  $^1\text{H}$  n.m.r. (400 MHz,  $\delta$ , ppm) 2.82 (*d*,  $J = 7.20 \text{ Hz}$ , 2 H,  $-\text{CH}_2\text{CO}_2\text{Me}$ ), 3.69 (*s*, 3 H,  $-\text{CO}_2\text{CH}_3$ ), 4.81 (*t*,  $J = 7.20 \text{ Hz}$ , 1 H,  $(\text{PhS})_2\text{CH}-$ ), 7.20–7.60 (10 H,  $\text{C}_6\text{H}_5\text{S}-$ );  $^{13}\text{C}$  n.m.r. (100 MHz,  $\delta$ , ppm) 41.0, 52.0, 53.4, 128.3, 129.1, 133.3, 170.4.

#### Methyl 3,3-propylenedimercaptopropanoate (**3c**).

Yield 71%;  $R_f = 0.45$  on t.l.c. (silica gel, hexane/ethyl acetate = 4/1); i.r. (neat) 2951, 2901, 1740, 1435, 1352  $\text{cm}^{-1}$ ;  $^1\text{H}$  n.m.r. (90 MHz,  $\delta$ , ppm) 1.70–2.30 (2 H,  $-\text{SCH}_2\text{CH}_2\text{CH}_2\text{S}-$ ), 2.79 (*d*,  $J = 7.29 \text{ Hz}$ , 2 H,  $-\text{CH}_2\text{CO}_2\text{Me}$ ), 2.80–3.00 (4 H,  $-\text{SCH}_2$ ), 3.72 (*s*, 3 H,  $-\text{CO}_2\text{CH}_3$ ), 4.41 (*t*,  $J = 7.29 \text{ Hz}$ , 1 H,  $(-\text{S})_2\text{CH}-$ );  $^{13}\text{C}$  n.m.r. (22.5 MHz,  $\delta$ , ppm) 25.2, 29.5, 40.4, 41.8, 52.0, 170.1.

#### Polyaddition: typical procedure

A polyaddition of methyl propiolate (**1**) with *p*-xylene- $\alpha,\alpha'$ -dithiol (**5**) was carried out as follows. To a THF (0.7 ml) solution of **1** (148 mg, 1.76 mmol) and **5** (300 mg, 1.76 mmol) was added tri-*n*-butylphosphine (178 mg, 0.881 mmol) at  $-30^\circ\text{C}$ . The temperature was allowed to rise to room temperature. After stirring for 24 h, the reaction mixture was diluted with THF (4.3 ml) and poured into hexane (100 ml). The precipitate was filtered and dried under vacuum. Compound **6**: 383 mg (85.4%); i.r. (neat) 2951, 2924, 1738, 1510, 1435  $\text{cm}^{-1}$ ;  $^1\text{H}$  n.m.r. (90 MHz,  $\delta$ , ppm) 2.73 (*d*,  $J = 7.47 \text{ Hz}$ , 2 H,  $-\text{CH}_2\text{CO}_2$

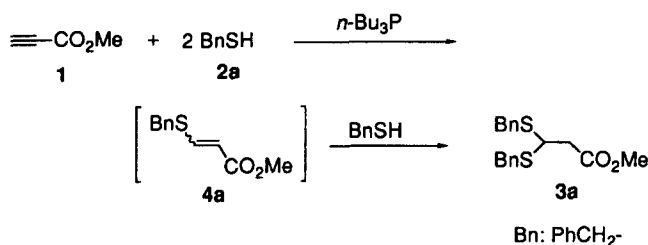


Scheme 3

Me), 3.63 (*s*, 3 H,  $-\text{CO}_2\text{CH}_3$ ), 3.80 (*s*, 4 H,  $\text{C}_6\text{H}_4\text{CH}_2\text{S}-$ ), 4.03 (*t*,  $J = 7.56$  Hz, 1 H,  $(-\text{S})_2\text{CH}-$ ), 7.16 (*s*, 4 H,  $-\text{C}_6\text{H}_4-$ );  $^{13}\text{C}$  n.m.r. (100 MHz,  $\delta$ , ppm) 34.6, 41.3, 46.7, 51.9, 129.3, 136.5, 170.1.

Similarly, a polymer (**8**) was prepared as follows.

Compound **8** (from **7** and **5**): yield 92.0%; i.r. (neat) 3053, 2915, 1684, 1597, 1510  $\text{cm}^{-1}$ ;  $^1\text{H}$  n.m.r. (90 MHz,  $\delta$ , ppm) 3.27 (*d*,  $J = 6.84$  Hz, 2 H,  $-\text{CH}_2\text{COPh}$ ), 3.81 (*s*, 4 H,  $\text{C}_6\text{H}_4\text{CH}_2\text{S}-$ ), 4.33 (*t*,  $J = 6.84$  Hz, 1 H,  $(-\text{S})_2\text{CH}-$ ), 7.19 (*s*, 4 H,  $-\text{C}_6\text{H}_4-$ ), 7.0–8.0 (5 H,  $\text{C}_6\text{H}_5-$ );  $^{13}\text{C}$  n.m.r. (22.5 MHz,  $\delta$ , ppm) 34.9, 45.1, 46.1, 128.0, 128.5, 129.2, 133.1, 136.4, 136.6, 195.8.



Scheme 4

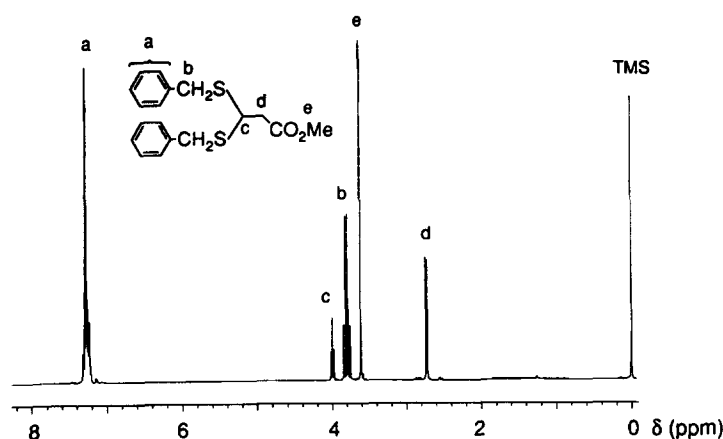


Figure 1  $^1\text{H}$  n.m.r. spectrum of **3a**

## RESULTS AND DISCUSSION

### Model reaction

The reaction of methyl propiolate (**1**) with 2 eq of benzylmercaptan (**2a**) was carried out in THF (1.0 M) for 24 h at ambient temperature using tri-*n*-butylphosphine (20 mol%) as catalyst to obtain a dithioacetal (**3a**) in 80% yield (Scheme 4). The structure of **3a** was confirmed by  $^1\text{H}$  n.m.r.,  $^{13}\text{C}$  n.m.r. and i.r. analyses. In the  $^1\text{H}$  n.m.r. spectrum, a methine proton in the dithioacetal moieties and those of a methylene adjacent to the ester group were observed at 4.00 and 2.73 ppm, respectively (Figure 1).

The reaction was examined under various concentrations of catalyst and reactants (Table 1). Although the monoadduct (**4a**) was obtained as a by-product in this reaction, the formation of **4a** could be suppressed by the higher concentrations of the catalyst and the reactants.

The reaction of the isolated monoadduct (**4a**) with **2a** was examined with as well as without tri-*n*-butylphosphine. The reaction in the presence of tri-*n*-butylphosphine proceeded smoothly to give **3a** in 95% yield. However,

**2a** was recovered almost quantitatively in the absence of the phosphine. Accordingly, the phosphine also served as a catalyst in the second addition of **2a** to **4a**. The mechanism of this reaction was considered as shown in Scheme 5. In the first addition step of thiol, the reaction may proceed by the addition of phosphine catalyst, the protonation and the vinylogous nucleophilic substitution (i.e. the addition-elimination) with the thiolate<sup>5</sup>. In the second addition step of thiols, the reaction may be also initiated by the addition of the phosphine catalyst\*, protonation and nucleophilic substitution with the thiolate. The equilibrium may be inclined towards the left side, because the electrophilicity of **4** may be decreased by the electron-donating mercapto group at the  $\alpha$ -position. The higher concentrations of the catalyst and substrate might increase the concentration of the zwitterionic intermediates to result in the effective conversion of **4**.

The rate of the first attack of thiols on **1** may be appreciably faster than that of the second attack, because the dithioacetal (**3a**) cannot be obtained by the stoichiometric reaction of thiols with **1**. Rates of the reactions of **1** with **2a** and that of **3a** with **2a** were estimated by kinetic

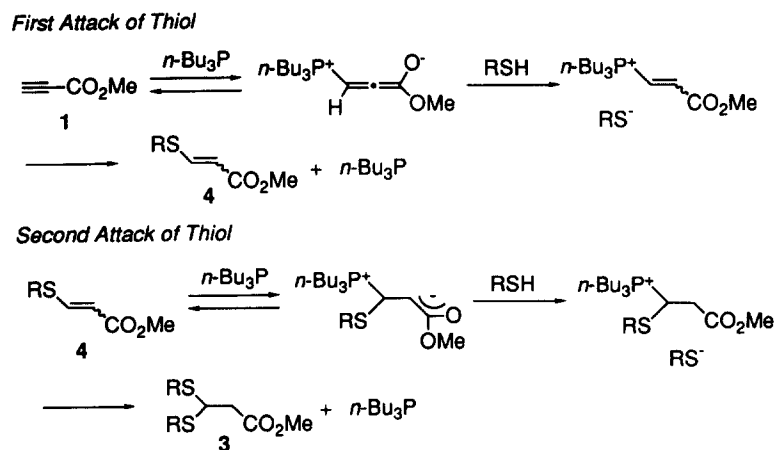
Table 1 Addition of benzylmercaptane to methyl propiolate<sup>a</sup>

Run	n-Bu <sub>3</sub> P (mol%)	Conc. (M)	Yield <sup>b</sup> (%)	
			<b>3a</b>	<b>4a</b>
1	0	1.0	6	0
2	20	1.0	80	20
3	50	1.0	84	10
4	100	1.0	91	6
5	50	0.5	75	22
6	50	2.0	88	7
7	50	4.0	91	0

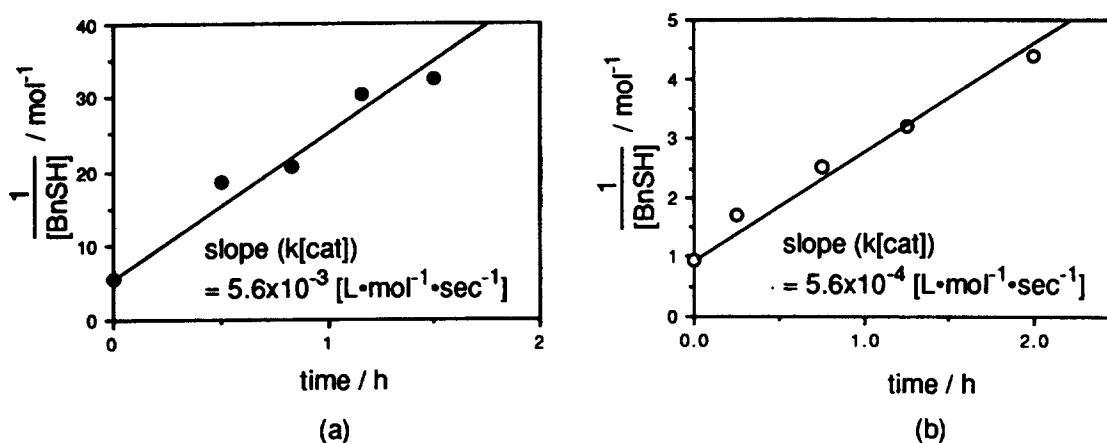
<sup>a</sup> The reaction was carried out in THF at room temp. for 24 h under nitrogen using n-Bu<sub>3</sub>P as catalyst

<sup>b</sup> Isolated as a mixture of **3a** and **4a** on silica gel. The ratio of **3a** and **4a** in the mixture was determined by  $^1\text{H}$  n.m.r. (400 MHz)

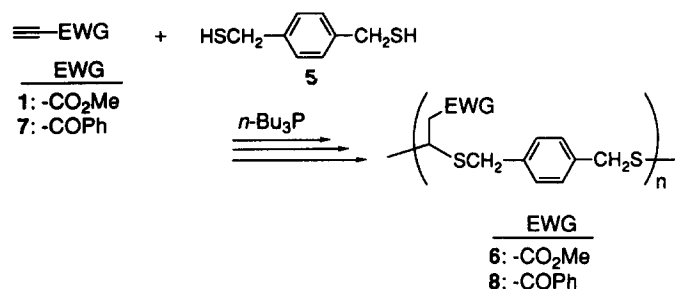
\* In order to detect the zwitterionic intermediate, the mixture of **4a** (75 mg, 0.36 mmol) and tri-*n*-butylphosphine (18 mg, 0.072 mmol) in THF (0.4 ml) was subjected to  $^{31}\text{P}$  n.m.r. measurement. Peaks attributable to phosphoniums were detected at 28.9, 41.7, 46.6 and 52.9 ppm accompanied by the peak at  $-33.1$  ppm (n-Bu<sub>3</sub>P), in the integral ratio of 2.5/8.6/1.8/1.0/107.3, respectively



Scheme 5



**Figure 2** Plot of  $1/[\text{BnSH}]$  versus time for (a) the reaction of benzyl propiolate with benzyl mercaptan ( $[\text{n-Bu}_3\text{P}] = 2.77 \times 10^{-3} \text{ mol l}^{-1}$ ) and (b) the reaction of methyl 2-benzylmercaptoenoate with benzyl mercaptan ( $[\text{n-Bu}_3\text{P}] = 2.66 \times 10^{-1} \text{ mol l}^{-1}$ )



Scheme 6

studies by using tri-*n*-butylphosphine ( $2.77 \times 10^{-3}$  and  $2.66 \times 10^{-1} \text{ mol l}^{-1}$ ), from which apparent kinetic coefficients ( $k$ ) were determined as  $2.0$  and  $2.0 \times 10^{-3} \text{ (l}^2 \text{ mol}^{-2} \text{ s}^{-1}\text{)}$ , respectively (Figure 2)<sup>†</sup>. That is, the second attack of thiols was found to be slower by  $1.0 \times 10^3$  times in comparison with the first attack. In the second addition step, the initiation step (i.e. addition of phosphine) may be suppressed, when compared with the first addition step, by an electron-donating mercapto group. Further, the reaction rate of  $\text{S}_{\text{N}}2$ -type substitution

<sup>†</sup> Regardless of the position of the rate determining step, the exact kinetic expression would become too complicated to solve on the basis of the proposed mechanism. However, the kinetics of the reactions were found to be approximated by the equation:  $-\text{d}[\text{BnSH}]/\text{d}t = k[\text{1 or 4a}][\text{BnSH}][\text{n-Bu}_3\text{P}]$

**Table 2** Addition of thiols to methyl propiolate<sup>a</sup>

Run	Thiols (eq)	Conditions		Yield <sup>b</sup> (%)	
		<i>n</i> -Bu <sub>3</sub> P (mol%)	Time (h)	3	4
1	BnSH (2a)	(2) 10	24	79	17
2	PhSH (2b)	(2) 20	89	17	78
3 <sup>c</sup>		(2) 20	42	80	13
4 <sup>d</sup>	HS(CH <sub>2</sub> ) <sub>3</sub> SH (2c)	(1) 30	12	71 <sup>e</sup>	0

<sup>a</sup> The addition was carried out in THF (0.5 M) at room temp. under nitrogen with *n*-Bu<sub>3</sub>P as a catalyst

<sup>b</sup> Isolated as a mixture of 3 and 4 on silica gel. The ratio of 3 and 4 in the mixture was determined by <sup>1</sup>H n.m.r. (400 MHz)

<sup>c</sup> The reaction was carried out at reflux temperature

<sup>d</sup> The addition was carried out in THF (0.1 M)

<sup>e</sup> Cyclic dithioacetal was obtained (C<sub>3</sub>-CO<sub>2</sub>Me)

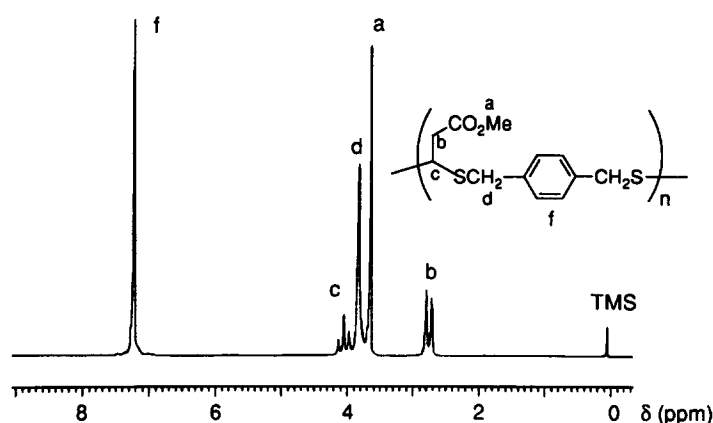


Figure 3  $^1\text{H}$  n.m.r. spectrum of **6**

by the thiolate may be considerably slower than addition-elimination by the thiolate in the first step, because phosphoniums are rarely employed as leaving groups in  $\text{S}_{\text{N}}2$ -type substitution reaction due to the relatively strong bonds. Thus, the larger rate differences between the first and second steps may be as a result of the reasons mentioned above.

The model reactions were performed by using various thiols (Table 2). In the case of thiophenol (**2b**), the corresponding dithioacetal (**3b**) could not be sufficiently obtained under the same conditions as for **2a** (run 2). More severe conditions were necessary to obtain **3b** in higher yield. In contrast to the case of **2a**, unidentified side reactions were sometimes observed in the case of **2b**, probably because of the requirement of the severe reaction conditions. A cyclic dithioacetal (**3c**) was also obtained in high yield in the case of propanedithiol (**2c**) under dilute conditions.

#### Polyaddition

Based on the results obtained by the model reactions, a polyaddition of **1** with *p*-xylene- $\alpha$ ,  $\alpha'$ -dithiol (**5**) was carried out under higher concentration of catalyst (50 mol%) and monomers (3 M) to obtain the corresponding polymer (**6**) having dithioacetal moieties in the backbone in 84% yield (Scheme 6). The structure of **6** was determined by  $^1\text{H}$  n.m.r.,  $^{13}\text{C}$  n.m.r. and i.r. spectroscopy. The number-average molecular weight ( $M_n$ ) and the molecular weight distribution ( $M_w/M_n$ ) of **6** were estimated as 8100 and 1.29, respectively (g.p.c.; polystyrene). The obtained polymer (**6**) is soluble in THF,  $\text{CH}_2\text{Cl}_2$  and  $\text{CHCl}_3$  and shows a colourless gum state. As expected, **6** exhibited a higher refractive index ( $n_D = 1.65$ ). In the  $^1\text{H}$  n.m.r. spectrum, the methine proton attributable to the dithioacetal moieties in the main chain was observed at 4.03 ppm, similar to that of the model compound (**3a**) (Figure 3). Because the signals assigned to the end-mercaptoenoate groups could not be observed, the polyaddition was found to proceed sufficiently under the conditions examined.

The polyaddition of **1** with **5** was carried out under various feed ratios of the two monomers (Table 3) to reveal that stoichiometric conditions were suitable for obtaining a polymer with higher molecular weight. The molecular weights and yields of the obtained polymers decreased by deviation from the stoichiometric conditions, as is usual for polyaddition reactions.

The consumption of monomer and the molecular weight of the resulting polymer were monitored by g.p.c.

after the designated reaction times (Figure 4). When the polyaddition was carried out by using tri-*n*-butylphosphine (50 mol%) in THF (3 M), the two monomers were consumed completely within a few minutes. Although the consumption of both monomers was relatively fast, similar to the case of the polyaddition of terminal bispropiolate with dithiol<sup>5</sup>, the polyaddition required a longer reaction time because of the slow

Table 3 Effect of the feed ratio of monomers<sup>a</sup>

Run	Feed ratio		$M_n$ ( $M_w/M_n$ ) <sup>c</sup>
	1/5	Yield <sup>b</sup> (%)	
1	1.0/1.2	74	2200 (1.52)
2	1.0/1.1	80	2900 (1.73)
3	1.0/1.0	84	8100 (1.29)
4	1.1/1.0	78	2900 (1.39)
5	1.2/1.0	44	2200 (1.17)

<sup>a</sup> The polymerization was carried out in THF (3 M) at room temp. for 4 h under nitrogen with *n*-Bu<sub>3</sub>P (50 mol%)

<sup>b</sup> Isolated yield after precipitation with hexane

<sup>c</sup> Estimated by g.p.c. (polystyrene; THF as eluent)

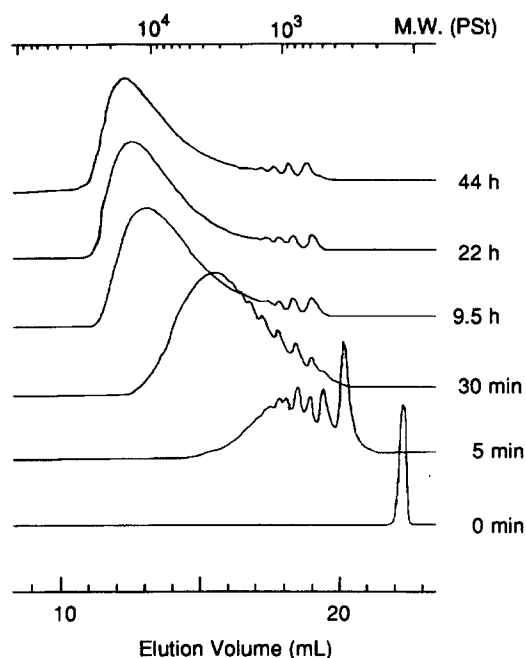


Figure 4 G.p.c. traces for the reaction of **1** with **5** after the designated reaction times

second attack of the mercapto group on  $\beta$ -alkylmercaptoenoate moieties.

Likewise, a terminal acetylene (7) bearing a ketone group (i.e. an ynone) can be used for the present polyaddition with 5 under similar conditions (Scheme 6). In this case, a polymer (8) having dithioacetal moieties in the main chain was obtained in almost quantitative yield (92%), whose  $M_n$  and  $M_w/M_n$  were estimated as 6900 and 1.70, respectively.

As the polymers obtained by the present polyaddition have novel dithioacetal moieties in the main chain, they are expected to have unique functions such as degradability, higher refractive indices, reactivity, etc. Applications of these polymers are in progress.

## REFERENCES

1. Seebach, D., *Synthesis*, 1969, 17.
2. Sandler, S. T. and Karo, W., *Organic Functional Group Preparations III*, 2nd edn. Academic Press, London, 1986, pp. 2-79.
3. Prilezhaeva, E. N. and Mikhelashvili, I. L., *Zh. Org. Khim.*, 1973, **9**, 1129.
4. Ranu, B. C., Bhar, S. and Chakraborti, R., *J. Org. Chem.*, 1992, **57**, 7349.
5. Kuroda, H., Tomita, I. and Endo, T., *Macromolecules*, 1995, **28**, 6020.
6. Yagi, T., Morishita, T. and Kobayashi, E., *Zairyo Gijutsu*, 1989, **7**, 272.
7. Brandsma, L., *Preparative Acetylenic Chemistry*, 2nd edn. Elsevier, Amsterdam, 1962, pp. 281.
8. Jones, E. R. H., Skattebøl, L. and Whiting, M. C., *Org. Syn.*, **4**, 792.