

A novel polyaddition of bifunctional acetylenes containing electron-withdrawing groups: 4. Synthesis of polymers having enone moieties by the reaction of ynones with bifunctional heteronucleophiles

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Phosphine-catalysed polyaddition of bifunctional ynones with diols or with dithiols is described. By the tri-*n*-butylphosphine-catalysed polyaddition of aromatic bis(ynone) having benzene ring as a spacer (without methylene group adjacent to carbonyl groups) or aliphatic bis(ynone) having octamethylene group as a spacer with *p*-xylene glycol, polymers having β -alkoxyenone moieties in the main chain were obtained in high yield. The polyaddition of the aromatic bis(ynone) gave a polymer composed of specifically *E*-unit, while that of the aliphatic bis(ynone)s produced a polymer containing both *E*- and *Z*-units. Further, the polyaddition with dithiols with bifunctional ynones was also carried out under similar conditions to yield the corresponding polymer composed of both *E*- and *Z*-units in almost quantitative yield. © 1997 Elsevier Science Ltd.

(Keywords: polyaddition; tri-*n*-butylphosphine; bis(ynone)s)

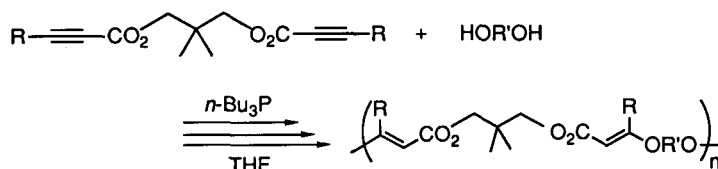
INTRODUCTION

Conjugate additions of heteronucleophiles toward unsaturated compounds activated with electron-withdrawing groups have been applied to the synthesis of various kinds of polymers having various functional groups¹. In spite of potential reactivities and functions of the resulting polymers, there are a few reports using diacetylenic compounds having electron-withdrawing groups as monomers².

Previously, we have reported the polyaddition of bifunctional propiolate with diols^{3,4}. The polyaddition proceeds smoothly in the presence of tri-*n*-butylphosphine as a catalyst to give polymers having β -alkoxyenoate moieties in the main chain (only composed of *E*-unit, Scheme 1). Because the polyaddition may proceed by the

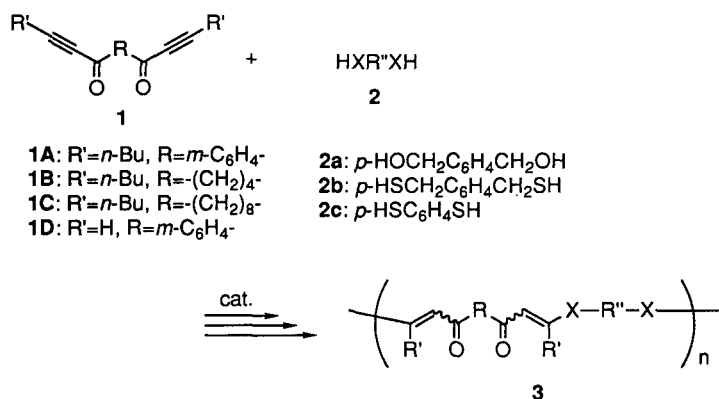
addition of the phosphine catalyst, the protonation, followed by the addition–elimination reaction, the polyaddition behaviour is expected to be dependent on both the structure of diacetylenic monomers and bifunctional heteronucleophiles used. The remarkable differences between dithiols and diols in the polyaddition were observed when dithiols were used as a monomer in comparison with diols. That is, the polyaddition with dithiols proceeds more smoothly to obtain polymers with higher molecular weights⁵. Further, the geometric selectivity of β -alkylmercaptoenoate moieties in the main chain was found to be dependent on the acidity of the used dithiols.

Based on the reported results, acyl groups may activate more strongly than ester moieties. Thus, bis(ynone)s might be served as more reactive monomers



Scheme 1

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Scheme 2

than bispropiolate for the polyaddition. Further, the resulting polymers are expected to have higher reactivity originated from enone moieties and photo-degradable functions based on carbonyl groups in the main chain. Polymers having analogous structure have been obtained by a polycondensation via the vinylogous nucleophilic substitution polymerization of bifunctional β -chloro-enones with dithiols⁶. However, this method may have difficulties in the designed synthesis of enone monomers. Herein, we wish to describe a phosphine-catalysed polyaddition of bifunctional ynones (**1A–D**) with *p*-xylylene glycol (**2a**) or dithiols (**2b–c**) (Scheme 2).

EXPERIMENTAL

Materials and instruments

Tetrahydrofuran (THF) was dried over sodium benzophenone ketyl and distilled under nitrogen. Pyridine and triethylamine were dried over calcium hydride and then purified by distillation. **2b**, **2c**, benzyl alcohol, and tri-*n*-butylphosphine were purified by distillation under reduced pressure. **2a** was purified by recrystallization from ethyl acetate and dried *in vacuo*. Triphenylphosphine was purified by recrystallization from ethyl acetate and dried *in vacuo*.

Infrared (i.r.) spectra were obtained with a JASCO FT/IR 5300 i.r. spectrophotometer. ¹H and ¹³C n.m.r. spectra were recorded on JNM-EX90, or 400 spectrometers in CDCl₃ (tetramethylsilane as an internal standard). Mass-spectra were obtained by the EI method by using a Hitachi M-80 mass spectrometer. Gel permeation chromatographic analyses (g.p.c.) were performed on a Tosoh HLC 8020 (TSKgel G5000HXL, G4000HXL, G3000HXL, and G2500HXL, THF as eluent).

Synthesis of monomers. 1,3-Bis(2-heptynoyl)benzene (**1A**)

1A was prepared by modification of the method described in the literature⁷. To a solution of 1-hexyne (10.0 g, 122 mmol) in THF (64 ml) was added dropwise *n*-butyllithium (1.65 M in hexane, 73.9 ml, 122 mmol) at -30°C under nitrogen. After 30 min, a solution of zinc chloride (16.6 g, 122 mmol) in THF (43 ml) was added, and then the temperature of the mixture was allowed to rise to 0°C. To the mixture was added tetrakis(triphenylphosphine)palladium (0.70 g, 0.610 mmol) and a solution of isophthaloyl dichloride (12.4 g, 61.1

mmol) in THF (30 ml) dropwise over a few min, while keeping the temperature between 0 and 5°C. After additional 20 min at 25°C, 200 ml of hexane was added and the mixture was poured into a saturated aqueous solution of ammonium chloride. After vigorous stirring, the layers were separated and the aqueous layer was extracted once with 100 ml of ethyl acetate. The combined organic solution was washed four times with 150 ml portions of a saturated aqueous solution of ammonium chloride and subsequently 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 9.51 g (32.3 mmol, 53.0%) of **1A**. *R*_f = 0.63 on t.l.c. (SiO₂, hexane/ethyl acetate = 4/1); i.r. (neat) 2959, 2872, 2205, 1649, 1298, 1225 cm⁻¹; ¹H n.m.r. (90 MHz, δ , ppm) 0.98 (*t*, *J* = 6.66 Hz, 6H, CH₃CH₂-), 1.20–2.00 (8H, -CH₂-), 2.54 (*t*, *J* = 6.62 Hz, 4H, -CH₂C \equiv C-), 7.60 (*t*, *J* = 7.92 Hz, 1H, -C₆H₄-), 8.34 (*dd*, *J* = 1.53 and 7.74 Hz, 2H, -C₆H₄-), 8.87 (*t*, *J* = 1.53 Hz, 1H, -C₆H₄-); ¹³C n.m.r. (22.5 MHz, δ , ppm) 13.6, 19.0, 22.2, 29.9, 79.6, 98.0, 128.9, 130.8, 134.2, 137.4, 177.2; m.s. (EI) *m/z* 294 (M⁺).

5,13-Octadecadiyn-7,12-dione (**1B**)

1B was prepared by modification of the method described in the literature⁸. To a solution of 1-hexyne (4.48 g, 54.6 mmol) in THF (30 ml) was added dropwise *n*-butyllithium (1.65 M in hexane, 33.1 ml, 54.6 mmol) at -30°C under nitrogen. After 30 min, a solution of zinc chloride (7.43 g, 54.6 mmol) in THF (20 ml) was added, and the temperature of the mixture was allowed to rise to 0°C. A solution of adipoyl dichloride (5.00 g, 27.3 mmol) in THF (13 ml) was added dropwise over a few min, maintaining between 5 and 10°C. After the addition, the cooling bath was removed and the temperature was allowed to rise to ambient temperature. Stirring was continued for an additional 1 h at room temperature, then the mixture was poured into a saturated aqueous solution of ammonium chloride. After vigorous stirring, the layers were separated and the aqueous layer was extracted three times with 30 ml portions of ethyl acetate. The combined organic solution was washed with 50 ml portions of a saturated aqueous solution of ammonium chloride four times and subsequently 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 3.06 g

(11.2 mmol, 40.9%) of **1B**. $R_f = 0.60$ on t.l.c. (SiO₂, hexane/ethyl acetate = 4/1); i.r. (neat) 2959, 2872, 2213, 1674, 1460 cm⁻¹; ¹H n.m.r. (90 MHz, δ , ppm) 0.93 (*bt*, $J = 6.57$ Hz, 6H, CH₃CH₂-), 1.20–2.00 (12H, -CH₂-), 2.37 (*t*, $J = 6.57$ Hz, 4H, -CH₂C≡C-), 2.55 (*bt*, $J = 6.84$ Hz, 4H, -CH₂CO-); ¹³C n.m.r. (22.5 MHz, δ , ppm) 13.4, 18.6, 21.9, 23.3, 29.7, 45.1, 80.8, 94.5, 187.6; m.s. (EI) m/z 274 (M⁺)

Similarly, 5,17-docosadiyn-7,16-dione (**1C**) was obtained in 67.5% yield: $R_f = 0.62$ on t.l.c. (SiO₂, hexane/ethyl acetate = 4/1); i.r. (neat) 2934, 2861, 2213, 1674, 1464 cm⁻¹; ¹H n.m.r. (90 MHz, δ , ppm) 0.93 (*bt*, $J = 6.57$ Hz, 6H, CH₃CH₂-), 1.20–2.00 (20H, -CH₂-), 2.37 (*t*, $J = 6.57$ Hz, 4H, -CH₂C≡C-), 2.52 (*t*, $J = 7.29$ Hz, 4H, -CH₂CO-); ¹³C n.m.r. (22.5 MHz, δ , ppm) 13.4, 18.6, 21.9, 24.0, 28.8, 29.0, 29.7, 45.4, 80.9, 94.1, 188.3; m.s. (EI) m/z 274 (M⁺) 330.

1,3-Bis(1-propynoyl)benzene (**1D**)

1D was prepared in two steps: to a solution (224 mmol) of ethynylmagnesium bromide⁸ in THF (260 ml) was added slowly a solution of isophthalaldehyde (15.0 g, 112 mmol) in THF (120 ml). After 30 min, the reaction mixture was poured into 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 ether. The organic extracts were combined with the first organic layer and the combined extract was dried over magnesium sulfate. After the evaporation of the solvent, the residue was purified by column chromatography on silica gel (hexane/ethyl acetate = 10/1) to give 15.2 g (81.7 mmol, 72.0%) of 1,3-bis(1-hydroxypropynyl)benzene: $R_f = 0.10$ on t.l.c. (SiO₂, hexane/ethyl acetate = 2/1); i.r. (neat) 3358, 2874, 2118, 1690, 1605 cm⁻¹; ¹H n.m.r. (90 MHz, δ , ppm) 2.58 (*br*, 1H, -OH), 2.67 (*d*, $J = 2.43$ Hz, 1H, HC≡C), 5.45 (*d*, $J = 2.25$ Hz, 1H, -CH(OH)-), 7.1–8.0 (4H, -C₆H₄-).

To a mixture of acetone (140 ml), water (43 ml), and concentrated sulfuric acid (15.9 g) was added 1,3-bis(1-hydroxypropynyl)benzene (13.1 g, 70.4 mmol) at 10°C. A solution of chromium(VI) oxide (10.1 g, 101 mmol) in water (34 ml) was added dropwise over 40 min, maintaining the temperature between 10 and 15°C. After 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 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 purified by column chromatography on silica gel (hexane/ethyl acetate = 15/1) to give 7.50 g (41.2 mmol, 58.6%) of **1D**: $R_f = 0.29$ on t.l.c. (SiO₂, hexane/ethyl acetate = 4/1); i.r. (KBr) 3227, 2101, 1638, 1597, 1208 cm⁻¹; ¹H n.m.r. (90 MHz, δ , ppm) 3.57 (*s*, 1H, HC≡C), 7.67 (*dt*, $J = 0.45$ and 7.29 Hz, 1H, -C₆H₄-), 8.41 (*dd*, $J = 1.71$ and 1.71 Hz, 2H, -C₆H₄-), 8.91 (*dt*, $J = 0.45$ and 1.80 Hz, 1H, -C₆H₄-); ¹³C n.m.r. (22.5 MHz, δ , ppm) 79.8, 81.9, 129.3, 130.8, 134.7, 136.6, 176.1.

Model reactions. Typical procedure

To a solution of **1A** (213 mg, 0.724 mmol) and benzyl alcohol (156 mg, 1.44 mmol) in THF (1.4 ml) was added tri-*n*-butylphosphine (29 mg, 0.144 mmol) at room temperature. After stirring for 12 h, the reaction mixture was

concentrated under vacuum. The residue was purified by column chromatography on silica gel (hexane/ethyl acetate = 20/1) to give 322 mg (0.631 mmol, 87.3%) of 1,3-bis(3-benzyloxy-2E-heptenoyl)benzene (**4A**); $R_f = 0.54$ on t.l.c. (hexane/ethyl acetate = 4/1); i.r. (neat) 3065, 3034, 2957, 2870, 1657, 1568 cm⁻¹; ¹H n.m.r. (90 MHz, δ , ppm) 0.95 (*bt*, $J = 6.39$ Hz, 6H, CH₃CH₂-), 1.2–2.0 (8H, -CH₂-), 2.94 (*t*, $J = 7.38$ Hz, 4H, -CH₂(BnO)C=), 5.01 (*s*, 10H, C₆H₅CH₂-), 6.25 (*s*, 2H, =CH-), 7.40 (*s*, 5H, C₆H₅-), 7.49 (*t*, $J = 8.19$ Hz, 1H, -C₆H₄-), 7.98 (*dd*, $J = 1.53$ and 8.19 Hz, 2H, -C₆H₄-), 8.39 (*t*, $J = 1.53$ Hz, 1H, -C₆H₄-); ¹³C n.m.r. (100 MHz, δ , ppm) 13.9, 22.7, 29.6, 32.9, 70.4, 96.9, 126.7, 127.5, 128.3, 128.5, 128.7, 130.8, 135.5, 140.7, 178.1, 189.4; m.s. (EI) m/z 510 (M⁺).

Similarly, the adduct (**4D**) was prepared as follows.

1,3-Bis(3-benzyloxy-2E-propenoyl)benzene (**4D**)

Yield 41.7%; $R_f = 0.10$ on t.l.c. (hexane/ethyl acetate = 4/1); i.r. (neat) 3065, 3034, 2934, 1663, 1601, 1580, 1316, 1148 cm⁻¹; ¹H n.m.r. (400 MHz, δ , ppm) 5.05 (*s*, 4H, C₆H₅CH₂-CH₂CO₂Me), 6.50 (*d*, $J = 12.0$ Hz, 2H, BnOCH=CHCO-), 7.41 (*m*, 10H, C₆H₅CH₂-), 7.54 (*t*, $J = 7.80$ Hz, 1H, -C₆H₄-), 7.88 (*d*, $J = 12.0$ Hz, 2H, BnOCH=CHCO-), 8.05 (*d*, $J = 7.60$ Hz, 2H, -C₆H₄-), 8.37 (*s*, 1H, -C₆H₄-); ¹³C n.m.r. (100 MHz, δ , ppm) 74.0, 102.7, 126.9, 127.6, 127.8, 128.5, 128.8, 134.6, 135.0, 138.9, 164.2, 189.7.

Polyadditions. Typical procedure

A polyaddition of **1A** with **2a** was carried out as follows: to a THF (1.6 ml) solution of **1A** (184 mg, 0.626 mmol) and **2** (86 mg, 0.626 mmol) was added tri-*n*-butylphosphine (63 mg, 0.312 mmol) at ambient temperature. After stirring for 3 h, the reaction mixture was diluted with THF (3.4 ml) and was poured into hexane (100 ml). The precipitate was filtered and was dried under vacuum. **3Aa**: 192 mg (71.1%); i.r. (neat) 2957, 2932, 2870, 1655, 1566, 1157, 1101 cm⁻¹; ¹H n.m.r. (90 MHz, δ , ppm) 0.95 (*bt*, $J = 6.39$ Hz, 6H, CH₃CH₂-), 1.10–2.00 (8H, -CH₂-), 2.94 (*bt*, $J = 7.29$ Hz, -CH₂CH=), 5.04 (*s*, 4H, -C₆H₄CH₂O-), 6.28 (*s*, 2H, =CH-), 7.41 (*s*, 4H, -C₆H₄-), 7.2–7.8 (1H, *m*-COC₆H₄CO-), 7.99 (*d*, $J = 7.74$ Hz, 2H, *m*-COC₆H₄CO-), 8.43 (*s*, 1H, *m*-COC₆H₄CO-); ¹³C n.m.r. (100 MHz, δ , ppm) 13.9, 22.7, 29.7, 32.9, 70.0, 96.9, 126.8, 127.4, 127.6, 127.9, 128.5, 130.9, 135.7, 140.6, 178.0, 189.3.

Similarly, other polymers (**3Ca**, **3Ab**, and **3Ac**) were prepared as follows:

3Ca (from **1C** and **2a**): Yield 84.4%; i.r. (neat) 2930, 2859, 1678, 1586, 1462, 1429, 1375 cm⁻¹; ¹H n.m.r. (90 MHz, δ , ppm) 0.98 (*bt*, $J = 6.66$ Hz, 6H, CH₃CH₂-), 1.00–2.00 (20H, -CH₂-), 2.40 (*bt*, $J = 6.39$ Hz, 4H, -CH₂(-CH₂O)C=), 2.80 (*bt*, $J = 7.47$ Hz, 4H, -CH₂CO-), 4.86 (*s*, 4H, -OCH₂C₆H₄-), 5.11 (*s*, Z=CHCO-), 5.52 (*s*, E=CHCO-), 7.39 (*s*, 4H, -C₆H₄-), E/Z = 87/13; ¹³C n.m.r. (100 MHz, δ , ppm) 13.8, 22.5, 24.7, 29.2, 29.6, 32.3, 69.5, 99.6, 127.8, 135.8, 175.1, 199.3.

3Ab (from **1A** and **2b**): Yield 96.0%; i.r. (neat) 2959, 2930, 2870, 1645, 1593, 1549, 1188 cm⁻¹; ¹H n.m.r. (90 MHz, δ , ppm) 0.94 (*bt*, $J = 6.66$ Hz, 6H, CH₃CH₂-), 1.00–2.00 (8H, -CH₂-), 2.63 (*br*, Z-CH₂(-CH₂S)C=), 2.89 (*br*, E-CH₂(-CH₂S)C=), 4.12 (*s*, 4H, -SCH₂C₆H₄-), 6.63 (*s*, E=CHCO-), 7.02 (*s*, Z=CHCO-), 7.20–7.75 (5H, -C₆H₄-, *m*-COC₆H₄CO-), 7.84 (*d*, $J = 7.74$ Hz,

E-m-COC₆H₄CO-), 8.05 (*d*, $J = 7.74$ Hz, *Z-m-COC₆H₄CO-*), 8.39 (*br*, 1H, *m-COC₆H₄CO-*), $E/Z = 69:31$; ¹³C n.m.r. (22.5 MHz, δ , ppm) 13.8, 22.0, 22.3, 22.7, 32.0, 32.3, 34.8, 35.1, 36.4, 113.1, 115.9, 127.2, 128.6, 129.1, 129.3, 129.6, 131.1, 134.0, 134.4, 135.9, 138.9, 139.9, 140.0, 167.1, 186.2, 187.3.

3Ac (from **1A** and **2c**): Yield 100.0%; i.r. (neat) 3063, 2957, 2930, 1637, 1534, 1470, 1194 cm⁻¹; ¹H n.m.r. (90 MHz, δ , ppm) 0.45–2.00 (14H, CH₃CH₂CH₂-), 2.31 (*br*, *Z-CH₂(-S)C=*), 2.93 (*br*, *E-CH₂(-S)C=*), 6.45 (*br*, *E=CHCO-*), 7.16 (*br*, *Z=CHCO-*), 7.20–8.70 (8H, *m-COC₆H₄CO-*, -C₆H₄-), $E/Z = 36/64$; ¹³C n.m.r. (100 MHz, δ , ppm) 13.6, 13.8, 21.9, 22.0, 22.7, 25.2, 31.9, 33.7, 33.9, 37.0, 115.8, 116.2, 127.4, 128.8, 128.9, 131.0, 131.5, 131.8, 132.4, 133.1, 133.8, 135.7, 136.0, 136.5, 136.7, 138.7, 139.3, 139.6, 165.3, 167.0, 186.8, 187.7.

3Bc (from **1B** and **2c**): Yield 98.4%; i.r. (neat) 2957, 2932, 2870, 1667, 1562, 1466, 1360 cm⁻¹; ¹H n.m.r. (90 MHz, δ , ppm) 0.72 (*bt*, $J = 6.03$ Hz, 6H, CH₃CH₂-), 0.80–1.95 (12H, -CH₂-), 2.17 (*br*, 4H, -COCH₂-), 2.55 (*br*, *Z-CH₂(-CH₂S)C=*), 2.80 (*br*, *E-CH₂(-CH₂S)C=*), 5.65 (*s*, *E=CHCO-*), 6.34 (*s*, *Z=CHCO-*), 7.53 (*s*, 4H, -C₆H₄-), $E/Z = 21/79$; ¹³C n.m.r. (22.5 MHz, δ , ppm) 13.6, 13.9, 22.0, 22.6, 24.1, 24.5, 29.1, 29.3, 31.6, 31.8, 33.4, 36.3, 36.4, 43.3, 44.3, 118.5, 118.7, 119.6, 119.8, 131.7, 132.2, 133.0, 133.6, 135.6, 135.9, 136.2, 136.6, 160.0, 160.3, 163.7, 197.3, 199.0.

3Cc (from **1C** and **2c**): Yield 92.3%; i.r. (neat) 2930, 2857, 1670, 1564, 1466, 1356 cm⁻¹; ¹H n.m.r. (90 MHz, δ , ppm) 0.72 (*bt*, $J = 6.39$ Hz, 6H, CH₃CH₂-), 0.80–1.95 (20H, -CH₂-), 2.15 (*br*, 4H, -COCH₂-), 2.45 (*t*, $J = 7.02$ Hz, *Z-CH₂(-CH₂S)C=*), 2.81 (*t*, $J = 7.29$ Hz, *E-CH₂(-CH₂S)C=*), 5.63 (*s*, *E=CHCO-*), 6.32 (*s*, *Z=CHCO-*), 7.53 (*s*, 4H, -C₆H₄-), $E/Z = 33/67$; ¹³C n.m.r. (22.5 MHz, δ , ppm) 13.1, 13.6, 13.8, 22.0, 22.1, 22.3, 22.6, 23.5, 23.7, 23.8, 24.1, 31.6, 31.8, 33.5, 36.3, 36.4, 43.0, 44.0, 118.4, 118.6, 119.0, 119.6, 119.7, 131.6, 132.2, 133.5, 135.6, 136.0, 136.2, 136.6, 160.4, 160.6, 164.0, 196.7, 198.3, 198.5.

RESULTS AND DISCUSSION

Model reaction

The model reaction of bis(ynone)s (**1A** and **1D**) with benzyl alcohol was carried out in THF for 12 h at ambient temperature using amines or phosphines as a catalyst (Scheme 3). In the case of a terminal ynone (**1D**) (Table 1, runs 1–3), the trialkylphosphine was effective to obtain adduct (**4D**) (run 3). However, the yields were rather low in the case of **1D** because of the formation of oligomeric side-products which were probably produced by the anionic chain reaction of ynone

moieties. A substituted ynone (**1A**) gave a better result by using tri-*n*-butylphosphine (run 6). In the case of triphenylphosphine (run 5), the α,γ -dienone which resulted from the isomerization of the ynone was found to be a major product^{9,10}.

Polyaddition

Polyaddition of **1A** with *p*-xylene glycol (**2a**) was carried out in THF (0.4 M) at room temperature for 8 h in the presence of tri-*n*-butylphosphine (20 mol%) to obtain the polymer having β -alkoxyenone moieties in the main chain in 72% yield. The number average molecular weight (M_n) and the molecular weight distribution (M_w/M_n) were estimated to be 5900 and 1.28, respectively (g.p.c., PSt).

The structure of the obtained polymer (**3Aa**) was identified by ¹H, ¹³C, and i.r. analyses. From the ¹H n.m.r. spectrum, a signal of olefinic protons in the main chain was observed at 6.27 ppm (Figure 1)¹¹. Thus, the geometry of the β -alkoxyenone moieties were confirmed to be only *E*-isomer, similar to the polyaddition of propiolates with diols^{3,4}. The double bonds were detected quantitatively from the integral ratio between the peak and other ones. Thus, any side reactions induced from the produced double bonds are negligible.

The molecular weight of the obtained polymer was monitored by g.p.c. after a designated reaction time (Figure 2). When the polyaddition of **1A** with **2a** was carried out in the presence of tri-*n*-butylphosphine (20 mol%) in THF (0.4 M), both monomers were consumed instantly and the increase in the molecular weight of the polymer was completed within 30 min. Because the internal bis(ynoate) monomers required 6 h to complete the polymerization with **2a** under similar conditions⁴, bis(ynone)s were found to have much higher polymerizability in comparison with bis(ynoate) systems.

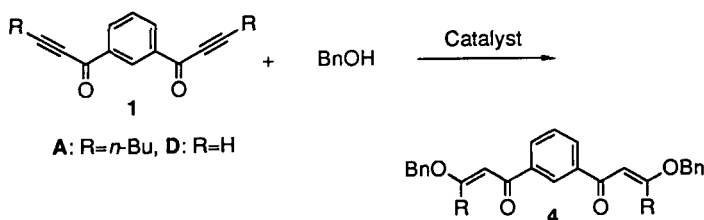
Table 1 Addition of benzyl alcohol (BnOH) to bisynones (**1A**, **1D**)^a

Run	R	Catalyst	Yield (%)
1	H	C ₂ H ₅ N	0 ^b
2		Ph ₃ P	37
3		<i>n</i> -Bu ₃ P	42
4	<i>n</i> -Butyl	Et ₃ N	0 ^b
5		Ph ₃ P	- ^c
6		<i>n</i> -Bu ₃ P	87

^a Reaction was carried out in THF (0.5 M) at r.t. for 12 h under nitrogen using a catalyst (20 mol%)

^b Bisynone was recovered quantitatively

^c A mixture containing β -alkoxyenone and α,γ -dienone moieties (isomerized product of ynone) was obtained (Y. 18 and 63%, respectively, from ¹H n.m.r.)



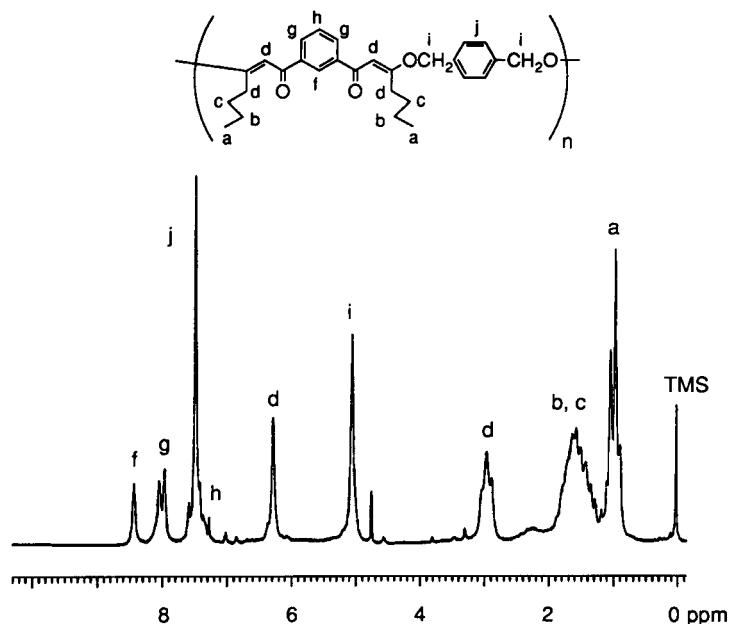


Figure 1 1H n.m.r. spectrum of 3Aa

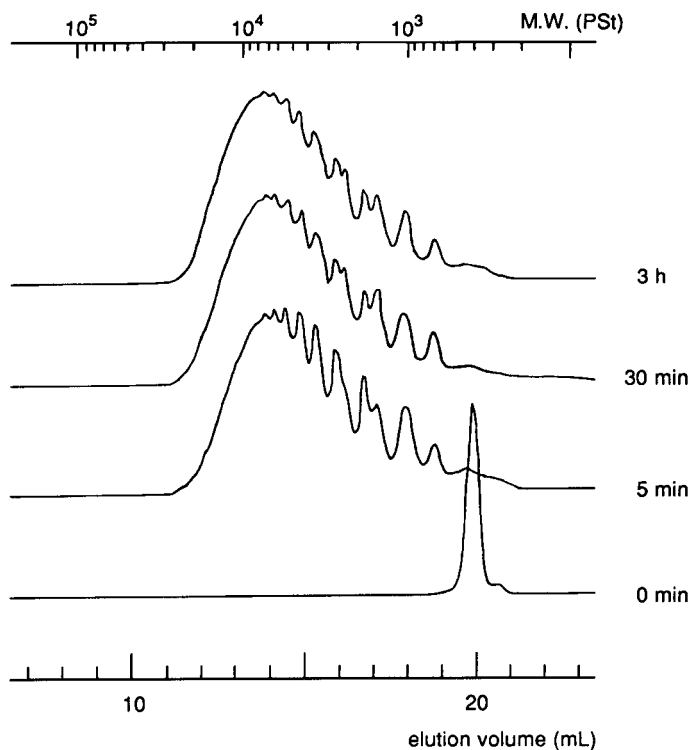


Figure 2 G.p.c. traces for the polymerization of 1A with 2a after designated reaction time

Polymerization conditions

The polyaddition of 1A with 2a was carried out in the presence of various concentrations of the catalyst (ranging from 5 to 80 mol%, Table 2). When 5 mol% of the catalyst was used, oligomers and 1A were obtained as a soluble part in hexane. This might be due to some side reactions that deactivated the phosphine catalyst, similar to the case of bis(ynoate) monomers^{3,4}. However, the polyaddition proceeded smoothly by using more than 10 mol% of the catalyst. Similar to the results obtained in

polyaddition of bis(ynoate) with diols^{3,4} or dithiols⁵, the higher concentration of catalyst was found to be suitable to obtain polymers with higher molecular weights.

The polyaddition of 1A with 2a was examined by varying concentrations of two monomers keeping the stoichiometric conditions (Table 3). Although the molecular weight and the yield were rather low due to the formation of oligomers at lower concentrations (0.1 M), the polyaddition at higher concentrations, gave the polymer having higher molecular weight in higher yields¹⁰.

Table 2 Effect of the concentration of the catalyst on the polyaddition of **1A** with **2a**^a

Run	<i>n</i> -Bu ₃ P (mol%)	Yield ^b /%	<i>M_n</i> (<i>M_w</i> / <i>M_n</i>) ^c
1	5	0	—
2	10	62	4900 (1.31)
3	20	72	5900 (1.28)
4	50	71	7000 (1.30)
5	80	74	6700 (1.29)

^a Polyaddition was carried out in THF (0.4 M) at room temperature for 3 h under nitrogen using *n*-Bu₃P as a catalyst

^b Isolated yield after precipitation with MeOH

^c Estimated by g.p.c. (PSt, THF as an eluent)

Table 3 Effect of the concentration of two monomers under stoichiometric concentrations^a

Run	Conc./M	Yield ^b /%	<i>M_n</i> (<i>M_w</i> / <i>M_n</i>) ^c
1	0.1	54	5500 (1.22)
2	0.2	67	5800 (1.26)
3	0.3	66	5900 (1.27)
4	0.4	71	7000 (1.30)
5	0.5 ^d	77	6600 (1.28)

^a Polyaddition was carried out in THF at room temperature for 3 h under nitrogen using *n*-Bu₃P (50 mol%) as a catalyst.

^b Isolated yield after precipitation with MeOH

^c Estimated by g.p.c. (PSt, THF as an eluent)

^d Saturated concentration of **2a**

Table 4 Effect of the feed ratio of monomers (**1A/2a**)^a

Run	Feed ratio 1A : 2a	Yield ^b /%	<i>M_n</i> (<i>M_w</i> / <i>M_n</i>) ^c
1	1.0 : 1.3	61	5100 (1.21)
2	1.0 : 1.2	65	5400 (1.23)
3	1.0 : 1.1	73	6200 (1.28)
4	1.0 : 1.0	71	7000 (1.30)
5	1.1 : 1.0	81	7500 (1.39)
6	1.2 : 1.0	83	7700 (1.44)
7	1.3 : 1.0	74	6300 (1.57)

^a The polymerization was carried out in THF (0.4 M) at room temperature for 8 h under nitrogen with *n*-Bu₃P (50 mol%)

^b Isolated yield after precipitation with MeOH

^c Estimated by g.p.c. (PSt, THF as an eluent)

Table 5 Polyaddition of various ynones with diol or dithiols

Run	R in (<i>n</i> -BuC≡CCO) ₂ R	X in <i>p</i> -HXC ₆ H ₄ XH	Yield ^c /%	<i>M_n</i> (<i>M_w</i> / <i>M_n</i>) ^e	<i>E</i> : <i>Z</i> ^f
1 ^a	<i>m</i> -C ₆ H ₄ - (1A)	-CH ₂ O- (2a)	70 ^d	7000 (1.30)	100 : 0
2 ^a	{CH ₂ } ₄ (1B)	-CH ₂ O- (2a)	0	—	—
3 ^a	{CH ₂ } ₈ (1C)	-CH ₂ O- (2a)	84	6800 (1.45)	87 : 13
4 ^b	<i>m</i> -C ₆ H ₄ - (1A)	-CH ₂ S- (2b)	96	10 800 (1.77)	69 : 31
5 ^b	<i>m</i> -C ₆ H ₄ - (1A)	-S- (2c)	100	18 100 (2.33)	36 : 64
6 ^b	{CH ₂ } ₄ (1B)	-S- (2c)	98	15 100 (1.72)	23 : 67
7 ^b	{CH ₂ } ₈ (1C)	-S- (2c)	92	20 100 (1.87)	36 : 64

^a The polyaddition was carried out in THF (0.4 M) at room temperature for 3 h under nitrogen with *n*-Bu₃P (50 mol%)

^b The polyaddition was carried out in THF (0.5 M) at room temperature for 1 h under nitrogen with *n*-Bu₃P (20 mol%)

^c Isolated yield after precipitation with hexane

^d Isolated yield after precipitation with MeOH

^e Estimated by g.p.c. (PSt, THF as an eluent)

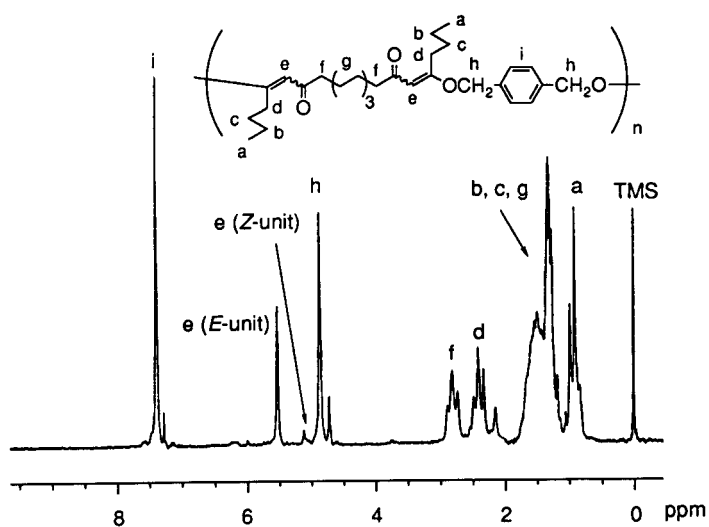
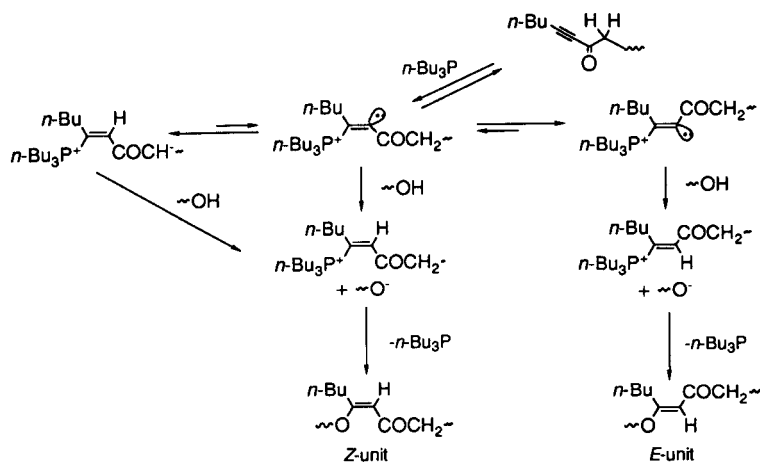
^f Determined by ¹H n.m.r. (90 MHz)

The polyaddition between **1A** and **2a** was performed under various feed ratios of two monomers (Table 4). The molecular weight of the resulting polymers decreased in the presence of excess **2a** as is usual for the polyadditions. However, the molecular weight did not decrease by using a slightly excess amount of **1A**, similar to the polyaddition of internal ynoate⁴. The result might be explained by the anionic chain reaction of end-ynone groups.

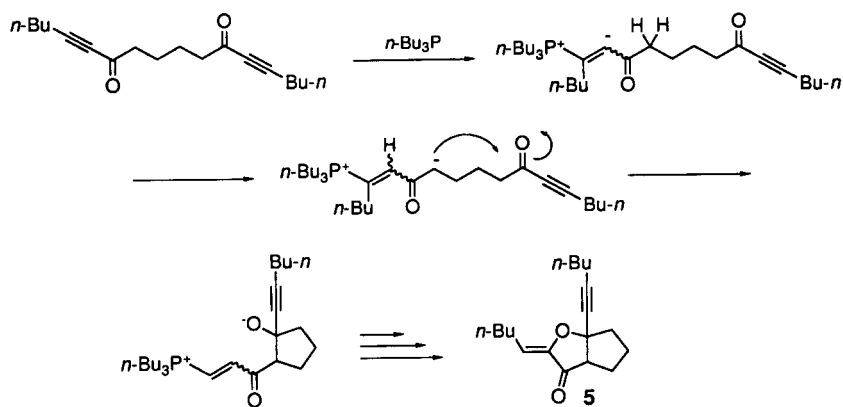
Polyaddition of various bis(ynone)s with diols or dithiols

The polyadditions of **2a** were carried out with various bis(ynone)s (**1A–C**) (Table 5). Both aromatic ynone (**1A**) and aliphatic ynone (**1C**) yielded the corresponding polymers in high yields (runs 1–3). Although the polymer (**3Aa**) composed of only *E*-unit was obtained in the case of the aromatic bis(ynone) (**1A**), the aliphatic bis(ynone) (**1C**) produced the polymer (**3Ca**) containing both *E*- and *Z*-units (87 and 13%, respectively) from ¹H n.m.r. spectrum (Figure 3)¹¹. In the polyaddition of bis(ynoate)s with dithiols⁵, the formation of *Z*-unit was found to be enhanced as the increase of acidity of the dithiols, which can be rationally explained by the more rapid protonation of zwitterionic intermediates produced by addition of the phosphine catalyst. In the present cases, the same diol (**2a**) was used for the polyaddition of both **1A** and **1C**. Thus, the rate of the protonation from hydroxyl groups should be the same. Accordingly, the difference might be originated from the bis(ynone) part. As proposed in Scheme 4, the formation of *Z*-unit can be explained by considering an intramolecular proton transfer process. The ynone moieties in **1C** possess acidic protons at the α -position of the carbonyl group, from which, the proton transfer might take place. After the intramolecular process, the reaction may proceed by the protonation with the hydroxyl group, followed by the addition–elimination reaction with the alkoxide.

By the reaction of **1B** with **2a**, the corresponding polymer (**3Ba**) was not obtained in spite of the complete conversion of **1B**. An unexpected bicyclic compound (**5**) was obtained presumably as a result of a cyclization reaction of **1B** induced by the anion generated at α -position of carbonyl group (Scheme 5)¹³. This result may support the presence of the intramolecular proton transfer process.


 Figure 3 ^1H n.m.r. spectrum of 3Ca


Scheme 4



Scheme 5

The polyaddition of dithiols (**2b–c**) with **1A** was also examined under similar conditions. Compared with the case of diols, the polyaddition proceeded more smoothly to give polymers (**3Ab** and **3Ac**) having higher molecular weights. Further, the resulting polymers contained both *E*- and *Z*-units, and the *Z*-selectivity increased as the increase in the acidity of dithiols used (runs 4 and 5), similar to the polyaddition of ynoates⁵. As proposed in the bis(ynoate)s system, the rate of the polyaddition is influenced by a protonation process in *Scheme 4*. Heteronucleophiles with higher protonation abilities, therefore, increase the rate of polymerization and *Z*-selectivity of the produced double bonds. Furthermore, the higher protonation ability of dithiols was found to suppress the side-reaction which occurred in the case of **2B** with **1a** (runs 2 vs 6).

As the polymers obtained from bis(ynone)s are composed of novel β -alkoxyenone moieties in the main chain, the unique character (e.g., reactivity, degradability, etc.) may be expected.

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11. The small peaks at 4.73 ppm can be attributed to the methylene groups adjacent to hydroxyl end-groups.
12. The oligomeric products may contain macrocyclic products as the result of intramolecular cyclization as is usual for polyaddition reactions. Thus, the intramolecular reaction might be decreased by performing the polyaddition under higher concentrations of both monomers. See ref. 3.
13. Kuroda, H., Tomita, I. and Endo, T., unpublished results.