# Nickel(0)-Catalyzed Cycloaddition Copolymerization of Ether Diynes with Carbon Dioxide to Poly(2-pyrone)s

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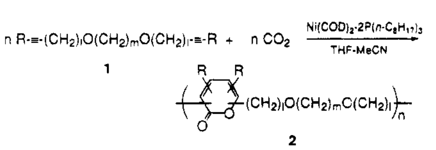
ABSTRACT: Nickel(0)-catalyzed cycloaddition copolymerization of $CO_2$ with five ether diynes ($RC{\equiv}C(CH_2)_lO(CH_2)_mO(CH_2)_lC{\equiv}CR$, $l = 2$, $m = 4$, R = Me (**1a**), $l = 2$, $m = 4$, R = Et (**1b**), $l = 2$, $m = 4$, R = $n$-Pr (**1c**), $l = 1$, $m = 4$, R = Me (**1d**), and $l = 1$, $m = 2$, R = Et (**1e**)) was studied. The corresponding five poly(2-pyrone)s with molecular weights of 3300-29 100 were obtained in 45-88% yield in a THF/MeCN solvent at 110 °C. Ternary copolymerization of $CO_2$ with equimolar amounts of **1a-c** and $EtC{\equiv}C(CH_2)_6C{\equiv}CEt$ (**4**) showed that an effect of three alkyl substituents (R = Me, Et, and $n$-Pr) on the copolymerizability of **1a-c** with $CO_2$ is mutually similar. The **1c**/$n$-$PrC{\equiv}C(CH_2)_{10}C{\equiv}C$-$n$-Pr (**6**)/$CO_2$ and **1e**/**4**/$CO_2$ ternary copolymerizations gave relative copolymerizabilities of 0.97 and 2.0, respectively, which indicated that an electron-withdrawing effect of an ether oxygen atom on the copolymerizability of a terminal C≡C bond of a copolymer operates through one methylene group to increase the ether diyne copolymerizability, while such an electronic effect of the ether oxygen atom does not act through two methylene groups.

## Introduction

Recently we developed the transition-metal-catalyzed 1:1 cycloaddition copolymerization of a diyne as a new polymerization reaction and reported the nickel(0)-catalyzed 1:1 cycloaddition copolymerization of various diynes with heterocumulenes such as $CO_2$[1] and isocyanates[2] to unprecedented poly(2-pyrone)s and poly(2-pyridone)s, respectively. The poly(2-pyrone) synthesis is an excellent example of the utilization of $CO_2$ as a source of carbon in polymer synthesis. It is also the first example of the efficient copolymerization of $CO_2$ with an unsaturated hydrocarbon. In the poly(2-pyrone) synthesis, three kinds of diynes without a heteroatom, namely, the aliphatic acyclic diyne,[1a,b] the aliphatic cyclic diyne,[1f] and the acyclic diyne[1d] having a phenylene group in the methylene chain tethering two C≡C bonds of the diyne, were used. If diynes with a heteroatom functionality can further be used, the nickel(0)-catalyzed cycloaddition copolymerization of a diyne with $CO_2$ will become quite useful.

In this study, we have chosen the important functionality of an ether group among various functionalities containing a heteroatom and have examined the synthesis of a poly(2-pyrone) having an oxyalkylene chain by the nickel(0)-catalyzed 1:1 cycloaddition copolymerization of ether diynes (**1**) with $CO_2$ (eq 1). Ether diynes




(1)

$l = 2$, $m = 4$: R = Me (**a**) $l = 1$, $m = 4$: R = Me (**d**)
R = Et (**b**) $l = 1$, $m = 2$: R = Et (**e**)
R = $n$-Pr (**c**)

with various structures can be prepared by a variety of combinations of acetylenic alcohol/alkylene dibromide or acetylenic chloride/alkylenediol using a phase-transfer catalyst.[3] Therefore, the effect of an ether diyne structure and an ether functional group on the copolymerizability of a C≡C bond of the ether diyne with $CO_2$ has also been studied.

## Experimental Section

Instrumentation and general procedures are described in the previous reports[1b-d] unless otherwise stated. $^1H$ NMR (400 MHz) and $^{13}C$ NMR (100 MHz) spectra were taken in $CDCl_3$ on a JEOL JX-400 instrument. Ether diynes **1a-e** were prepared by two substrate combinations of acetylenic alcohol/alkylene dibromide and acetylenic chloride/alkylenediol using NaOH and tetrabutylammonium bromide as a phase-transfer catalyst.[3] Carbon dioxide was a commercial reagent (assay: minimum 99.99 vol %) supplied by Teisan, Inc., and was used without further purification.

**Copolymerization of Ether Diynes 1a-c with $CO_2$.** The reaction was carried out under nitrogen. $Ni(COD)_2$ (0.0550 g, 0.200 mmol) in a THF solution (2.50 mL), $P(n\text{-}C_8H_{17})_3$ (0.179 mL, 0.400 mmol), MeCN (2.50 mL), and **1b** (0.532 mL, 2.00 mmol) were placed in this order in a 50-mL stainless steel autoclave under magnetic stirring at ambient temperature. $CO_2$ gas was compressed up to 50 kg/cm$^2$, and the reaction mixture was heated at 110 °C for 20 h. After the reaction mixture was cooled by ice water, the remaining $CO_2$ gas was purged off. The resulting mixture was concentrated in vacuo. Addition of ether (20 mL) to a residue precipitated copolymer **2b**, which was purified by dissolving in $CH_2Cl_2$ (1.0 mL) and adding ether (20 mL). Drying in vacuo at room temperature gave **2b** as a pale brown solid (0.52 g, 88%). GPC analysis of **2b** showed $M_n = 16\,100$ and $M_w/M_n = 1.8$. **2b**: IR (film, cm$^{-1}$) 1706, 1636, 1550, 1111; $^1H$ NMR $\delta$ 0.90-1.35 (m, 6 H), 1.35-1.70 (m, 4 H), 2.20-2.85 (m, 8 H), 3.25-3.75 (m, 8 H); $^{13}C$ NMR $\delta$ 12.0-31.8 (m), 67.6-71.2 (m), 111.0-111.3 (br s), 111.7-111.9 (br s), 118.1-118.3 (br s), 118.3-118.6 (br s), 119.1-119.4 (br s), 119.6-120.0 (br s), 125.8-126.2 (br s), 126.4-126.8 (br s), 149.7-150.0 (br s), 150.4-150.6 (br s), 154.6-154.9 (br s), 155.2-155.6 (br s), 157.5-157.9 (br d), 160.1-160.3 (br s), 160.9-161.2 (br s), 162.9-163.4 (br d), 163.4-163.6 (br s).

The copolymerization of **1a** or **1c-e** with $CO_2$ was carried out similarly to the **1b**/$CO_2$ copolymerization. **2a**: IR (film, cm$^{-1}$) 1718, 1654, 1560, 1108; $^1H$ NMR $\delta$ 1.35-1.75 (m, 4 H), 1.75-2.30 (m, 6 H), 2.50-2.90 (m, 4 H), 3.20-3.75 (m, 8 H). The $^{13}C$ NMR spectrum of **2a** showed broad singlets centered

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at 112.5, 112.9, 113.1, 113.2, 119.9, 120.0, 120.1, 120.6, 151.4, 152.6, 153.0, 154.2, 154.3, 155.7, 155.9, 163.3, 163.4, and 163.8 ppm, which are assigned to the C=O and C=C absorptions of four regioisomeric 2-pyrone rings in the copolymer, together with multiplets at 12.8–32.0 and 65.7–71.0 ppm. **2c**: IR (film, $cm^{-1}$) 1705, 1634, 1551, 1109; $^1H$ NMR $\delta$ 0.80–1.35 (m, 6 H), 1.35–1.80 (m, 8 H), 2.20–2.85 (m, 8 H), 3.25–3.75 (m, 8 H); $^{13}C$ NMR $\delta$ 13.7–32.8 (m), 67.8–70.8 (m), 111.4–112.7 (br d), 116.6–117.2 (br s), 119.1–120.6 (br d), 124.3–125.5 (br d), 150.0–151.1 (br d), 154.0–156.0 (br d), 156.0–156.8 (br s), 158.7–160.2 (br d), 162.7–164.0 (br s). **2d**: IR (film, $cm^{-1}$) 1708, 1654, 1553, 1096; $^1H$ NMR $\delta$ 1.40–1.90 (m, 4 H), 1.90–2.40 (m, 6 H), 3.30–3.70 (m, 4 H), 4.10–4.60 (m, 4 H); $^{13}C$ NMR $\delta$ 11.7–31.9 (m), 63.5–71.2 (m), 112.2–112.7 (br s), 113.3–113.7 (br s), 114.2–114.6 (br s), 115.0–115.5 (br s), 118.8–119.3 (br s), 120.3–121.4 (br s), 122.0–122.4 (br s), 124.1–124.5 (br s), 147.6–148.2 (br s), 152.2–152.7 (br s), 153.9–154.5 (br s), 156.0–156.7 (br s), 157.8–158.2 (br s), 159.6–160.1 (br s), 162.3–162.8 (br d), 163.1–163.7 (br d). Copolymer **2d** did not show a satisfactory result for elemental analysis. Anal. Calcd for $(C_{13}H_{18}O_4)_n$: C, 65.53; H, 7.61. Found: C, 59.67; H, 7.21. **2e**: IR (film, $cm^{-1}$) 1708, 1636, 1553, 1094; $^1H$ NMR $\delta$ 0.90–1.50 (m, 6 H), 2.10–2.80 (m, 4 H), 3.40–3.90 (m, 4 H), 4.10–4.60 (m, 4 H); $^{13}C$ NMR $\delta$ 111.4–112.5 (m), 118.1–118.8 (br s), 120.3–121.5 (m) 128.0–128.4 (br s), 146.5–147.7 (m), 152.6–153.6 (br s), 154.9–155.9 (br s), 160.6–162.0 (m), 162.5–163.5 (br d). For the analysis of the $^{13}C$ NMR spectrum of **2e**, see the text.

**Preparation of Cooligomer 3b from 7,12-Dioxa-3,15-octadecadiyne (1b) and $CO_2$.** The reaction was carried out under nitrogen. $Ni(COD)_2$ (0.110 g, 0.400 mmol) in a THF (10.0 mL) solution, $P(n\text{-}C_8H_{17})_3$ (0.357 mL, 0.800 mmol), MeCN (10.0 mL), and **1b** (1.06 mL, 4.00 mmol) were placed in this order in a 50-mL stainless steel autoclave under magnetic stirring at ambient temperature. $CO_2$ gas was compressed up to 50 kg/$cm^2$. The reaction mixture was heated at 110 °C for 15 min under magnetic stirring. After the reaction mixture was cooled by ice water, the remaining $CO_2$ gas was purged off. The reaction mixture was concentrated under vacuum to give a residue, which was purified three times by PLC (AcOEt/hexane = 2/1 (v/v)), (AcOEt/hexane = 1/1 (v/v)), and (AcOEt/hexane = 2/3 (v/v)), respectively, to give cooligomer **3b** (0.068 g, 6.3%). Cooligomer **3b**: IR (film, $cm^{-1}$) 1707, 1633, 1551, 1112; $^1H$ NMR $\delta$ 1.09 (t, $J$ = 7.5 Hz), 1.20 (t, $J$ = 7.6 Hz), 1.21 (t, $J$ = 7.5 Hz), 1.53–1.63 (m, 8 H), 2.14 (qt, $J$ = 7.6 and 2.4 Hz, 4 H), 2.36–2.43 (m, 4 H), 2.43–2.81 (m, 8 H), 3.37–3.70 (m, 16 H); $^{13}C$ NMR $\delta$ 12.3–32.0 (m), 68.2–71.3 (m), 76.5, 82.7, 111.7, 112.3, 118.5, 118.8, 119.6, 120.2, 126.2, 126.8, 150.4, 151.1, 155.3, 156.0, 157.8, 158.1, 160.5, 161.2, 163.15, 163.28, 163.55, 163.63; MS $m/e$ (relative intensity) 55 (>100), 71 (100), 81 (>100), 111 (88), 153 (64), 278 (39), 375 (18), 544 ($M^+$, 10). Cooligomer **3b** did not give satisfactory results for elemental analyses. Anal. Calcd for $C_{33}H_{52}O_6$: C, 72.76; H, 9.62. Found: C, 71.73; H, 9.72. The purity of **3b** was estimated to be >95% on the basis of its $^1H$ NMR spectrum.

**Ternary Copolymerization of Ether Diynes 1a–c, 3,11-Tetradecadiyne (4), and $CO_2$.** The reaction was carried out under nitrogen. In a 50-mL stainless steel autoclave, $Ni(COD)_2$ (0.0275 g, 0.100 mmol) in a THF solution (2.50 mL), $P(n\text{-}C_8H_{17})_3$ (0.0893 mL, 0.200 mmol), MeCN (2.50 mL), **1a** (0.118 mL, 0.500 mmol), and **4** (0.115 mL, 0.50 mmol) were placed in this order under magnetic stirring at ambient temperature. $CO_2$ gas was compressed up to 50 kg/$cm^2$. The reaction mixture was heated at 110 °C for 15 min under magnetic stirring. After the reaction mixture was cooled by ice water, the remaining $CO_2$ gas was purged off. The solution was concentrated in vacuo. Addition of hexane (20 mL) to a resulting residue precipitated a copolymer, which was purified by dissolving in $CH_2Cl_2$ (1.0 mL) and adding hexane (20 mL). Drying in vacuo at room temperature gave copolymer **5a** as a pale brown solid (0.17 g, 67%). Copolymer **5a**: IR (film, $cm^{-1}$) 1702, 1636, 1560, 1109; $^1H$ NMR $\delta$ 0.80–1.85 (m), 1.85–2.90 (m), 3.10–3.80 (m); $^{13}C$ NMR $\delta$ 12.3–32.1 (m), 67.6–71.5 (m), 79.2–80.0 (m), 81.6–82.5 (m), 112.1–114.5 (m), 114.5–118.4 (m), 119.7–121.2 (m), 122.7–125.5 (m), 151.2–152.3 (m), 152.3–154.0 (m), 154.0–155.0 (m), 155.0–156.7 (m), 157.7–160.0 (m), 160.0–162.7 (m), 163.2–164.7 (m). The ternary copolymerizations of **1b**/**4**, **1c**/**4**, **1e**/**4**, and **1c**/**6** with $CO_2$ were carried out similarly to the **1a**/**4**/$CO_2$ copolymerization to give copolymers **5b**, **5c**, **5e**, and **7**, respectively. Copolymer **5b**: IR (film, $cm^{-1}$) 1702, 1654, 1560, 1110; $^1H$ NMR $\delta$ 0.05–1.85 (m), 2.05–2.90 (m), 3.20–3.80 (m); $^{13}C$ NMR $\delta$ 12.0–32.0 (m), 67.7–71.7 (m), 78.8–79.7 (m), 81.2–82.0 (m), 87.3–90.5 (m), 114.5–118.0 (m), 118.0–120.4 (m), 122.5–125.4 (m), 125.4–127.1 (m), 148.9–150.9 (m), 153.5–154.3 (m), 157.7–159.5 (m), 159.5–162.0 (m), 162.9–164.3 (m). Copolymer **5c**: IR (film, $cm^{-1}$) 1706, 1629, 1458, 1109; $^1H$ NMR $\delta$ 0.70–1.83 (m), 1.83–2.95 (m), 3.10–4.85 (m); $^{13}C$ NMR $\delta$ 11.3–31.8 (m), 67.7–71.5 (m), 78.9–80.0 (m), 81.5–82.5 (m), 87.9–90.7 (m), 111.6–113.0 (m), 114.8–118.0 (m), 119.3–120.7 (m), 122.7–125.9 (m), 150.0–151.3 (m), 154.0–157.8 (m), 157.8–160.4 (m), 160.4–162.1 (m), 163.1–164.4 (m). **5e**: IR (film, $cm^{-1}$) 1708, 1654, 1560, 1096; $^1H$ NMR $\delta$ 0.90–1.75 (m), 2.05–2.85 (m), 3.40–3.90 (m), 4.10–4.50 (m); $^{13}C$ NMR $\delta$ 12.1–31.9 (m), 64.3–70.9 (m), 78.9–79.8 (m), 81.3–82.4 (m), 111.2–112.6 (m), 114.2–117.2 (m), 118.0–118.7 (m), 120.0–121.3 (m), 122.6–124.8 (m), 127.7–128.4 (m), 146.7–147.7 (m), 152.6–156.4 (m), 157.1–159.6 (m), 160.5–162.4 (m), 162.4–163.9 (m). **7**: IR (film, $cm^{-1}$) 1716, 1628, 1550, 1111; $^1H$ NMR $\delta$ 0.75–1.15 (m), 1.15–1.85 (m), 2.05–2.85 (m), 3.20–3.80 (m); $^{13}C$ NMR $\delta$ 13.5–32.1 (m), 67.8–71.3 (m), 81.9–82.4 (m), 111.6–112.2 (m), 115.1–116.0 (m), 116.6–117.2 (m), 119.3–120.2 (m), 122.9–123.8 (m), 124.5–125.5 (m), 149.6–150.6 (m), 154.2–156.6 (m), 157.7–160.0 (m), 160.8–162.0 (m), 163.3–164.0 (m).

**Table 1. Nickel(0)-Catalyzed Cycloaddition Copolymerization of Diyne 1b with $CO_2$ to Poly(2-pyrone) 2b (eq 1)[a]**

| | | 2b | | |
|---|---|---|---|---|
| **1b**, mmol | temp, °C | yield,[b] % | $M_n$[c] | $M_w/M_n$[c] |
| 1 | 60 | (18) | 2 000 | 1.5 |
| | 90 | (77) | 3 500 | 2.2 |
| | 110 | 51 | 13 400 | 2.1 |
| | | 53[d] | 15 800 | 2.2 |
| | | 38[e] | 22 500 | 3.9 |
| 2 | | 88 | 16 100 | 1.8 |
| 1 | 130 | 51 | 4 000 | 7.1 |

[a] $Ni(COD)_2$/**1b** = 0.1; $P(n\text{-}C_8H_{17})_3$/Ni = 2; $CO_2$, 50 kg/$cm^2$ (initial pressure at room temperature); solvent, 5 mL, THF/MeCN = 1/1 (v/v); time, 20 h. [b] Based on the quantitative formation of **2b**. The values in parentheses are yields of ether-soluble and hexane-insoluble **2b**. [c] Determined by GPC with polystyrene standards in chloroform. [d] $CO_2$, 20 kg/$cm^2$. [e] $CO_2$, 10 kg/$cm^2$.

## Results and Discussion

A nickel(0) catalyst generated from bis(1,5-cyclooctadiene)nickel ($Ni(COD)_2$) (10 mol %) and 2 equiv of $P(n\text{-}C_8H_{17})_3$ as a ligand effected the 1:1 cycloaddition copolymerization of ether diynes **1a–e** with $CO_2$ to afford poly(2-pyrone)s **2a–e** having a repeating unit of a 2-pyrone ring substituted with an oxyalkylene chain (eq 1). Several copolymerization factors such as a reaction temperature, a substrate concentration, and a $CO_2$ pressure were examined in the **1b**/$CO_2$ copolymerization. The results are summarized in Table 1.

The copolymerization depended upon the reaction temperature. At the reaction temperature below 90 °C, the copolymerization proceeded slowly to give a hexane-insoluble but ether-soluble copolymer with a low molecular weight. The copolymerization took place efficiently at 110 °C to afford poly(2-pyrone) **2b** with a molecular weight around 15 000. Raising the reaction temperature to 130 °C, however, did not give a good result and produced a copolymer with a broader molecular weight distribution. This finding suggests formation of a branched copolymer.[2c] Increase of a diyne concentration raised a copolymer yield. The $CO_2$ pressure as low as 10 kg/$cm^2$ was sufficient to effect the 1:1

**Table 2. Nickel(0)-Catalyzed Cycloaddition Copolymerization of Diynes 1 with $CO_2$ to Poly(2-pyrone)s 2 (eq 1)[a]**

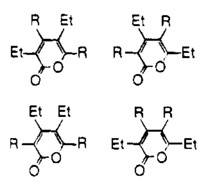
| 1 (mmol) | temp, °C | 2 | yield,[b] % | $M_n$[c] | $M_w/M_n$[c] |
|---|---|---|---|---|---|
| **a** (1) | 110 | **a** | 41 | 13 000 | 2.6 |
| (2) | | | 77 | 15 500 | 2.6 |
| (1) | 130 | | 84 | 6 100 | 7.4 |
| **c** (1) | 110 | **c** | 23 | 29 100 | 2.4 |
| (2) | | | 45 | 27 000 | 2.5 |
| **d** (1) | | **d** | 59 | 3 500 | 1.5 |
| (2) | | | 63 | 5 900 | 2.1 |
| **e** (1.5) | 100 | **e** | 74[d] | 3 300 | 2.8 |
| (1) | 110 | | 30 | 2 200 | 1.4 |
| (1.5) | | | 31 | 3 300 | 1.2 |

[a] $Ni(COD)_2/1 = 0.1$; $P(n\text{-}C_8H_{17})_3/Ni = 2$; $CO_2$, 50 kg/cm$^2$ (initial pressure at room temperature); solvent, 5 mL, THF/MeCN = 1/1 (v/v); time, 20 h. [b] Based on the quantitative formation of 2. [c] Determined by GPC with polystyrene standards in chloroform. [d] Solvent, 2.5 mL.

copolymerization. The copolymerization of **1a** or **1c** with $CO_2$ proceeded well also at 110 °C (Table 2). Ether diynes **1d,e** gave poly(2-pyrone)s **2d,e** although their molecular weight was not high (Table 2). A thermogravimetric analysis (TGA) of **2b** and **2d** showed a rapid weight loss around 200 °C in air.

Poly(2-pyrone)s **2a–e** gave reasonable IR and $^1H$ NMR spectra. They exhibited three IR absorptions characteristic of a 2-pyrone ring in the regions of 1700, 1600, and 1500 cm$^{-1}$. Poly(2-pyrone) **2a** and poly(2-pyrone)s **2a–c** showed $^1H$ NMR $CH_3C{=}C$ and $CH_2C{=}C$ absorptions at 1.75–2.30 and 2.20–2.90 ppm, respectively. Poly(2-pyrone)s **2d** and **2e** showed $^1H$ NMR $C{=}CCH_2O$ absorptions at 4.10–4.60 ppm along with absorptions of a $CH_3C{=}C$ group and a $CH_2C{=}C$ group at 1.90–2.40 and 2.10–2.80 ppm, respectively.

To confirm further the poly(2-pyrone) formation, cooligomer **3b** consisting of two **1b** molecules and one



cooligomer **3b**
( R = $-(CH_2)_2O(CH_2)_4O(CH_2)_2-C{\equiv}CEt$ )
cooligomer **3e**
( R = $-CH_2O(CH_2)_2OCH_2-C{\equiv}CEt$ )

$CO_2$ molecule was prepared by shortening a reaction time. Its $^{13}C$ NMR C=O and C=C absorptions are shown in Figure 1. Cooligomer **3b** exhibited 4 C=O absorptions and 16 C=C absorptions with similar intensities. This result indicates that **3b** consists of approximately equal amounts of four regioisomers, and accordingly the 2-pyrone repeating unit of **3b** is nonregioselectively formed. Correspondence of the C=O and C=C absorptions of **2b** to those of **3b** (Figure 1) confirms the formation of **2b**. $^{13}C$ NMR C=O and C=C absorptions of **2a**, **2c**, and **2d** are shown in Figure 1. Poly(2-pyrone) **2c** showed C=O and C=C absorptions similar to those of **2b**. Poly(2-pyrone) **2a** exhibited $^{13}C$ NMR C=O and C=C absorptions different from those of **2b** and **2c**, but its absorption pattern is compatible with a poly(2-pyrone) structure. Poly(2-pyrone) **2d** showed also C=O and C=C absorptions assignable to a 2-pyrone ring.

Copolymer **2e** showed $^{13}C$ NMR C=O and C=C absorptions at 111.4–112.5 (m), 118.1–118.8 (br s), 120.3–121.5 (m), 128.0–128.4 (br s), 131.0–131.6 (br s), 146.5–147.7 (m), 152.6–153.6 (br s), 154.9–155.9 (br s), 160.6–162.0 (m), 162.5–163.5 (br d), and 165.8–166.6 (br s) ppm (Figure 1). To elucidate these absorptions, preparation of cooligomer **3e** was attempted under reaction conditions similar to those employed for the preparation of **3b**. Cooligomer **3e**, however, could not be obtained as a pure compound. PLC purification (AcOEt/hexane = 2/1 (v/v)) followed by a repeated one (AcOEt/hexane = 1/1 (v/v)) of reaction products gave two fractions A and B containing regioisomers of **3e** in ca. 11% yield, but fractions A and B contained impurities and showed their $^{13}C$ NMR absorptions at 126.7 and 136.6 plus 126.7 ppm, respectively, which were not observed in the spectrum of **2e**. Besides these absorptions, fractions A and B showed C=O and C=C absorptions assignable to a 2-pyrone ring; fraction A exhibited two C=O absorptions (163.0 and 163.4 ppm) and eight C=C absorptions (112.6, 118.7, 120.8, 121.3, 155.6, 161.3, 161.6, and 162.0 ppm) and fraction B showed two sets of C=C absorptions (147.6/147.9 and 161.4/161.6 ppm) together with three C=O and C=C absorptions (112.3, 128.4, and 163.4 ppm). These findings indicate that each of two fractions A and B contains two regioisomers of **3e**, and accordingly **3e** consists of four regioisomers. Good correspondence of the $^{13}C$ NMR C=O and C=C absorptions between **2e** and **3e** was observed except the absorptions (126.7 and 136.6 ppm) of **3e** due to the impurities and two other absorptions (131.0–131.6 and 165.8–166.6 ppm) of **2e**. The absorption around 166 ppm appeared in both spectra of **2e** and fraction A of **3e** but was not observed in the spectra of **2a–d** (Figure 1). Two absorptions at 131.0–131.6 and 165.8–166.6 ppm of **2e** therefore may be ascribed to its irregular structures, which were not identified at the present time. Thus the formation of **2e** was confirmed.

The effect of an ether diyne structure and an ether functional group on the copolymerizability of the ether

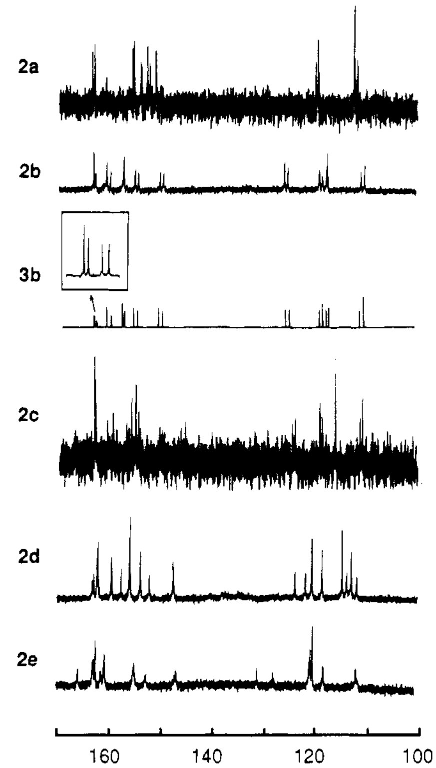


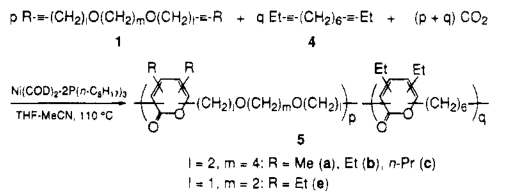

**Figure 1.** $^{13}C$ NMR C=O and C=C absorptions of poly(2-pyrone)s **2a–e** and cooligomer **3b** (ppm).

**Table 3. Ternary Copolymerization Involving Diyne 1, $CO_2$, and 3,11-Tetradecadiyne (4) or 4,16-Eicosadiyne (6) to Poly(2-pyrone) 5 or 7[a]**

| 1 + 4 or 6 | time, min | poly(2-pyrone) | | | | |
|---|---|---|---|---|---|---|
| | | | yield,[b] % | $M_n$[c] | $M_w/M_n$[c] | [1]/[4 or 6][d] |
| **1a** + **4** | 15 | **5a** | 67 | 3400 | 1.7 | 0.81 |
| **1b** + **4** | 30 | **5b** | 53 | 3000 | 1.9 | 0.82 |
| **1c** + **4** | 25 | **5c** | 61 | 3100 | 1.6 | 0.72 |
| **1e** + **4** | 30 | **5e** | 18 | 1400 | 1.2 | 2.0 |
| **1c** + **6** | 180 | **7** | 57 | 8900 | 1.1 | 0.97 |

[a] **1** = **4** or **6** = 0.5 mmol; Ni/**1** + **4** or **6** = 0.1; $P(n\text{-}C_8H_{17})_3$/Ni = 2; $CO_2$, 50 kg/cm$^2$ (initial pressure at room temperature); solvent, 5 mL, THF/MeCN = 1/1 (v/v); temperature, 110 °C. [b] Based on the quantitative formation of **5** or **7**. [c] Determined by GPC with polystyrene standards in chloroform. [d] The relative copolymerizability of **1** to **4** or **6**: the molar ratio of **1** to **4** or **6** components in **5** or **7** determined by $^1$H NMR.

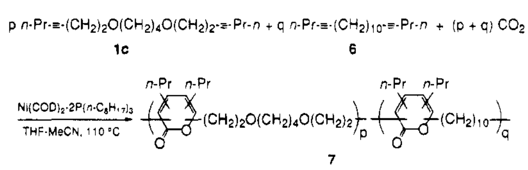
diyne with $CO_2$ was examined by ternary copolymerization involving $CO_2$ and equimolar amounts of two diynes. First, the ternary copolymerization of **1a–c**, 3,-11-tetradecadiyne (**4**), and $CO_2$ was carried out to disclose an effect of a Me, Et, or $n$-Pr substituent upon the ether diyne copolymerizability (eq 2). Determina-



(2)

tion of a copolymer composition, i.e., the molar ratio of **1a–c** to **4** components in copolymers **5a–c**, by $^1$H NMR spectroscopy gave a relative copolymerizability of **1a–c** to **4** (Table 3). Three relative copolymerizabilities obtained indicate that the effect of the Me, Et, or $n$-Pr substituent upon the copolymerizability of the ether diyne with $CO_2$ is mutually similar. Previously we obtained the following copolymerizability order of three acyclic diynes with $CO_2$ in the nickel(0)-catalyzed poly-(2-pyrone) formation: EtC≡C$(CH_2)_6$C≡CEt > MeC≡C-$(CH_2)_2$C≡CMe > 1,4-$n$-PrC≡C$CH_2C_6H_4CH_2$C≡C-$n$-Pr.[1c] The effect of the alkyl substituent found in this study indicates that the difference among the Me, Et, and $n$-Pr substituents does not influence the above copolymerizability order remarkably and accordingly supports the previous proposal;[1c] the copolymerizability of MeC≡C-$(CH_2)_2$C≡CMe and 1,4-$n$-PrC≡C$CH_2C_6H_4CH_2$C≡C-$n$-Pr is reduced by the rigidity of a terminal diyne component of a copolymer originating from a short methylene chain and the presence of a phenylene group, respectively.

The ternary copolymerization of **1c**/**6**/$CO_2$ (eq 3) and



(3)

**1e**/**4**/$CO_2$ (eq 2) disclosed an effect of an ether oxygen atom upon the ether diyne copolymerizability. A relative copolymerizability (0.97) of **1c** to **6** determined by the **1c**/**6**/$CO_2$ ternary copolymerization (Table 3) shows that an electron-withdrawing effect of the ether oxygen atom on the copolymerizability of a terminal C≡C bond of a copolymer does not act through two methylene groups. On the other hand, the relative copolymerizability (2.0) of **1e** to **4** (Table 3) indicates that such an electronic effect of the ether oxygen atom operates through one methylene group to increase the ether diyne copolymerizability. A detailed elucidation of the electronic effect of the ether oxygen atom upon the poly(2-pyrone) formation, however, is not clear at the present time because the nickel(0)-catalyzed 2-pyrone ring formation involves several intermediates such as five- and seven-membered nickel(II) metallacycles along with a nickel(0) complex coordinated with a diyne and/or $CO_2$.[4]

Poly(2-pyrone)s **5a–c**, **5e**, and **7** were identified by IR, $^1$H NMR, and $^{13}$C NMR spectroscopies. The $^1$H or $^{13}$C NMR spectrum of the poly(2-pyrone) obtained by the ternary copolymerization of two diynes and $CO_2$ was almost a superposition of that prepared from the copolymerization of each diyne and $CO_2$.

Utilization of $CO_2$ as a source of carbon in polymer synthesis is an interesting research subject.[1g] Examples of $CO_2$ copolymers, however, are very limited. The present study provides a new entry of a $CO_2$ copolymer. In addition, the successful copolymerization of the ether diyne with $CO_2$ suggests that the ether diyne acts as a useful diyne comonomer in the transition-metal-catalyzed cycloaddition copolymerization of a diyne and can be used in the copolymerization involving other various cycloaddition components such as isocyanates,[2] alkenes,[5] and nitriles.[6]

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## References and Notes

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