Macromolecules **1995,** *28,* 433–436

A Novel Polyaddition of Diols with Bifunctional Acetylenes Having Electron-Withdrawing Groups

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 July 28, 1994; Revised Manuscript Received October 28, 1994®

ABSTRACT: Tri-*n*-butylphosphine-catalyzed polyadditions of bifunctional acetylenes having ester groups [*i.e.*, bis(propiolate)s (**5**)] with diols (**6**) are described. Polyadditions with primary diols (**6a–f**) proceeded under mild conditions, and polymers having β-alkoxyenoate moieties in the main chain (only composed of *E* isomer) were obtained in almost quantitative yield. For instance, the reaction of **5A** and **6a** gave a polymer (**7Aa**) in 94% yield whose M_n and M_w/M_n were estimated as 12 800 and 2.57, respectively. The obtained polymers were stable upon storage under air. Within the examined reaction conditions, more than 5 mol % of a catalyst and an appropriate concentration of monomers (>0.2 M) with stoichiometric conditions were suitable to obtain polymers with higher molecular weights. When the polyaddition was carried out with a small excess of **5**, a gelation took place as a result of the cross-linking reaction of end-acetylene moieties.

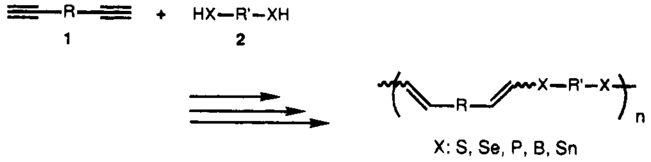
Introduction

Polyadditions between bifunctional acetylenes (**1**) and monomers (**2**) having heteroatom-hydrogen linkages are excepted to produce polymers with heteroatom-substituted vinyl groups in the main chains (Scheme 1). Various kinds of bifunctional monomers containing S–H,[1a] Se–H,[1b] P–H,[1c] B–H,[1d] Sn–H,[1e] *etc.* have been examined for the polyaddition with diacetylenes. The resulting polymers are known to have unique characteristics such as reactivity or functionality (electroconductivity, thermal stability, *etc.*) depending on the introduced heteroatoms as well as the structure of the polymers. In spite of a better availability of diols in comparison with the above-mentioned heteroatom-containing monomers, few reports have dealt with polyaddition using these monomers. Polyaddition of bifunctional acetylenes with diols is expected to yield polymers containing vinyl ether moieties in the main chain that may show unique reactivities as well as degradabilities.

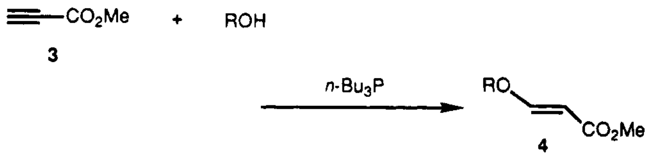
Recently, we have reported a proton-catalyzed polyaddition between bisallenyl ether and diols, from which polymers having vinyl groups in the side chains and acetal moieties in the main chain are obtained.[2] Consequently, these polymers showed degradability under acidic conditions.

Trialkylphosphine-catalyzed conjugate addition of alcohols to methyl propiolate (**3**) has been reported to proceed smoothly under mild conditions and to give β-alkoxyenoates (**4**) (predominantly *E* isomer) in high yields (Scheme 2).[3] In this paper, we wish to report a novel polyaddition of bifunctional acetylenes (**5A** and **5B**) with diols (**6a–g**) (Scheme 3).

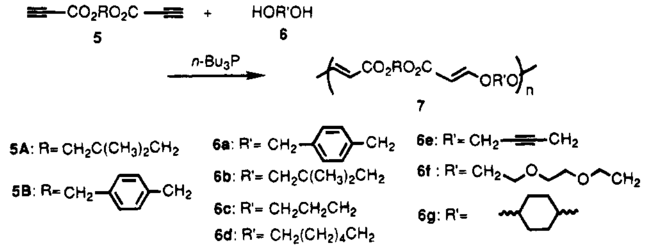
Scheme 1



Scheme 2



Scheme 3



Experimental Section

Materials and Instruments. Tetrahydrofuran (THF) was dried over sodium benzophenone ketyl and distilled under nitrogen. **6a**, **6b**, **6d**, **6e**, and **6g** were purified by recrystallization from ethyl acetate and dried in vacuo. **6c** and **6f** were dried over sodium and then purified by distillation.

Infrared (IR) spectra were obtained with a JASCO FT/IR 5300 infrared spectrometer. ^{1}H- and ^{13}C-NMR spectra were recorded on a JNM-EX90 spectrometer in $CDCl_3$ (tetramethylsilane as an internal standard). Gel permeation chromatographic analyses (GPC) were performed on a Tosoh HLC 8020 (TSKgel G5000HXL, G4000HXL, and G2500XL, THF as eluent).

Synthesis of Monomers. 2,2-Dimethylpropylene 1,3-Dipropiolate (5A). To a solution of propiolic acid (10.1 g, 144 mmol) in benzene (100 mL) were added neopentyl glycol (6.20 g, 59.6 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, the remaining materials were extracted three times with ethyl acetate, and the combined extracts were dried over magnesium sulfate. After the evaporation of the solvents, the residue was purified by column chromatography on silica gel (hexane/ethyl acetate = 10/1) to give 10.1 g (48.6 mmol, 83.5%) of **5A** as white crystals: $R_f = 0.40$ on TLC (hexane/ethyl acetate = 4:1); mp 59.0–61.0 °C; IR (KBr) 3239, 2984, 2969, 2897, 2114, 1711, 1263 cm^{-1}; ^{1}H NMR (90 MHz, δ, ppm) 1.03 (s, 6H, $C(CH_3)_2$), 2.93 (s, 2 H, $HC{\equiv}C$), 4.03 (s, 4 H, CO_2CH_2); ^{13}C NMR (22.5 MHz, 8, ppm) 21.5, 34.7, 70.4, 74.4, 75.1, 152.5.

® Abstract published in *Advance ACS Abstracts,* December 15, 1994.

0024-9297/95/2228-0433$09.00/0

p-Xylylene dipropiolate (**5B**) was similarly obtained from propiolic acid (10.1 g, 144 mol) and p-xylylene glycol (8.22 g, 59.6 mmol) in 62.3% yield (8.98 g, 37.7 mmol): $R_f = 0.40$ on TLC (SiO_2, hexane/ethyl acetate = 2/1); mp 66.0–67.5 °C [recrystallized from ethyl acetate/hexane (1/4)]; IR (KBr) 3264, 2982, 2118, 1709, 1254 cm^{-1}; ^1H NMR (90 MHz, δ, ppm) 2.92 (s, 2 H, $HC{\equiv}C$), 5.23 (s, 4 H, CO_2CH_2), 7.39 (s, 4 H, C_6H_4); ^{13}C NMR (22.5 MHz, δ, ppm) 67.3, 74.4, 75.2, 128.7, 135.1, 152.4.

Polyaddition. Typical Procedure. The polyaddition of 2,2-dimethylpropylene 1,3-dipropiolate (**5A**) with p-xylylene glycol (**6a**) was carried out as follows: To a THF (2.4 mL) solution of dipropiolate (**5A**) (200 mg, 0.962 mmol) and p-xylylene glycol (**6a**) (133 mg, 0.962 mmol) was added tri-n-butylphosphine (39 mg, 0.192 mmol) at room temperature. After stirring for 3 h, the reaction mixture was diluted with THF (7.6 mL) and poured into methanol (200 mL). The precipitate was filtered and dried under vacuum. **7Aa**: 313 mg (94%); IR (neat) 3094, 2965, 2880, 1707, 1624, 1128 cm^{-1}; ^1H NMR (90 MHz, δ, ppm) 1.00 (s, 6 H, $CH_2C(CH_3)_2$), 3.95 (s, 4 H, OCH_2CMe_2), 4.90 (s, 4 H, $CH_2C_6H_4$), 5.32 (d, $J = 12.8$ Hz, 2 H, $=CHCO_2$), 7.34 (s, 4 H, C_6H_4), 7.68 (d, $J = 12.8$ Hz, 2 H, $OCH=$); ^{13}C NMR (22.5 MHz, δ, ppm) 21.3, 34.8, 68.6, 72.2, 97.2, 127.9, 135.5, 161.9, 167.3.

Similarly, all the other polymers (**7**) were prepared in almost quantitative yield.

7Ab (from **5A** and **6b**): IR (neat) 3094, 2967, 2880, 1711, 1626, 1128 cm^{-1}; ^1H NMR (90 MHz, δ, ppm) 0.96 (s, 6 H, $OCH_2C(CH_3)_2$), 1.02 (s, 6 H, $CO_2CH_2C(CH_3)_2$), 3.64 (s, 4 H, OCH_2CMe_2), 3.94 (s, 4 H, $CO_2CH_2CMe_2$), 5.21 (d, $J = 12.6$ Hz, 2 H, $=CHCO_2$), 7.59 (d, $J = 12.9$ Hz, 2 H, $=CHO$); ^{13}C NMR (22.5 MHz, δ, ppm) 21.5, 21.8 68.6, 96.4, 162.3, 167.5.

7Ac (from **5A** and **6c**): IR (neat) 3094, 2965, 2890, 1711, 1626, 1134 cm^{-1}; ^1H NMR (90 MHz, δ, ppm) 0.98 (s, 6 H, CH_2CMe_2), 2.12 (m, 2 H, $CH_2CH_2CH_2$), 3.94 (s, 4 H, $=CHOCH_2CH_2$), 3.70–4.10 (t, $J = 5.94$ Hz, 4 H, $=CHOCH_2CH_2$), 5.22 (d, $J = 12.9$ Hz, 2 H, $=CHCO_2$), 7.58 (d, $J = 12.6$ Hz, 2 H, $=CHOCH_2$); ^{13}C NMR (22.5 MHz, δ, ppm) 21.9, 28.3, 34.9, 66.6, 68.6, 96.7, 162.0, 167.4.

7Ad (from **5A** and **6d**): IR (neat) 3094, 2941, 2874, 1711, 1624, 1130 cm^{-1}; ^1H NMR (90 MHz, δ, ppm) 0.98 (s, 6 H, $CH_2C(CH_3)_2$), 1.20–2.00 (m, 8 H, $(CH_2)_4$), 3.85 (t, $J = 6.2$ Hz, 4 H, $CH_2OCH=$), 3.94 (s, 4 H, $CO_2CH_2CMe_2$), 5.19 (d, $J = 12.6$ Hz, 2 H, $=CHCO_2$), 7.59 (d, $J = 12.8$ Hz, 2 H, $=CHOCH_2$); ^{13}C NMR (22.5 MHz, δ, ppm) 21.8, 25.5, 28.7, 34.9, 68.6, 70.8, 96.1, 162.6, 167.8.

7Ae (from **5A** and **6e**): IR (neat) 3094, 2966, 2878, 1709, 1626, 1125 cm^{-1}; ^1H NMR (90 MHz, δ, ppm) 0.99 (s, 6 H, $CH_2C(CH_3)_2$), 3.63 (s, $=CHOCH_2CMe_2$), 3.95 (s, $CO_2CH_2CMe_2$), 4.60 (s, ${\equiv}CCH_2OCH=$), 4.60 (s, $CO_2CH_2C{\equiv}$), 5.10 (d, $J = 12.6$ Hz, ${\equiv}CCH_2OCH=CHCO_2CH_2$), 5.33 (d, $J = 12.6$ Hz, $=CHO$), 7.55 (d, $J = 12.9$ Hz, ${\equiv}CCH_2OCH=CHCO_2CH_2$), 7.59 (d, $J = 12.6$ Hz, $=CHCO_2$); ^{13}C NMR (22.5 MHz, δ, ppm) 21.6, 34.8, 58.1, 68.8, 81.7, 98.1, 160.5, 166.9. From the ^1H NMR spectrum, the structure of **7Ae** was contaminated with 14% of the transesterification units.

7Af (from **5A** and **6f**): IR (neat) 3092, 2961, 2878, 1709, 1626, 1127 cm^{-1}; ^1H NMR (90 MHz, δ, ppm) 0.98 (s, 6 H, $CH_2C(CH_3)_2$), 3.68 (s, 4 H, OCH_2CH_2O), 3.78 (m, 4 H, $=CHOCH_2CH_2O$), 3.94 (s, 4 H, $CO_2CH_2CMe_2$), 4.02 (m, 4 H, $=CHOCH_2CH_2O$), 5.22 (d, $J = 12.9$ Hz, 2 H, $=CHCO_2$), 7.61 (d, $J = 12.6$ Hz, 2 H, $=CHO$); ^{13}C NMR (22.5 MHz, δ, ppm) 21.7, 34.9, 68.6, 69.3, 70.3, 70.8, 96.5, 162.4, 167.5.

7Ba (from **5B** and **6a**): IR (neat) 3096, 3036, 2942, 2880, 1707, 1622, 1125 cm^{-1}; ^1H NMR (90 MHz, δ, ppm) 4.88 (s, 4 H, $=CHOCH_2$), 5.14 (s, 4 H, CO_2CH_2), 5.34 (d, $J = 12.9$ Hz, 2 H, $=CHCO_2$), 7.34 (s, 8 H), 7.69 (d, $J = 12.8$ Hz, 2 H, $=CHOCH_2$); ^{13}C NMR (22.5 MHz, δ, ppm) 65.3, 72.3, 97.32, 127.9, 128.2, 135.5, 136.2, 162.2, 167.2.

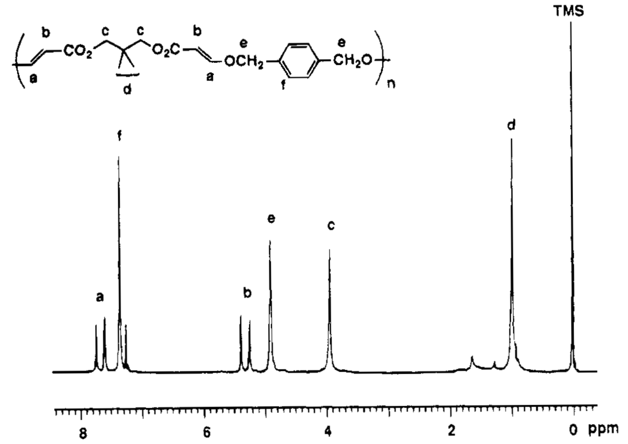


Figure 1. ^1H NMR spectrum of **7Aa**.

Scheme 4

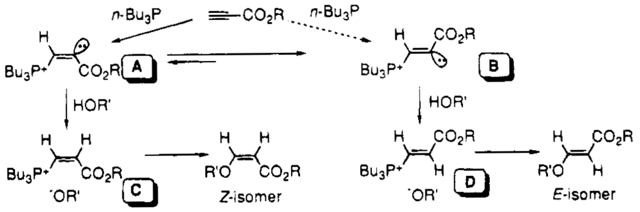


Table 1. Effect of the Concentration of the Catalyst on the Polyaddition of 5A with 6a[a]

run	Bu_3P (mol %)	M_n (M_w/M_n)[b]
1	1	700 (1.37)
2	5	10 800 (2.31)
3	20	11 200 (2.24)
4	50	12 200 (2.40)
5	70	11 700 (2.15)

[a] Polyaddition was carried out in THF (0.4 M) at room temperature for 3 h under nitrogen using n-Bu_3P as a catalyst. [b] Estimated by GPC (PSt, THF as an eluent).

Table 2. Effect of the Concentration of Two Monomers (5A/6a) under Stoichiometric Conditions[a]

run	conc/M	M_n (M_w/M_n)[b]
1	0.1	8 600 (2.55)
2	0.3	11 700 (2.47)
3	0.4	11 200 (2.24)
4	0.5	12 800 (2.57)

[a] Polyaddition was carried out in THF (0.4 M) at room temperature for 3 h under nitrogen using n-Bu_3P (20 mol %) as a catalyst. [b] Estimated by GPC (PSt, THF as an eluent).

7Bb (from **5B** and **6b**): IR (neat) 3094, 2965, 2880, 1707, 1624, 1128 cm^{-1}; ^1H NMR (90 MHz, δ, ppm) 0.99 (s, 6 H, $CH_2C(CH_3)_2$), 3.62 (s, $=CHOCH_2CMe_2$), 3.94 (s, $CO_2CH_2CMe_2$), 4.89 (s, $=CHOCH_2C_6H_4$), 5.10–5.45 (m, $CH=CHCO_2CH_2CMe_2$), 5.14 (s, $CO_2CH_2C_6H_4$), 5.24 (d, $J = 12.8$ Hz, $=CHOCH_2C_6H_4$), 7.35 (s, 4 H, C_6H_4), 7.50–7.70 (m, $=CHOCH_2CMe_2$), 7.61 (d, $J = 12.8$ Hz, $=CHOCH_2C_6H_4$); ^{13}C NMR (22.5 MHz, δ, ppm) 21.5, 35.4, 65.2, 75.4, 96.4, 128.3, 136.2, 162.7, 167.3. From the ^1H NMR spectrum, the structure of **7Bb** was contaminated with 15% of the transesterification units.

7Bc (from **5B** and **6c**): IR (neat) 3094, 3034, 2957, 2890, 1709, 1624, 1130 cm^{-1}; ^1H NMR (90 MHz, δ, ppm) 2.09 (m, 2 H, $CH_2CH_2CH_2$), 3.94 (t, $J = 5.9$ Hz, $=CHOCH_2$), 4.21 (t, $J = 5.9$ H, $CO_2CH_2CH_2CH_2$), 4.89 (s, $=CHOCH_2C_6H_4$), 5.14 (s, $CO_2CH_2C_6H_4$), 5.10–5.45 (m, $=CHCO_2$), 5.25 (d, $J = 12.7$ Hz, $CH_2CH_2OCH=CHCO_2CH_2C_6H_4$), 7.35 (s, 4 H, C_6H_4), 7.40–7.80 (m, $=CHO$), 7.60 (d, $J = 12.6$ Hz, $CH_2CH_2OCH=CHCO_2CH_2C_6H_4$); ^{13}C NMR (22.5 MHz, δ, ppm) 28.3, 65.3, 66.7, 96.6, 128.2, 136.2, 162.3, 167.3. From the ^1H NMR spectrum, the structure of **7Bc** was contaminated with 19% of the transesterification units.

7Bd (from **5B** and **6d**): IR (neat) 3096, 3059, 3028, 2942, 2865, 1709, 1624, 1130 cm^{-1}; ^1H NMR (90 MHz, δ, ppm) 1.20–1.90 (m, 8 H, $(CH_2)_4$), 3.83 (t, $J = 6.0$ Hz, $=CHOCH_2CH_2$), 3.90–4.20 (m, $CO_2CH_2CH_2$), 5.10 (s, $=CHOCH_2C_6H_4$), 5.15 (s, $CO_2CH_2C_6H_4$), 5.1–5.45 (m, $=CHCO_2$), 5.21 (d, $J = 12.8$ Hz, $CH_2CH_2OCH=CHCO_2CH_2C_6H_4$), 7.30 (s, 4 H, C_6H_4), 7.40–7.85 (m, $=CHO$), 7.62 (d, $J = 12.8$ Hz, $CH_2CH_2OCH=CHCO_2CH_2C_6H_4$); ^{13}C NMR (22.5 MHz, δ, ppm) 25.3, 28.6, 65.2, 70.8, 95.9, 128.2, 136.3, 162.8, 167.5. From the ^1H NMR spectrum,

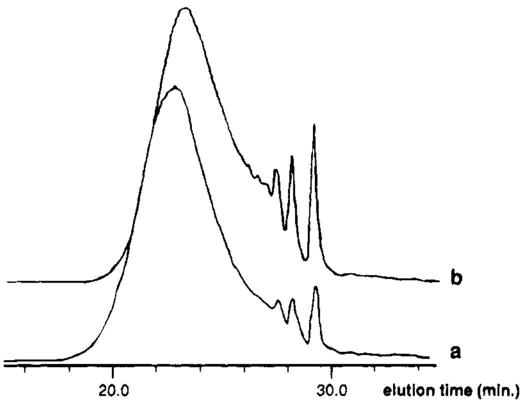


Figure 2. GPC trace of polymers obtained by polyaddition of **5A** with **6a** under different monomer concentrations [0.5 M (a) and 0.1 M (b)].

Table 3. Effect of the Feed Ratio of Monomers (5A/6a)[a]

run	feed ratio **5A**:**6a**	yield[b]/%	M_n (M_w/M_n)[c]
1	1.0:1.2	82	7 300 (1.36)
2	1.0:1.1	90	8 500 (1.49)
3	1.0:1.0	94	13 000 (1.84)
4	1.1:1.0	*d*	
5	1.2:1.0	*d*	

[a] Polyaddition was carried out in THF (0.4 M) at room temperature for 3 h under nitrogen using *n*-Bu_3P (20 mol %). [b] Isolated yield after precipitation with methanol. [c] Estimated by GPC (PSt, THF as an eluent). [d] Gelation took place.

the structure of **7Bd** was contaminated with 6% of the transesterification units.

7Be (from **5B** and **6e**): IR (neat) 3088, 2936, 2882, 1709, 1626, 1123 cm^{-1}; ^{1}H NMR (90 MHz, δ, ppm) 4.57 (s, $OCH_2C\equiv$), 4.76 (s, $CO_2CH_2C\equiv$), 4.89 (s, $=CHOCH_2C_6H_4$), 5.16 (s, $CO_2CH_2C_6H_4$), 5.20–5.50 (m, $=CHCO_2$), 5.35 (d, J = 12.6 Hz, $\equiv CCH_2OCH=CHCO_2CH_2C_6H_4$), 7.37 (s, 4 H, C_6H_4), 7.40 (m, $=CHOCH_2$), 7.58 (d, J = 12.8 Hz, $\equiv CCH_2OCH=CHCO_2CH_2C_6H_4$); ^{13}C NMR (22.5 MHz, δ, ppm) 58.1, 65.4, 81.6, 98.1, 128.3, 136.1, 160.8, 166.8. From the ^{1}H NMR spectrum, the structure of **7Be** was contaminated with 22% of the transesterification units.

7Bf (from **5f** and **6f**): IR (neat) 3094, 3026, 2936, 2878, 1707, 1624, 1125 cm^{-1}; ^{1}H NMR (90 MHz, δ, ppm) 3.65 (s, 4 H, OCH_2CH_2O), 3.76 (m, 4 H, $CH_2CH_2OCH_2$), 3.97 (m, $=CHOCH_2$), 4.25 (m, $CO_2CH_2CH_2O$), 4.89 (s, $=CHOCH_2C_6H_4$), 5.14 (s, $CO_2CH_2C_6H_4$), 5.10–5.50 (m, $=CHCO_2$), 5.26 (d, J = 12.8 Hz, $CH_2CH_2OCH=CHCO_2CH_2C_6H_4$), 7.35 (s, 4 H, C_6H_4), 7.50–7.90 (m, $=CHO$), 7.64 (d, J = 12.6 Hz, $CH_2CH_2OCH=CHCO_2CH_2C_6H_4$); ^{13}C NMR (22.5 MHz, δ, ppm) 65.2, 69.3, 70.4, 70.8, 96.5, 128.2, 136.3, 162.9, 167.3. From the ^{1}H NMR spectrum, the structure of **7Bf** was contaiminated with 10% of the transesterification units.

Results and Discussion

The polyaddition of **5A** and **6a** was carried out at room temperature in THF (0.5 M) for 3 h by using tri-*n*-butylphosphine (20 mol %).[4] The polyaddition proceeded exothermically to obtain polymer **7Aa** having a β-alkoxyenoate structure in the main chain in almost quantitative yield. The number-average molecular weight (M_n) and the molecular weight distribution (M_w/M_n) of **7Aa** were estimated as 12 800 and 2.57, respectively (GPC, PSt).

The structure of the obtained polymer (**7Aa**) was confirmed by ^{1}H-NMR, ^{13}C-NMR, and IR analyses. From the ^{1}H-NMR spectrum[5] (Figure 1), olefinic protons in the main chain of the polymer were observed at 5.3 and 7.7 ppm. From the integral ratio between these peaks and other protons, the double bond was detected quantitatively, indicating that no undesired side reactions such as the second attack of the alkoxy group toward β-alkoxyenoate moieties took place. The geometry of the olefin was confirmed to be only *E* isomer from the chemical shifts as well as the coupling constant.

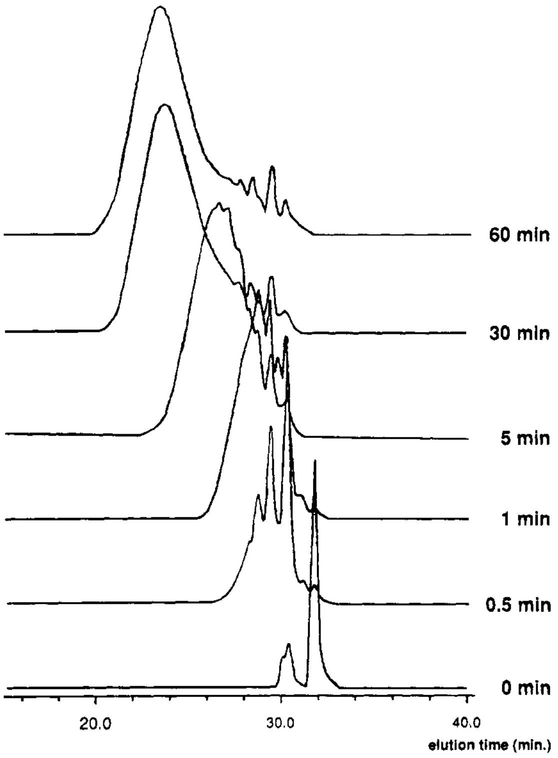


Figure 3. GPC traces for the reaction of **5A** with **6a** after the designated reaction time.

The present polyaddition can be considered to proceed as shown in Scheme 4. At first, the nucleophilic attack of tri-*n*-butylphosphine at the β-carbon of the propiolate moieties may occur in an anti fashion to give an intermediate (**A**),[6] which undergoes isomerization to the geometric isomer (**B**), since **B** will be thermodynamically more stable. If protonation of **A** is much faster than the equilibration, **C** may be obtained.[7] The protonation with alcohol is, however, known to be rather slow,[8] which may shift the equilibrium so as to favor the path **A** → **B** → **D**. Many addition–elimination reactions are known to proceed with complete retention regardless of the geometry of the starting alkenes.[9] Thus, the attack of alkoxide toward phosphonium intermediates may also proceed *via* the retention (*i.e.*, *E*-phosphonium intermediates provide *E*-enoates).

Effect of Concentration of the Catalyst. The polyaddition of **5A** with **6a** was examined at ambient temperature in THF by varying the concentration of the catalyst from 1 to 70 mol % (Table 1). When 1 mol % of the catalyst was used, the consumption of monomer was not completed even at the longer reaction time and oligomers were obtained (run 1). This might be due to some side reactions that deactivate the phosphine catalyst.[10] On the other hand, the polyaddition with 5 mol % of the catalyst proceeded smoothly to yield the polymer (M_n = 12 000) in almost quantitative yield. Further excess of the catalyst, however, gave no more effect on the molecular weight of the resulting polymer.

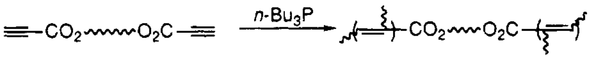
Effect of Concentration of Monomers. Polyaddition of **5A** with **6a** was performed under various concentrations of the two monomers, keeping the stoichiometric conditions (Table 2). As expected, polyaddition at lower concentration (0.1 M) gave a polymer having a lower M_n (8600, run 1) in comparison with that at higher concentrations [0.3–0.5 M (saturated)]. From

Table 4. Synthesis of Various Polymers for 5A,B with 6a–g[a]

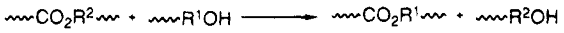
run	$HC{\equiv}CCO_2R^2O_2CC{\equiv}CH$	HOR^1OH	M_n (M_w/M_n)[b]	transesterification[c]/%
1	$CH_2C(CH_3)_2CH_2$ (**5A**)	$CH_2C_6H_4CH_2$ (**6a**)	12 800 (2.57)	<5
2		$CH_2C(CH_3)_2CH_2$ (**6b**)	7 100 (1.92)	nd[d]
3		$CH_2CH_2CH_2$ (**6c**)	4 800 (2.22)	nd[d]
4		$CH_2(CH_2)_4CH_2$ (**6d**)	5 000 (1.81)	nd[d]
5		$CH_2{\equiv}CH_2$ (**6e**)	5 800 (2.78)	14
6		$(CH_2CH_2O)_2CH_2CH_2$ (**6f**)	4 400 (2.42)	nd[d]
7		1,4-cyclohexylene (**6g**)	*e*	nd[d]
8	$CH_2C_6H_4CH_2$ (**5B**)	$CH_2C_6H_4CH_2$ (**6a**)	13 800 (2.16)	nd[d]
9		$CH_2C(CH_3)_2CH_2$ (**6b**)	7 100 (2.46)	15
10		$CH_2CH_2CH_2$ (**6c**)	5 200 (2.22)	19
11		$CH_2(CH_2)_4CH_2$ (**6d**)	4 500 (1.81)	6
12		$CH_2{\equiv}CH_2$ (**6e**)	7 500 (2.94)	22
13		$(CH_2CH_2O)_2CH_2CH_2$ (**6f**)	4 700 (2.44)	10
14		1,4-cyclohexylene (**6g**)	*e*	nd[d]

[a] Polyaddition was carried out in THF (0.5 M) at room temperature for 3 h under nitrogen using *n*-Bu_3P (20 mol %) as a catalyst. [b] Estimated by GPC (PSt, THF as an eluent). [c] Determined by ^1H-NMR (90 MHz). [d] Not determined. [e] Gelation took place.

Scheme 5



Scheme 6



the GPC analyses of the polymers obtained in runs 1 and 4 (Figure 2), the content of oligomeric products was dependent on the reaction concentration.[11]

Effect of Feed Ratio of Monomers. Polyaddition of **5A** and **6a** was carried out under various feed ratios of monomers. As summarized in Table 3, the stoichiometric condition was suitable to obtain the polymer with higher molecular weight. The molecular weights of the resulting polymers decreased in the presence of excess **6a** as is usual for polyaddition reactions. Interestingly, a gelation took place when an excess of **5A** was used. In the presence of an excess of **5A**, it is expected that a polymer having propiolate moieties as end groups will be produced, from which a cross-linking reaction might take place. To clarify this possibility, methyl propiolate was treated with tri-*n*-butylphosphine under similar conditions, and oligomers ($M_n = 530$) were obtained in 59% yield. Further, the reaction of fibunctional acetylene **5A** with a catalyst produced a gel in 49% yield. Thus, the gelation in the presence of an excess of **5A** should be due to the anionic polymerization among the terminal propiolate moieties (Scheme 5).

Rate of Polyaddition. The consumption of **5A** and **6a** and the molecular weight of the resulting polymer were monitored by GPC after the designated reaction time (Figure 3). When the reaction was carried out by using tri-*n*-butylphosphine (5 mol %) in THF (0.3 M), both monomers were consumed completely within 1 min and the molecular weight of the polymer gradually increased until reaction for 30 min. The fast consumption of the monomer and the gradual increase of the molecular weight of the polymer can be represented by the usual polyaddition process.

Polyaddition with Various Diols. Polyadditions were carried out by using various acetylene monomers (**5A** and **5B**) and diols (**6a–g**). From the diols containing primary alcohol moieties, the corresponding polymers were obtained in almost quantitative yield (Table 4). Although the ester groups in the main chain were partially transesterificated with the diol monomers used, as shown in Scheme 6, soluble polymers containing only *E* geometric units and quantitative contents of double bonds were obtained. Among the obtained polymers, **7Aa**, **7Ae**, **7Ba**, **7Bb**, and **7Be** showed better film-forming character when cast from dichloromethane solution. On the other hand, gels were obtained when a secondary diol (**6g**) was used (runs 7 and 14). The gelation may take place by the anionic chain propagation of acetylene moieties, as mentioned above (in the section on the effect of feed ratio). That is, secondary alcohols are known to have rather poor proton-donating ability, which may enhance the chain polymerization of the acetylene moieties initiated by zwitterionic phosphonium intermediates.

As the polymers obtained by the present polyaddition have novel β-alkoxyenoate moieties in the main chain, unique reactivites as well as degradabilities may be expected, which are currently being investigated.

References and Notes

(1) (a) Kobayashi, E.; Metaka, N.; Aoshima, S.; Furukawa, J. *J. Polym. Sci., Part A* **1990**, *28*, 2461. (b) Kobayashi, E.; Jiang, J.; Ohta, H.; Furukawa, J. *J. Polym. Sci., Polym. Chem. Ed.* **1992**, *30*, 227. (c) Kobayashi, E.; Obata, T.; Aoshima, S.; Furukawa, J. *Polym. Prepr. Jpn.* **1990**, *37*, 1648. (d) Chujo, Y.; Tomita, I.; Hashiguchi, Y.; Saegusa, T. *Macromolecules* **1992**, *25*, 33. (e) Luneva, L. K.; Sladlov, A. M.; Korshak, V. V. *Vysokomol. Soedin.* **1965**, *7*, 427.

(2) Sato, E.; Yokozawa, T.; Endo, T. *Chem. Lett.* **1993**, 1113.

(3) Inanaga, J.; Baba, Y.; Hanamoto, T. *Chem. Lett.* **1993**, 241.

(4) We have tried sodium hydride-catalyzed polyaddition of **5A** with **6a** to compare with the phosphine-catalyzed system. Although a polymer ($M_n = 5000$) was also obtained in high yield in the case of the sodium hydride-catalyzed system, the structure of the polymer was contaminated with a moderate amount of transesterifcated and unknown units.

(5) The small peaks at 1–2 ppm can be attributed to the alkyl groups in tri-*n*-butylphosphine used as a catalyst, which can be also detected by the ^{31}P NMR spectrum. The intensities of these peaks were affected by the precipitation conditions, indicating that tri-*n*-butylphosphine is not included in the structure of the polymer.

(6) (a) Dykstra, C. E.; Arduengo, A. J.; Fukunaga, T. *J. Am. Chem. Soc.* **1978**, *100*, 6007. (b) Strozier, R. W.; Caramella, P.; Houk, K. N. *J. Am. Chem. Soc.* **1979**, *101*, 1340. (c) Caramella, P.; Houk, K. N. *Tetrahedron Lett. 22*, 819. (d) Houk, K. N. *J. Am. Chem. Soc.* **1982**, *104*, 323.

(7) Huisgen, R.; Herbig, K.; Siegel, A.; Huber, H. *Chem. Ber.* **1966**, *99*, 2526.

(8) (a) Winterfeldt, E.; Preuss, H. *Chem. Ber.* **1966**, *99*, 450. (b) Winterfeldt, E.; Preuss, H. *Chem. Ber.* **1966**, *99*, 2572.

(9) (a) Truce, W. E.; Gorbaty, M. L. *J. Org. Chem.* **1970**, *35*, 211. (b) Lodder, G.; Van Dorp, J. W. J.; Avramovitch, B.; Rappoport, Z. *J. Org. Chem.* **1989**, *54*, 2574.

(10) The oxidation reaction of the phosphine catalyst and/or the anionic polymerization of acetylene moieties initiated by phosphine might be a part of possible side reactions.

(11) The oligomeric products may contain macrocyclic products as the result of intramolecular cyclization.

MA9411080