



Radical polymerization of methacrylates having acetylenic moiety activated by electron-withdrawing group as a reactive functional group

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Received 18 March 2005; received in revised form 1 July 2005; accepted 11 July 2005
Available online 21 September 2005

Abstract

The synthesis of methacrylates having an acetylene moiety activated by an electron-withdrawing group and a radical polymerization of the methacrylates are described. The methacrylates were prepared from alkynoic acids via ω -hydroxyalkyl alkynoates in two steps. This was done by the radical polymerization of the synthesized methacrylates, polymethacrylates having the acetylene moieties activated by the electron-withdrawing group as the side-chain that were obtained in high yields. In the radical polymerization, the acetylene moiety slightly hindered the polymerization of the methacrylate moiety. The influences of the acetylene moiety decreased with the introduction of substituents at the acetylene moiety. The polymer reaction of the obtained polymer having the acetylenic side chain with thiols gave the corresponding polymers having the β -alkylmercaptoenoate moiety in high yields.

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Keywords: Radical polymerization; Methacrylates; Acetylenes; Electron-withdrawing groups; Reactive polymer

1. Introduction

Functionalized polymers are frequently synthesized by the polymer reactions of polymers having reactive functional groups [1]. In this method, the reactivity of the functional groups is one of the

important factors because the reactivity of the functional groups in the polymer is generally lower than the reactivity of the functional groups in the monomer by the steric affect and the interaction of the functional groups in the polymer. Consequently, more reactive functional groups, more active reagents, harder conditions, and so on are required in the reactions of polymers compared with those of low molecular weight compounds.

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Acetylenes activated by electron-withdrawing groups are one of the relatively highly reactive compounds, and it is known the anionic reactivity of the acetylenic compounds is higher than that of the corresponding olefins [2]. In organic synthesis, such acetylenes are the one of most important substrates and widely used as a key intermediate [3]. Therefore, acetylene moieties activated by the electron-withdrawing group are also one of the interesting reactive functional groups in the polymer synthesis. We have reported upon polymer synthesis using the high anionic reactivity of acetylene activated by electron-withdrawing as a functional group for polymerization [4]. For example, the polyaddition of bifunctional acetylenes activated by an electron-withdrawing group with diols proceeded smoothly under the mild conditions observed in the presence of trialkylphosphine as a mild catalyst to give polymers having C–C double bonds in the main chain in high to almost quantitative yields [4a,4b]. Thus, an acetylenic skeleton activated by the electron-withdrawing group might also be one of the attractive functional groups in polymer reactions.

Generally, radical additions to C–C triple bonds are much less common than such additions to C–C double bonds [5]. In fact, it is much more difficult to obtain polyacetylenes effectively by the radical polymerization of acetylenes [6]. Therefore, in a molecular design of the monomers having acetylene moieties activated by the electron-withdrawing group as a reactive functional group, the selection of methacrylates as radically polymerizable monomers may be preferable to the chemical properties of acetylenes. Thus, we have designed methacrylates (**1**) having acetylene moieties activated by the electron-withdrawing group as a novel reactive monomer. Both the property of the polymer obtained from **1**, and the radical polymerization

behavior of **1** are interesting. Herein, we wish to describe the synthesis and radical polymerization of **1** (Scheme 1).

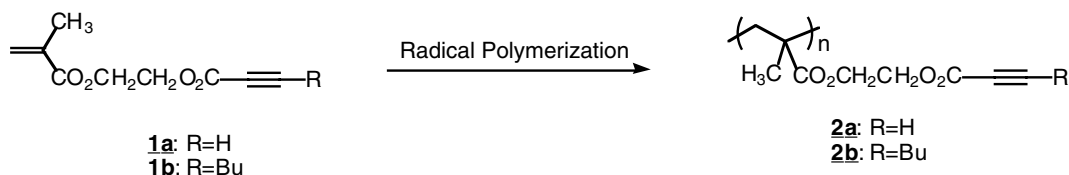
2. Experimental

Materials and instruments. Tetrahydrofuran (THF) was dried over sodium benzophenone ketyl and distilled under nitrogen. Dichloromethane and dimethylformamide (DMF) were dried over calcium hydride and then purified by distillation. Methyl methacrylate (MMA) was distilled under vacuum. Other commercially available chemicals were used without purification. Methyl 2-heptynoate was prepared from methyl chloroformate and 1-hexyne in 78% yield according to the method described in the literature [6].

The infrared (IR) spectra were obtained with a JASCO FT/IR 8000 infrared spectrometer. The ¹H- and ¹³C NMR spectra were recorded on JNM-FX90 or AL400 spectrometers, in CDCl₃ (using tetramethylsilane as an internal standard). Gel permeation chromatographic analysis (GPC) was performed on a GPC system equipped with SHODEX KF-804L and KF-80M (PSt, THF as an eluent).

2.1. 2-Heptynoic acid (**3b**)

3b was prepared by the modification of the method described in the literature [7]. *n*-Butyllithium (1.56 M in hexane, 63.0 mL, 98.3 mmol) was added dropwise to a solution of 1-hexyne (5.00 g, 61.0 mmol) in diethyl ether (40 mL) at –80 °C under nitrogen and the mixture was then stirred for 30 min at this temperature. Carbon dioxide was gently introduced into the mixture, which was kept at a temperature of between 0



Scheme 1.

and -10°C . After the exothermic reaction had ceased, the resulting solution was cautiously poured into 200 mL of ice water. The organic layer was separated and then extracted twice with 40 mL of water. To the combined aqueous layer was added concentrated hydrochloric acid in small portions with cooling in an ice bath until a pH of one had been reached. The mixture was extracted five times with 40 mL of diethyl ether. The extracts were dried over magnesium sulfate and then the drying agent was filtered off. After the evaporation of the solvents, the residue was purified by vacuum distillation to give **3b** (10.3 g, 81.8 mmol, 81%: colorless oil, bp₂ 76–79 °C); IR (neat) 2961, 2242, 1699, 1281 cm^{-1} ; ^1H NMR (90 MHz, δ , ppm) 0.89 (t, $J = 7.4$ Hz, 3H, CH_3CH_2-), 1.36–1.58 (m, 4H, $-\text{CH}_2-$), 2.33 (t, $J = 7.2$ Hz, 2H, $\text{CH}_2\text{C}\equiv\text{C}-$), 11.24 (bs, 1H, $-\text{CO}_2\text{H}$).

2.2. 2-Hydroxyethyl 2-propynoate (**4a**)

To a solution of 2-propynoic acid (3.50 g, 50.0 mmol) and ethylene glycol (46.8 mL, 755 mmol) was added *p*-toluenesulfonic acid monohydrate (1.63 g, 8.64 mmol). The mixture was stirred at 60°C for 24 h and then poured into 100 mL of saturated aqueous sodium bicarbonate. The organic layer was extracted four times with 30 mL of ethyl acetate. The combined organic layers were dried over magnesium sulfate. After the evaporation of the solvents, the residue was purified by vacuum distillation to give 3.87 g (33.9 mmol, 67.9%) of **4a** (bp_{1.0} 63–64 °C, colorless oil); IR (neat) 3400, 3266, 2962, 2120, 1715, 1455, 1372, 1246 cm^{-1} ; ^1H NMR (90 MHz, δ , ppm) 2.88 (bs, 1H, $-\text{OH}$), 2.98 (s, 1H, $\text{HC}\equiv\text{C}$), 3.80 (t, $J = 4.8$ Hz, 2H, CH_2OH), 4.22 (t, $J = 4.8$ Hz, 2H, $-\text{CO}_2\text{CH}_2-$).

2.3. 2-Hydroxyethyl 2-heptynoate (**4b**)

Similarly, **4b** (bp_{0.01} 91–93 °C, colorless oil) was synthesized from **3b** and ethylene glycol in 93.6% yield. IR (neat) 3378, 2926, 2245, 1725, 1456, 1371, 1269 cm^{-1} ; ^1H NMR (90 MHz, δ , ppm) 0.86 (t, $J = 7.4$ Hz, 3H, CH_3-), 1.32–1.54 (m, 4H, $-\text{CH}_2\text{CH}_2\text{CH}_3$), 2.28 (t, $J = 7.4$ Hz, 2H,

$-\text{CH}_2\text{C}\equiv\text{C}$), 2.37 (bs, 1H, $-\text{OH}$), 3.68 (t, $J = 5.4$ Hz, 2H, $-\text{CH}_2\text{OH}$), 4.22 (t, $J = 5.4$ Hz, 2H, $-\text{CO}_2\text{CH}_2-$).

2.4. Ethylene methacrylate propynoate (**1a**)

To a solution of **4a** (2.50 g, 21.9 mmol) and methacrylic anhydride (4.05 g, 26.3 mmol) in CH_2Cl_2 were added *p*-toluenesulfonic acid monohydrate (0.418 g, 2.19 mmol) and 4-*t*-butylcatechol (0.010 g, 0.06 mmol). The mixture was refluxed for 12 h and then poured into 10 mL of saturated aqueous sodium bicarbonate. After extraction with 10 mL of ethyl acetate three times, the combined organic layers were concentrated in a vacuum. The residue was treated with 0.1 M sodium hydroxide (50 mL) for 15 min and then the mixture was extracted three times with 20 mL of ethyl acetate. The combined organic layers were washed with 20 mL of saturated aqueous ammonium chloride, dried over magnesium sulfate and then the drying agent was filtered off. After evaporation of the solvents, the residue was purified by column chromatography on silica gel (ethyl acetate/hexane = 200:1–50:1) to obtain 2.22 g (12.2 mmol, 55.7%) of **1a** ($R_f = 0.28$, ethyl acetate/hexane = 1/4, colorless oil); IR (neat) 3258, 2963, 2122, 1719, 1638, 1455, 1229, 1165 cm^{-1} . ^1H NMR (400 MHz, δ , ppm) 1.88 (s, 3H, CH_3-), 2.90 (s, 1H, $\text{HC}\equiv\text{C}$), 4.31 (m, 2H, CO_2CH_2-), 4.39 (t, $J = 5.2$ Hz, 2H, $-\text{CO}_2\text{CH}_2-$), 5.54 (s, 1H, $\text{CH}_2=$), 6.07 (s, 1H, $\text{CH}_2=$). ^{13}C NMR (100 MHz, δ , ppm) 18.3 (CH_3-), 61.9 ($-\text{CO}_2\text{CH}_2-$), 63.6 ($-\text{CO}_2\text{CH}_2-$), 74.2 ($\text{HC}\equiv\text{C}-$), 75.5 ($\text{HC}\equiv\text{C}$), 126.1 ($\text{CH}_2=$), 135.5 ($\text{CH}_2=\text{C}<$), 152.1 ($\text{HC}\equiv\text{CCO}_2-$), 166.7 ($=\text{CMeCO}_2-$). ^{13}C NMR (22.5 MHz, δ , ppm) 18.2 (CH_3-), 61.9 ($-\text{CO}_2\text{CH}_2-$), 63.7 (CO_2CH_2-), 74.4 ($\text{HC}\equiv\text{C}-$), 75.4 ($\text{HC}\equiv\text{C}$), 126.2 ($\text{CH}_2=$), 135.8 ($\text{CH}_2=\text{C}<$), 152.3 ($\text{HC}\equiv\text{CCO}_2-$), 167.0 ($=\text{CMeCO}_2-$).

2.5. Ethylene 2-hexynoate methacrylate (**1b**)

Similarly, **1b** ($R_f = 0.45$, ethyl acetate/hexane = 1/4, colorless oil) was prepared from **4b** and methacrylic anhydride in 81.7% yield. IR (neat) 2961, 2874, 2235, 1718, 1637, 1454, 1371, 1321, 1298, 1250, 1165 cm^{-1} . ^1H NMR (400 MHz, δ ,

ppm) 0.89 (t, $J = 7.2$ Hz, 3H, CH_3), 1.40 (m, 2H, CH_3CH_2), 1.53 (m, 2H, $-\text{CH}_2\text{CH}_2$), 1.92 (s, 3H, CH_3), 2.31 ($J = 7.0$ Hz, 2H, $-\text{CH}_2\text{C}\equiv$), 4.31 (m, 2H, $-\text{CO}_2\text{CH}_2$), 4.39 (m, 2H, $-\text{CO}_2\text{CH}_2$), 5.56 (s, 1H, CH_2), 6.10 (s, 1H, CH_2). ^{13}C NMR (100 MHz, δ , ppm) 13.4 ($-\text{CH}_2\text{C}\equiv$), 18.2 (CH_3), 18.4 (CH_3), 22.0 ($-\text{CH}_2$), 29.5 ($-\text{CH}_2$), 62.1 ($-\text{CO}_2\text{CH}_2$), 63.2 ($-\text{CO}_2\text{CH}_2$), 72.8 ($-\text{CH}_2\text{C}\equiv\text{C}$), 90.6 ($-\text{CH}_2\text{C}\equiv$), 126.1 (CH_2), 135.9 ($\text{CH}_2=\text{C}$), 153.5 ($-\text{C}\equiv\text{CCO}_2$), 167.1 ($=\text{CMeCO}_2$).

2.6. Radical polymerization of **1**

Typical procedure. The polymerization of **1a** was carried out as follows: To a solution of **1a** (0.500 g, 2.74 mmol) in DMF (5.0 mL) in a glass tube was added 2,2'-azobis(isobutyronitrile) (AIBN) (0.013 g 0.082 mmol). The tube was cooled, degassed, sealed off, and heated at 60 °C for 15 h. The reaction mixture was poured into methanol (100 mL). The precipitate was filtered and dried under vacuum to obtain **2a** (0.458 g, 91.6%). IR (neat) 3252, 2959, 2120, 1725, 1451, 1229, 1152 cm^{-1} . ^1H NMR (400 MHz, δ , ppm) 0.7–1.4 (3H, CH_3), 1.7–2.1 (2H, CH_2CMe), 2.6–3.5 (1H, $\text{HC}\equiv$), 4.13 (m, 2H, $-\text{CO}_2\text{CH}_2$), 4.30 (m, 2H, CO_2CH_2).

Similarly, **2b** was prepared by the radical polymerization of **1b**. **2b**: IR (neat) 2959, 2236, 1717, 1455, 1256, 1150, 1078 cm^{-1} . ^1H NMR (400 MHz, δ , ppm) 0.9 (t, $J = 7.1$ Hz, 3H, CH_3CH_2), 0.7–1.1 (3H, CH_3), 1.40 (m, 2H, $-\text{CH}_2$), 1.55 (m, 2H, $-\text{CH}_2$), 1.7–2.1 (2H, $-\text{CH}_2\text{CMe}$), 2.32 (t, $J = 6.1$ Hz, 2H, $-\text{CH}_2\text{C}\equiv$), 3.9–4.6 (4H, $-\text{CO}_2\text{CH}_2\text{CH}_2$).

2.7. Radical polymerization of MMA in the presence of acetylenic compounds

Typical procedure. The polymerization of MMA in the presence of methyl propiolate was carried out as follows: To a solution of MMA (0.102 g, 1.02 mmol) in DMF (1.8 mL) in a glass tube were added AIBN (0.005 g, 0.0306 mmol) and methyl propiolate (0.0857 g, 1.02 mmol). The tube was cooled, degassed, sealed off, and heated at 60 °C for 15 h. The reaction mixture was poured into methanol (100 mL). A precipitate was not obtained.

Similarly, the radical polymerizations of MMA in the absence of acetylenic compounds and in the presence of methyl 2-hexynoate were also carried out to obtain poly(methyl methacrylate) (PMMA) in 43% and 22% yields, respectively.

2.8. Radical copolymerization of **1b** with vinyl monomers

The copolymerization of **1b** with MMA was carried out as follows: To a solution of **1b** (0.127 g, 0.532 mmol) and MMA (0.117 g, 1.17 mmol) in DMF (3 mL) in a glass tube was added AIBN (0.008 g 0.0487 mmol). The tube was cooled, degassed, sealed off, and heated to 60 °C for 24 h. The reaction mixture was poured into methanol (60 mL). The precipitate was filtered and dried under vacuum to obtain the corresponding copolymer (0.197 g, 80.8%). IR (neat) 2959, 2237, 1718, 1450, 1257, 1149 cm^{-1} . ^1H NMR (90 MHz, δ , ppm) 0.95 (CH_3), 0.71–2.20 ($-\text{CH}_2\text{CH}_2\text{CH}_3$, $-\text{CH}_2\text{C}(\text{CH}_3)\text{CO}$), 2.18 ($-\text{CH}_2\text{C}\equiv$), 3.58 (CO_2CH_3), 4.00–4.60 ($-\text{CO}_2\text{CH}_2$). From the integral ratio in the ^1H NMR spectrum, the unit ratio of the copolymer was estimated to be ca. 1:2 [poly(**1b**):PMMA].

Similarly, the copolymerization of **1b** (0.115 g, 0.485 mmol) with styrene (0.109 g, 1.05 mmol) was also carried out to obtain the corresponding copolymer in 53% yield. IR (neat) 2934, 2237, 1717, 1454, 1253, 702 cm^{-1} . ^1H NMR (90 MHz, δ , ppm) 0.92 (CH_3), 0.51–2.12 ($-\text{CH}_2\text{CHPh}$, $-\text{CH}_2\text{CH}_2\text{CH}_3$, $-\text{CH}_2\text{C}(\text{CH}_3)\text{CO}$), 2.20–2.57 ($\text{CH}_2\text{C}\equiv$, CH_2CHPh), 3.48–4.53 ($-\text{CO}_2\text{CH}_2$), 6.18–7.51, Ph). From the integral ratio in the ^1H NMR spectrum, the unit ratio of the copolymer was estimated to be ca. 1:2 [poly(**1b**):PSt].

2.9. Phosphine-catalyzed polymer reaction of **2** with thiols

The reaction of **2a** with benzylmercaptane was carried out to obtain **5aA** as follows: To a solution of polymer (**2a**) (0.100 g, 0.549 mmol of unit) in THF (0.6 mL) and benzylmercaptane (0.075 g, 0.604 mmol) was added tributylphosphine (0.022 g, 0.110 mmol) under nitrogen at room temperature. The reaction mixture was poured into

hexane (20 mL). The precipitate was filtered and dried under vacuum to obtain **5aA** (0.157 g, 93.4%). IR (neat) 2957, 1732, 1574, 1454, 1232, 1161 cm^{-1} . ^1H NMR (400 MHz, δ , ppm) 0.7–1.0 (3H, CH_3), 1.7–2.1 (2H, CH_2CMe), 3.8–4.3 (6H, PhCH_2S - and $-\text{OCH}_2\text{CH}_2\text{O}$ -), 5.6–5.8 (1H, $\text{SCH}=\text{CH}$ -), 7.2 (5H, Ph), 7.6–7.7 (1H, $-\text{SCH}=\text{CH}$ -).

Similarly, the reactions of **2b** with benzylmercaptane or thiophenol were carried out to obtain **5bA** or **5bB**, respectively.

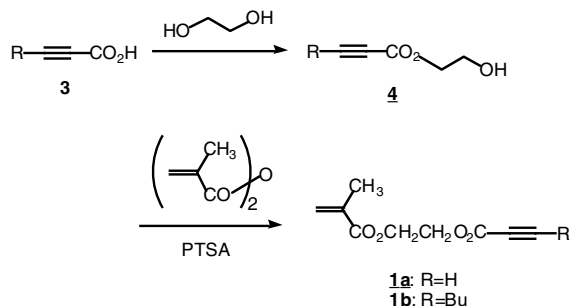
5bA: Yield 80.2%, IR (neat) 2959, 1715, 1590, 1455, 1248, 1169 cm^{-1} . ^1H NMR (400 MHz, δ , ppm) 0.7–1.1 (6H, CH_3CH_2 - and $-\text{CH}_2\text{CMe}$), 1.1–2.0 (6H, CH_2CMe , and $\text{CH}_3\text{CH}_2\text{CH}_2$ -), 2.70 (2H, $-\text{CH}_2\text{C}\equiv\text{C}$ -), 3.8–4.3 (6H, PhCH_2S - and $-\text{OCH}_2\text{CH}_2\text{O}$ -), 5.5 (1H, $\text{S}(\text{Bu})\text{C}=\text{CH}$ -), 7.1–7.3 (5H, Ph).

5bB: Yield 83.1%, IR (neat) 2959, 1732, 1705, 1580, 1441, 1441, 1171 cm^{-1} . ^1H NMR (400 MHz, δ , ppm) 0.5–1.1 (6H, CH_3CH_2 - and $-\text{CH}_2\text{CMe}$), 1.5–2.0 (6H, CH_2CMe , and $\text{CH}_3\text{CH}_2\text{CH}_2$ -), 2.30 (2H, $Z\text{-CH}_2\text{C}\equiv\text{C}$ -), 2.8 (2H, $E\text{-CH}_2\text{C}\equiv\text{C}$ -), 3.8–4.3 (4H, $-\text{OCH}_2\text{CH}_2\text{O}$ -), 5.2 (1H, $E\text{-S}(\text{Bu})\text{C}=\text{CH}$ -), 5.8 (1H, $Z\text{-S}(\text{Bu})\text{C}=\text{U}/\text{ES}/\text{DTD501}/\text{React}/1994\text{CH}$ -), 7.1–7.3 (5H, Ph) ($E:Z = 1:2$).

3. Results and discussion

3.1. Synthesis of methacrylates (**1**) having the acetylene moiety activated by the electron-withdrawing group

Methacrylates (**1**) having the acetylene moiety activated by the electron-withdrawing group were synthesized from 2-alkanoic acids (**3**) via ω -hydroxyalkyl alkynoate (**4**) in two steps (Scheme 2). Acetylenic compounds activated by the electron-withdrawing group are generally labile under basic conditions, and a conjugate addition [4a,4c] of alcohols to such acetylenes takes place easily under those conditions because of the high anionic reactivity. So we attempted the preparation of methacrylates (**1**) under acidic conditions. The esterification of alkanolic acid with excess amounts of ethylene glycol in the presence of *p*-toluenesulf-



Scheme 2.

onic acid (PTSA) was carried out to yield **4** in 68–94% yield. For the preparation of **1**, the esterification of **4** with methacrylic acid in the presence of trifluoroacetic anhydride [8] as an activator of carboxylic acid was tried as a reaction under acidic and mild conditions. However, pure **1** was not obtained due to contamination by trifluoroacetate because the removal of the by-product was very difficult. As another method of preparation, we tried the esterification of **4** using methacrylic anhydride in the presence of PTSA as a catalyst with slight heating. In this method, we were able to obtain pure **1** in 56–82% yields.

3.2. Radical polymerization of **1**

The radical polymerization of **1** was examined at 60 °C in DMF in the presence of AIBN at various concentrations to obtain **2** (Table 1). When the polymerization of **1a** and **1b** was carried out without solvents, the obtained polymers were insoluble in common organic solvents such as THF, DMF, CHCl_3 and so on (Runs 1 and 5). In the IR spectra of these insoluble polymers, the absorption due to the C–C triple bond was clearly observed. Furthermore, the polymerization was performed with DMF as a solvent under various concentrations. Although the soluble polymer was not obtained at high monomer concentrations in the polymerization of **1a** (Runs 1 and 2), the soluble polymer (**2a**) was obtained in high yield by performing the polymerization at 0.5 M of the monomer concentration (Run 3). The number-average molecular weight (M_n) and the molecular distribution (M_w/M_n) were estimated to be 8,100

Table 1
Radical polymerization of **1** at various concentrations^a

Run	R	Solvent/ <i>M</i>	Yield ^b (%)	<i>M_n</i> (<i>M_w</i> / <i>M_n</i>) ^d
1	H (1a)	Bulk	89 ^c	— ^c
2		DMF/1.0	88 ^c	— ^c
3		DMF/0.5	86	8100 (2.03)
4		DMF/0.2	7	5500 (1.40)
5	<i>n</i> -Bu(1b)	Bulk	88 ^c	— ^c
6		DMF/2.0	92	60,400 (6.68)
7		DMF/1.0	91	46,600 (2.00)
8		DMF/0.7	88	24,400 (1.92)
9		DMF/0.5	87	20,700 (1.92)
10		DMF/0.2	66	13,800 (1.56)

^a The polymerization of **1** was examined at 60 °C in DMF in the presence of AIBN (3 mol%) at various concentrations.

^b Isolated yield after precipitation with methanol.

^c The obtained polymer was insoluble in common organic solvents (DMF, THF, CH₂Cl₂, etc.).

^d Estimated by GPC (PSt, THF as an eluent).

^e Not estimated.

and 2.03, respectively, from the GPC analysis. The structures of the obtained polymers were confirmed by ¹H NMR and IR analysis. Both of the spectra of **2a** are shown in Figs. 1 and 2. In the IR spectrum of **2a**, the absorptions were observed at about 3250 (an attributable absorption to H–C≡) and 2120 (an attributable absorption to C≡C) cm⁻¹ similarly to **1a**. In the ¹H NMR spectrum of **2a**, the signals of the olefinic protons assigned to the methacrylate moiety of **1a** disappeared and a signal of the acetylenic proton was observed at 2.6–3.5 ppm in a similar way to **1a**. The C–C triple bond in the obtained polymer was detected quantitatively from the integral ratio

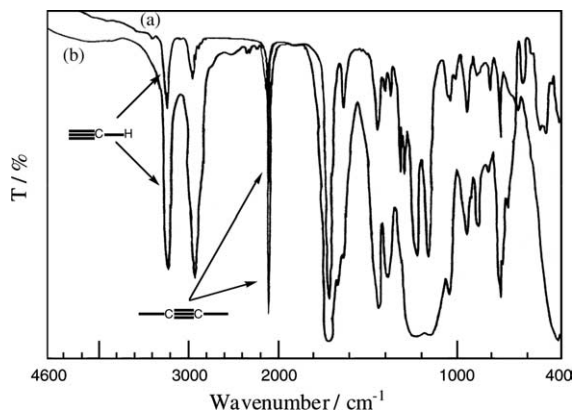


Fig. 1. IR spectra of **1a** (a) and **2a** (b).

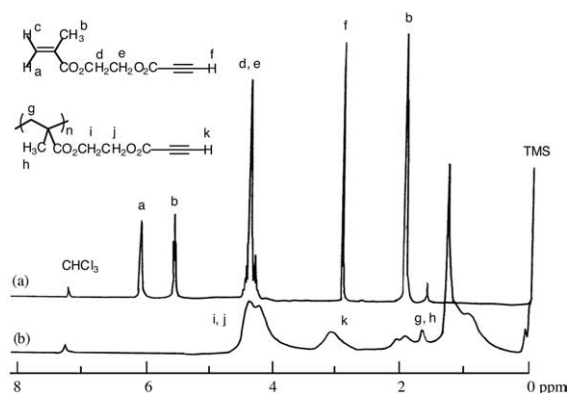
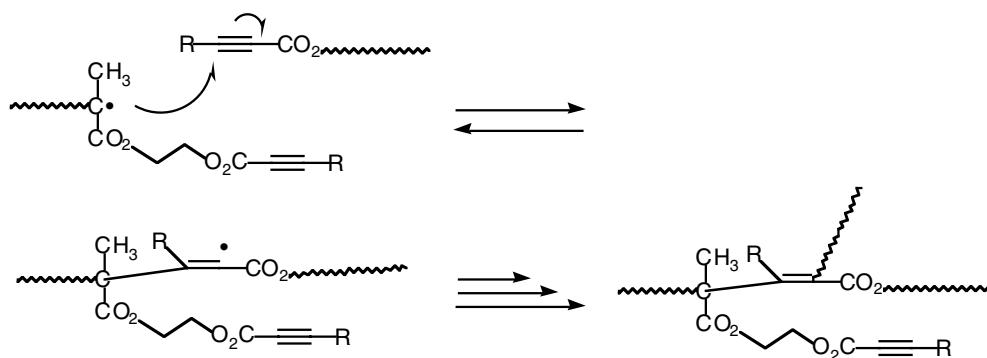


Fig. 2. ¹H NMR spectra (90 MHz, CDCl₃) of **1a** (a) and **2a** (b).

between this peak and the peaks of other protons. An almost quantitative existence of the acetylene moiety was verified in both spectra.

The yield of the polymer decreased at lower monomer concentrations (0.2 M, Run 4). In the polymerization of **1b** in DMF (2.0–0.2 M), the soluble polymer was also obtained. The molecular distribution of **2b** obtained at 2.0 M was broad compared with those of **2b** obtained at lower monomer concentrations (Runs 6–10). Gelation might take place depending on the monomer concentrations because of the addition of radical species to the acetylene moiety slightly proceeding at high monomer concentrations (Scheme 3) [9]. The effects of the monomer concentration was



Scheme 3.

prominent in the case of **1a** compared with **1b**. The tendency might be due to a difference between the reactivity of the two acetylene moieties: the terminal acetylenes are more reactive compared with internal acetylenes. It was found from the results that the polymerization at appropriate monomer concentrations has to be carried out in order to obtain soluble polymers having the acetylene moieties as a side chain in higher yield.

The radical polymerization of methyl methacrylate (MMA) was carried out in the presence (1 equiv.) of methyl propiolate or methyl 2-heptynoate in order to investigate the influence of the acetylenic skeleton toward the radical polymerization of the methacrylate moiety (Table 2). When the radical polymerization of MMA was carried out in DMF (0.5 M) at 60 °C, poly(methyl methacrylate) (PMMA) ($M_n = 23,600$, $M_w/M_n = 1.42$) was obtained in 44% yield (run 1). However, PMMA was not obtained in the presence of methyl propi-

olate (run 2). Furthermore, in the presence of methyl 2-heptynoate, the yield of PMMA decreased by about half compared with in the absence of acetylenic compounds (run 3). The presence of acetylenic compounds hindered the radical polymerization of methacrylate and the tendency was particularly noticeable in the case of terminal acetylene. Such an inhibition of polymerization by acetylenes has also been reported by Doak [5c]. In the paper, it has been described that the addition of a small amount of phenylacetylene reduced the overall rate of polymerization, accompanied by a decrease in a molecular weight of the polymer because of the formation of a vinyl radical derived from phenylacetylene formed radicals, which do not readily propagate the chain. Therefore, the acetylene moiety in **1** might inhibit the polymerization of the methacrylate moiety at lower monomer concentrations by the formation of a vinyl radical whose propagation ability is relatively low.

The polymerization of MMA in the presence of acetylenic compounds (1 equiv.) was also carried out without solvent at 60 °C for 24 h and the components of the reaction mixture were estimated by ¹H NMR spectroscopy (400 MHz). In the case of copolymerization with methyl propiolate, the conversions of MMA and methyl propiolate were estimated to be ca. 84% and ca. 34% [10], respectively. Similarly, the conversions of MMA and methyl 2-heptynoate were estimated to be 99% and 19%, respectively, when methyl 2-heptynoate was employed as the comonomer. From these results, it was found that the influence of methyl 2-heptyno-

Table 2
Radical polymerization of MMA in the presence of acetylenic compounds^a

Run	R R—C≡C—CO ₂ Me	Yield ^b (%)	M_n (M_w/M_n) ^c
1	None	43	23,600 (1.42)
2	H	0	—
3	<i>n</i> -Bu	22	26,400 (1.22)

^a The polymerization of methyl methacrylate (MMA) was carried out in the presence (1 equiv.) of acetylenic compounds by using AIBN (3 mol %) in DMF (0.5 M) at 60 °C.

^b Isolated yield after precipitation with methanol.

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

Table 3
Radical polymerization of **1** at various temperatures

Run	R	Initiators ^a	Temp (°C)	Yield ^b (%)	$M_n (M_w/M_n)^c$
1 ^d	H (1a)	AIBN	60	86	8100 (2.03)
2 ^d		BPO	80	91	13,600 (2.78)
3 ^d		DTBP	120	17	16,100 (2.34)
4 ^f	<i>n</i> -Bu (1b)	AIBN	60	99	– ^e
5 ^f		BPO	80	100	– ^e
6 ^f		DTBP	120	74	5500 (1.97)
7 ^f		AIBN	60	89	38,600 (2.25)
8 ^f		BPO	80	98	– ^e
9 ^f		DTBP	120	82	38,600 (3.68)

^a AIBN, 2,2'-azobis(isobutyronitrile); BPO, benzoyl peroxide; DTBP, Di-*t*-butyl peroxide.

^b Isolate yield after precipitation with methanol.

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

^d The polymerization was carried out in DMF (0.5 M).

^e The obtained polymer was insoluble in common organic solvent (DMF, THF, CH₂Cl₂, etc.).

^f The polymerization was carried out in DMF (1.0 M).

ate toward radical polymerization is slight compared with methyl propiolate. The gelation in high monomer concentrations might be due to the addition of radical species to the acetylene moiety because the consumption of acetylenes in the polymerization of MMA in the presence of acetylenes without solvents was confirmed.

The polymerization of **1** was also tried at various temperatures. The results are shown in Table 3. When the polymerization of **1a** was carried out in DMF (0.5 M) at various temperatures, **2a** having the higher molecular weight and broader molecular weight distribution was obtained in higher yield at 80 °C compared with the case at 60 °C (Runs 1 and 2). In contrast, the yield of **2a** decreased significantly at 120 °C (Run 3). Furthermore, the polymerization of **1a** was examined at a higher monomer concentration (1.0 M) and various temperatures (Runs 4–6). The soluble **2a** was obtained in high yield at 120 °C although the gela-

tion took place at both 60 and 80 °C (Runs 4 and 5). The polymerization of MMA was carried out at various temperatures in order to investigate the variation of the polymerizability of the methacrylate moiety in **1a** (Table 4). As shown in Table 4, the molecular weights of the obtained PMMA increased with rising polymerization temperature. From these results, the difference in the polymerization behavior in Table 3 (Runs 1–6) may be due to the propagation ability of the vinyl radical derived from the acetylene moiety of **1a**, as shown in Scheme 3, changing in response to varying temperatures. The radical polymerizability of the acetylene moiety might increase due to the moderate rise in the polymerization temperature and the decrease at higher polymerization temperatures. Therefore, in the case of Run 6 in Table 3, the soluble **2a** might be obtained in spite of a high monomer concentration. In the case of Run 3 in Table 3, the yield of **2a** might decrease due to that acetylene

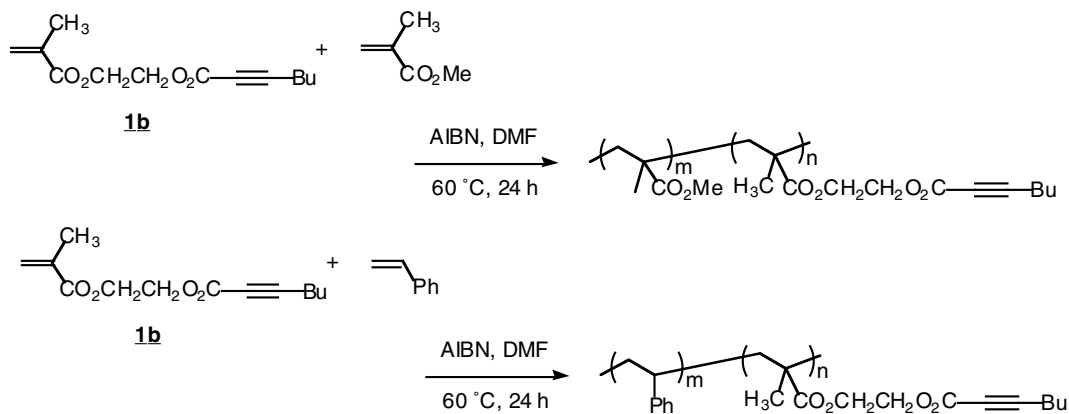
Table 4
Radical polymerization of MMA at various temperatures^a

Run	Initiators	Temp (°C)	Yield ^b (%)	$M_n (M_w/M_n)^c$
1	AIBN	60	60	57,000 (1.42)
2	BPO	80	74	63,000 (1.59)
3	DTBP	120	69	78,000 (1.76)

^a The polymerization was carried out in the presence of various initiators (3 mol%) in DMF (1.0 M).

^b Isolate yield after precipitation with methanol.

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



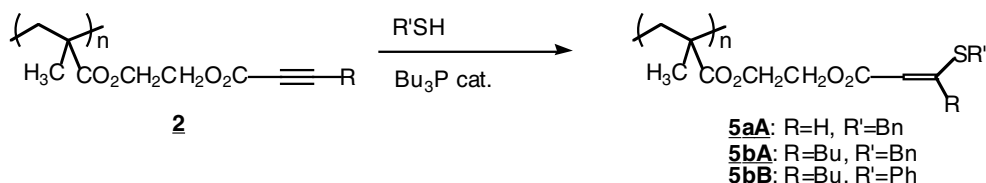
moiety preventing the desired polymerization in the low monomer concentration. This tendency on the variation of the polymerization temperature was also observed in the case of **1b** (Runs 7–9 in Table 3).

The copolymerization of **1b** with common vinyl monomers (2 equiv.) such as styrene and MMA was carried out in the presence of AIBN in DMF (monomers concentration; 0.5 M) at 60 °C (Scheme 4). When MMA was used as the comonomer, the copolymer having $M_n = 17,300$ and $M_w/M_n = 2.19$ was obtained in 81% yield as an insoluble part in methanol. In the case of styrene, the copolymer having ($M_n = 9200$, $M_w/M_n = 1.54$) was also obtained in 53% yield. The unit ratios of the obtained copolymers reflected the monomer feed ratio.

3.3. Polymer reaction of **2**

The anionic reactivity of acetylenes activated by the electron-withdrawing group is high, as described above. The polymer reaction of **2a** and

2b with thiols in the presence of tributylphosphine as a catalyst was tried (Scheme 5). The reaction was carried out in THF under nitrogen at room temperature. When benzylmercaptane or thiophenol were used as the thiols, the corresponding polymers (**5**) having a β -alkylmercaptoenoate moiety as a side chain were obtained in high yield. The polymers were soluble in common organic solvents such as THF, DMF, and CHCl_3 . It was suggested that the acetylene moiety in **2** was converted quantitatively to a β -alkylmercaptoenoate moiety in all cases because the strong absorption of the C–C triple bond conjugated with a carbonyl group in the IR spectroscopy disappeared in the reaction and the integral value of the phenyl group, and the newly formed double in the ^1H NMR spectroscopy almost agreed with the theoretical values. When **2a** ($M_n = 8000$, $M_w/M_n = 1.73$) and **2b** ($M_n = 38,600$, $M_w/M_n = 3.62$) were employed as the starting polymer, the polymers whose molecular weights and molecular distributions were 5800 and 1.33 (**5aA**), 25,400 and 3.04 (**5bA**), and 13,300 and 1.99 (**5bB**), respectively, were obtained. In the



Scheme 5.

GPC measurement, all of the obtained polymers showed lower molecular weights than the starting polymers. Although it is known that the transesterification in the anionic reaction of alkynoates with alcohols take place as a side reaction [4a], such a side reaction is not observed in the phosphine catalyzed reaction of the alkynoates with thiols, and the corresponding adducts are obtained in almost quantitative yields [4b]. Furthermore, it is difficult to believe that the fission of some of the covalent bonds occurred by the phosphine-catalyzed reaction from the reaction mechanism [4,11]. Based on this, the decrease in the molecular weight by the polymer reaction may not be due to some of the side reactions. We think the degree of polymerization may not change [12].

4. Conclusion

The synthesis of methacrylates (**1**) having an acetylene moiety activated by the electron-withdrawing group and radical polymerization of **1** were described. Methacrylates (**1**) were prepared from alkynoic acids via ω -hydroxyalkyl alkynoates in two steps. By the radical polymerization of **1**, polymethacrylates (**2**) having an acetylene moiety activated by the electron-withdrawing group as the side-chain were obtained in high yields. The acetylene moiety in **1** slightly hindered the polymerization of the methacrylate moiety in the radical polymerization. The influences of the acetylene moiety decreased with the introduction of substituents at the acetylene moiety. The polymer reaction of the obtained polymer (**2**) having the acetylenic side chain with thiols gave the corresponding polymers having β -alkylmercaptoenoate moieties in high yields.

As the polymers (**2**) having acetylene moieties activated by an electron-withdrawing group are a novel reactive polymer, studies on other polymer reactions and applications of **2** are in progress.

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- [17] An acetylenic skeleton is linear and rigid. From which, the apparent size of polymers containing acetylene moieties may be bigger compared with the size of common polymers such as polystyrene, assuming the molecular weight of both is the same. GPC is a way to determine the molecular weight from the difference in the apparent size for standard polymers. We think that the apparent size of polymers obtained by the polymer reaction may become compact by transforming the acetylenic skeleton to olefinic skeleton. A detailed investigation into the variation of molecular weight by the polymer reaction is in progress with applications of **2**.