Nickel(0)-Catalyzed Cycloaddition Copolymerization Involving Two Diynes and Carbon Dioxide to Poly(2-pyrone)

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Received March 30, 1993; Revised Manuscript Received June 7, 1993

ABSTRACT: A copolymerizability order of five diynes, i.e., 3,11-tetradecadiyne (**A**), 2,6-octadiyne (**B**), 1,4-di(2-hexynyl)benzene (**C**), 1,3-di(2-hexynyl)benzene (**D**), and 1,7-cyclotridecadiyne (**E**), in the nickel(0)-catalyzed 1:1 cycloaddition copolymerization of the diyne with CO_2 to the poly(2-pyrone) was determined by the nickel(0)-catalyzed copolymerization involving two diynes and CO_2. The copolymerizability order obtained by analyzing the copolymer composition using ^1H NMR spectroscopy was **A** > **E** > **B** > **C** > **D**. This order was explained in terms of the steric hindrance exerted by the substituent on the terminal C≡C bond of the cooligomer or the copolymer to its cycloaddition along with mobility of its terminal C≡C bond moiety for the cycloaddition. An order of cycloaddition reactivity of the diyne, which is related to formation of the cooligomer, was determined by measuring the unreacted diyne in the copolymerization involving five diynes and CO_2 using gas chromatography. The result was **E** > **B** > **C** > **D** > **A**. Thus high copolymerizability of diyne **A** is noteworthy.

Introduction

Recently, we reported the nickel(0)-catalyzed 1:1 cycloaddition copolymerization of diynes with CO_2 to poly(2-pyrone)s (Chart I, eqs 1-5).[1-3] Five diynes were used: 3,11-tetradecadiyne (**A**),[1] 2,6-octadiyne (**B**),[2] 1,4-di(2-hexynyl)benzene (**C**),[3] 1,3-di(2-hexynyl)benzene (**D**),[3] and 1,7-cyclotridecadiyne (**E**).[1] The 1:1 cycloaddition copolymerization is formally expressed as shown in eq 6, and the 2-pyrone ring formation is proposed to proceed according to eq 7 on the basis of the nickel(0)-catalyzed 2-pyrone formation from a monoyne and CO_2.[4] Here we have studied the nickel(0)-catalyzed copolymerization involving two diynes and CO_2 to determine the copolymerizability order of five diynes **A**-**E**, which clarifies the relationship between the diyne copolymerizability and the diyne structure along with the characteristics of this novel copolymerization reaction.

Experimental Section

General Procedures. IR spectra were determined on a Perkin-Elmer 1600 spectrophotometer. ^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were taken in $CDCl_3$ on a JEOL JNM-JX-400 instrument. ^1H NMR (200 MHz) were taken in $CDCl_3$ on a Varian GEMINI-200 instrument. Chemical shifts are reported in ppm on the δ scale relative to tetramethylsilane as 0 ppm. GPC was performed in chloroform using SHODEX AC-803 and AC-804 gel columns with polystyrene standards. VPO was conducted in chloroform on a Corona 117 vapor pressure osmometer. TGA was performed on a Shimadzu DT-30 instrument. Gas chromatographic analysis (GC) was performed on a Shimadzu GC-12A instrument employing a 20% silicone DC 550 on Celite 545 column with *n*-tetradecane and/or *n*-nonadecane as a GC internal standard. 3,11-Tetradecadiyne (A), 2,6-octadiyne (B), and 1,7-cyclotridecadiyne (E) were commercial reagents and were distilled under nitrogen. 1,4-Di(2-hexynyl)benzene (C) and 1,3-di(2-hexynyl)benzene (D) were prepared according to our previous report.[3] Tetrahydrofuran (THF) was distilled from $LiAlH_4$ under nitrogen. Acetonitrile (MeCN) was distilled from CaH_2 under nitrogen. Bis(1,5-cyclooctadiene)nickel(0) ($Ni(COD)_2$) was purchased from Kanto Kagaku, Inc. Tri-*n*-octylphosphine was a commercial reagent and was used without further purification. Carbon dioxide was a commercial reagent (assay: minimum 99.99 vol %) supplied by Teisan, Inc., and was used without further purification.

Copolymerization of 3,11-Tetradecadiyne (A), 2,6-Octadiyne (B), and CO_2. The reaction was carried out under nitrogen. $Ni(COD)_2$ (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), **A** (0.115 mL, 0.500 mmol), and **B** (0.064 mL, 0.50 mmol) were placed in this order in a 50-mL steel stainless steel autoclave under magnetic stirring at ambient temperature. CO_2 gas was compressed up to 20 kg/cm². The reaction mixture was heated at 60 °C for 3 h 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 ether (20 mL) to a resulting residue precipitated a copolymer. Drying in vacuo at room temperature gave copolymer **AB** as pale yellow solids (0.036 g, 19%). GPC analysis of the copolymer showed M_n = 1700 and M_w/M_n = 1.6. Copolymer **AB**: IR (KBr, cm^{-1}) 1703, 1632, 1553, 1073, 1056; ^1H NMR (200 MHz) 0.70-1.33 (m), 1.33-1.80 (m), 1.80-3.10 (m); ^{13}C NMR 12.0-32.0 (m), 112.0-113.0 (m), 114.6-115.2 (m), 115.2-116.0 (m), 116.7-117.0 (m), 117.3-118.0 (m), 119.0-120.5 (m), 121.2-122.0 (m), 122.0-122.8 (m), 122.8-123.6 (m), 124.4-125.0 (m), 151.0-153.0 (m), 153.0-155.0 (m), 155.3-156.3 (m), 157.6-158.6 (m), 158.6-159.8 (m), 163.0-163.4 (m), 163.4-164.5 (m).

Copolymerization of 2,6-Octadiyne (B), 1,3-Di(2-hexynyl)benzene (D), and CO_2. The reaction was carried out under nitrogen. $Ni(COD)_2$ (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), **B** (0.064 mL, 0.50 mmol), and **D** (0.123 mL, 0.500 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 20 kg/cm². The reaction mixture was heated at 80 °C for 20 h 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 ether (20 mL) to the resulting residue precipitated a copolymer. Loss of the copolymer by the use of ether was examined because the copolymer obtained by the copolymerization of diyne **D** with CO_2 was precipitated with methanol.[3] Evaporation of the filtrate in vacuo and subsequent addition of methanol (20 mL) did not precipitate any copolymer. This finding indicates that copolymer **BD** precipitated with ether was satisfactorily obtained without extensive loss. Drying in vacuo at room temperature gave copolymer **BD** as pale yellow solids (0.14 g, 65%). GPC analysis of the copolymer showed M_n = 2100 and M_w/M_n = 2.7. Copolymer **BD**: IR (KBr, cm^{-1}) 1707, 1635, 1604, 1552, 1059, 780; ^1H NMR (200 MHz, CD_2Cl_2) 0.60-1.15 (m), 1.15-1.80 (m), 1.80-3.10 (m), 3.35-4.10 (m), 6.70-7.50 (m); ^{13}C NMR 12.0-38.0 (m), 110.4-113.0 (m), 113.0-116.0 (m), 116.5-117.7 (m), 119.8-120.8 (m), 121.1-123.3 (m), 124.0-130.0 (m), 134.0-143.0 (m), 150.4-154.0 (m), 154.0-158.0 (m), 158.8-161.0 (m), 162.2-164.6 (m).

Copolymerizations with Other Diyne Combinations Involving CO_2. Copolymerizations with other diyne combinations involving CO_2 were similarly carried out to copolymerizations of

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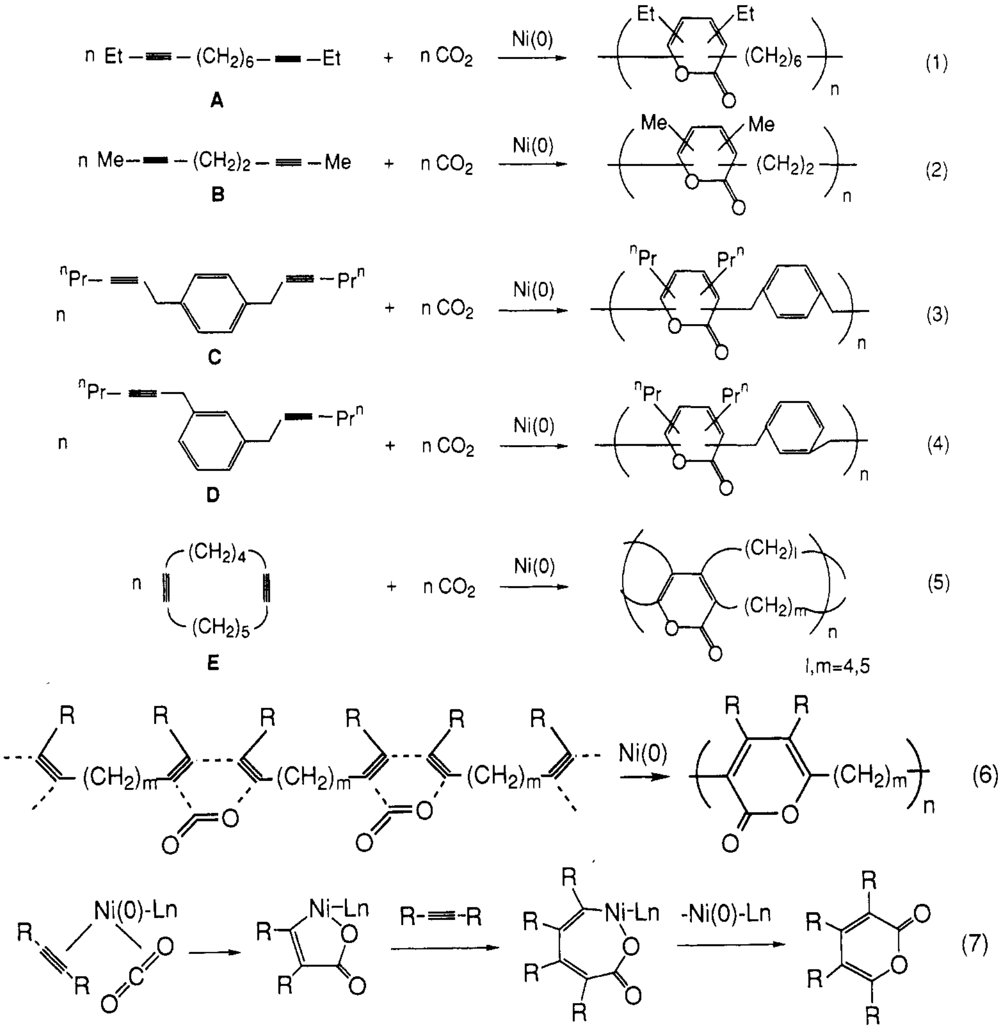
Chart I

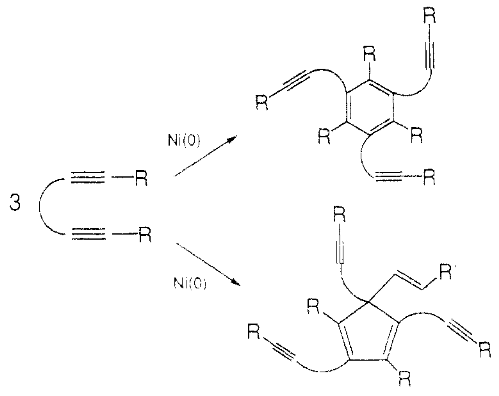


A/**B**/CO$_2$ and **B**/**D**/CO$_2$, and the copolymers obtained were characterized as follows. Copolymer **AE**: IR (KBr, cm^{-1}) 1703, 1624, 1542, 1070, 1050; ^{1}H NMR (200 MHz) 0.70–1.30 (m), 1.30–2.00 (m), 2.00–3.00 (m); ^{13}C NMR 12.0–38.0 (m), 114.2–117.6 (m), 122.4–125.4 (m), 152.9–156.7 (m), 156.7–159.8 (m), 162.3–164.4 (m). Copolymer **BC**: IR (KBr, cm^{-1}) 1706, 1635, 1551, 1511, 1059, 784; ^{1}H NMR (200 MHz, CD$_2$Cl$_2$) 0.60–1.13 (m), 1.13–1.83 (m), 1.83–3.20 (m), 3.40–4.10 (m), 6.80–7.40 (m); ^{13}C NMR 11.0–38.0 (m), 110.0–113.0 (m), 113.0–116.4 (m), 116.4–117.8 (m), 119.0–121.0 (m), 121.0–123.7 (m), 124.8–127.0 (m), 127.0–131.5 (m), 133.6–143.0 (m), 150.5–154.0 (m), 154.8–158.0 (m), 159.2–161.2 (m), 162.5–164.8 (m). Copolymer **BE**: IR (KBr, cm^{-1}) 1703, 1632, 1553, 1073, 1056; ^{1}H NMR (400 MHz) 0.80–2.03 (m), 2.03–3.10 (m); ^{13}C NMR 12.3–33.0 (m), 111.3–113.0 (m), 114.0–118.8 (m), 118.8–120.8 (m), 120.8–123.2 (m), 123.2–125.2 (m), 149.7–153.2 (m), 153.2–157.0 (m), 157.0–159.8 (m), 162.5–164.4 (m).

Gas Chromatographic Analysis of Unreacted Diynes in the Copolymerization. The reaction was carried out under nitrogen. Ni(COD)$_2$ (0.0330 g, 0.120 mmol) in a THF solution (2.81 mL), P(*n*-C$_8$H$_{17}$)$_3$ (0.107 mL, 0.240 mmol), MeCN (2.81 mL), **A** (0.092 mL, 0.40 mmol), **B** (0.0512 mL, 0.400 mmol), **E** (0.0752 mL, 0.400 mmol), and *n*-tetradecane (0.0794 g, 0.400 mmol) in a THF solution (0.443 mL) as a GC internal standard 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 20 kg/cm^2. The reaction mixture was heated at 80 °C for 30 min under magnetic stirring. After the reaction mixture was cooled by ice water, the remaining CO$_2$ gas was purged off. Unreacted diynes were determined by gas chromatographic analysis of the reaction mixture. The copolymerization containing five diynes **A**–**E** was similarly carried out and was analyzed using two GC internal standards of *n*-tetradecane and *n*-nonadecane.

Results and Discussion

Nickel(0)-catalyzed copolymerization of two diynes and CO$_2$ was carried out similarly to the previously reported nickel(0)-catalyzed copolymerization[1-3] of the diyne with CO$_2$ using the reaction conditions to effect the 1:1 copolymerization. Thus an equimolar mixture of two diynes was treated with CO$_2$ under pressure in a mixed THF/MeCN solvent at a prescribed reaction temperature in the presence of a nickel(0) catalyst generated from Ni(COD)$_2$ (10 mol %) and 2 equiv of a tri-*n*-octylphosphine ligand. The copolymer of poly(2-pyrone) was obtained by concentration of the reaction mixture under vacuum followed by precipitation with ether. The copolymer is pale yellow solids. It is soluble in methylene chloride, chloroform, and THF but is insoluble in ether and hexane. Formation of poly(2-pyrone) was confirmed by IR, ^{1}H NMR, and ^{13}C NMR spectroscopic analyses as previously.[1-3] The poly(2-pyrone) exhibited the following characteristic spectral data of the 2-pyrone ring: IR ν(C=O) absorption at 1700–1710 cm^{-1}; ^{1}H NMR CH$_2$C=C absorptions at δ 2.0–3.2, and ^{13}C NMR C=C and C=O absorptions at δ 112–118, 120–127, 150–157, 157–161, and 162–165. Each group of the ^{13}C NMR C=C and C=O absorptions appeared as a multiplet due to regioisomeric 2-pyrone rings (vide post). The copolymer showed only negligible or very small ^{13}C NMR C=C absorption due to diyne homopolymer units depicted in eq 8,[5] which indicates efficient 1:1 copolymerization of the diyne with CO$_2$ to the poly(2-pyrone). The ^{1}H or ^{13}C NMR spectrum of the copolymer from two diynes and CO$_2$ was almost a



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superposition of that of the poly(2-pyrone) obtained from the copolymerization of each diyne and CO_2.

The yields and molecular weights of the copolymers obtained under various reaction conditions are summarized in Table I. For example, the poly(2-pyrone) obtained from the copolymerization of **A**, **B**, and CO_2 is expressed as **AB**. The copolymerization reaction was mostly not allowed to proceed to completion to determine the relative copolymerizability of two diynes with CO_2 by analyzing the copolymer composition. The molecular weight of the copolymer was measured by GPC in chloroform with polystyrene standards. A GPC curve of the copolymer generally showed only one peak.

The composition of the copolymer was determined by ^1H NMR spectroscopic analysis using peak areas of a key absorption and other absorptions. The key absorption and the other absorptions of the copolymer are as follows: CH_3 and CH_2 absorptions of the diyne **A** moiety at δ 0.70–1.85 as the key absorption and $CH_3C{=}C$ plus $CH_2C{=}C$ absorptions of the diyne **A** and **B** moieties at δ 1.70–3.10 (copolymer **AB**), CH_3 absorptions of the diyne **A** moiety at δ 0.70–1.45 as the key absorption and CH_2 absorptions of the diyne **A** and **E** moieties at δ 1.10–3.00 (copolymer **AE**), CH_2 absorptions of the diyne **E** moiety at δ 0.80–2.20 as the key absorption and $CH_3C{=}C$ plus $CH_2C{=}C$ absorptions of the diyne **B** and **E** moieties at δ 1.50–3.10 (copolymer **BE**), C_6H_5 absorptions of the diyne **C** moiety at δ 6.80–7.40 as the key absorption and CH_3 plus CH_2 absorptions of the diyne **B** and **C** moieties at δ 0.60–4.10 (copolymer **BC**), and C_6H_5 absorptions of the diyne **D** moiety at δ 6.70–7.50 as the key absorption and CH_3 plus CH_2 absorptions of the diyne **B** and **D** moieties at δ 0.60–4.10 (copolymer **BD**). The results of the composition analysis of the copolymer obtained from an equimolar feed of two diynes are summarized in Table I and indicate that the copolymerizability order of the five diynes is **A** > **E** > **B** > **C** > **D**. Copolymerizability means the ease with which the diyne is incorporated into the copolymer.

Our previous studies[1,2] on the copolymerization of **A** or **B** with CO_2 show a lower copolymerizability of **B** than **A**, which has now been confirmed by formation of poly(2-pyrone) **AB** with copolymer composition [**A**]/[**B**] = 3.0. The lower copolymerizability of **B** than **A** was further demonstrated by the copolymerization with the diyne feed differing from **A**/**B** = 1 and also by an effect of the content of **B** in the diyne feed upon the molecular weight of **AB** as follows.

Results of the copolymerization of **A**, **B**, and CO_2 using diyne feeds of **A**/**B** = 3/7 and 7/3 and a copolymerization time of 20 h are shown in Table II. The copolymer composition indicates the higher copolymerizability of **A** than **B** although the copolymer yield is high. The relationship between the molecular weight of copolymer **AB** and the composition of the diyne feed is illustrated in Figure 1 on the basis of data in Table II. It is noteworthy that the molecular weight of **AB** decreased with increasing content of **B** in the diyne feed.

Table I. Nickel(0)-Catalyzed Ternary Copolymerization Involving Two Diynes (I + II) and CO_2 to Poly(2-pyrone)[a]

			poly(2-pyrone)				
I + II	temp, °C	time, h		yield,[b] %	M_n[c]	M_w/M_n[c]	[I]/[II][d]
A + B	60	3	**AB**	19	1700	1.6	3.0
A + E	90	4	**AE**	50	2800	2.6	2.1
E + B	80	1	**BE**	36	1200	1.5	2.7
B + C	80	4	**BC**	67	2200 (2400)[e]	2.0	2.2
B + D	80	4	**BD**	65	2100	2.7	2.8

[a] I = II = 0.500 mmol; Ni/I + II = 0.10; tri-*n*-octylphosphine/Ni = 2; CO_2, 20 kg/cm^2 (initial pressure at room temperature); solvent, 5 mL, THF/MeCN = 1/1 (v/v). [b] Based on quantitative formation of the copolymer from I, II, and CO_2. [c] Determined by GPC with polystyrene standards in chloroform. [d] Molar ratio of I and II components in the copolymer determined by ^1H NMR. [e] Determined by VPO in chloroform.

Table II. Nickel(0)-Catalyzed Ternary Copolymerization of Two Diynes A and B with CO_2 to Poly(2-pyrone) AB[a]

	AB			
A/**B**[b]	yield,[c] %	M_n[d]	M_w/M_n[d]	[**A**]/[**B**][e]
0[f]	78	1700	2.0	
1/10	83	2000	2.3	
2/8	73	2700	2.1	
3/7	81	3000	2.2	0.72
7/3	77	5000	2.7	3.4
3/7[g]	83	11400	15	
5/5[h]	77	3800	5.4	

[a] **A** + **B** = 1.00 mmol; Ni/**A** + **B** = 0.10; tri-*n*-octylphosphine/Ni = 2; CO_2, 50 kg/cm^2 (initial pressure at room temperature); solvent, 5 mL, THF/MeCN = 1/1 (v/v); temperature, 60 °C; time, 20 h. [b] Diyne feed, molar ratio. [c] Based on quantitative formation of **AB**. [d] Determined by GPC with polystyrene standards in chloroform. [e] Molar ratio of **A** and **B** components in **AB** determined by ^1H NMR. [f] Binary copolymerization of **B** with CO_2.[2] [g] **A** + **B** = 4.00 mmol. [h] CO_2, 20 kg/cm^2 (initial pressure at room temperature); temperature, 80 °C; time, 14 h.

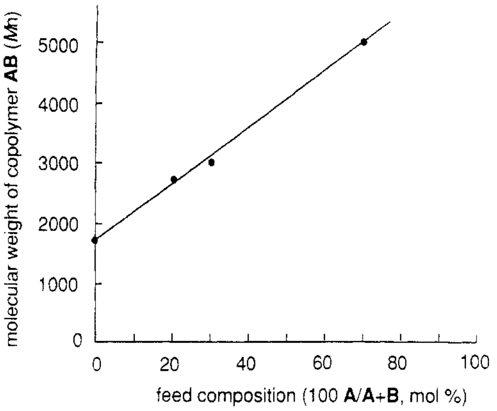


Figure 1. Relationship between the feed composition and the molecular weight of copolymer **AB** in the ternary copolymerization of 3,11-tetradecadiyne (**A**), 2,6-octadiyne (**B**), and CO_2 under the reaction conditions of footnotes *a* and *f* in Table II.

Previously, the copolymerization of **A** or **B** with CO_2 was found to be dependent upon the diyne concentration.[1,2] For example, under the diyne concentration of footnote *a* in Table II, the copolymerization of **B** with CO_2 almost stops after formation of the copolymer with the molecular weight of ca. 1700[2] as shown in Figure 1, which suggests that the cycloaddition reactivity of the terminal C≡C bond of the copolymer (vide infra) is reduced as its degree of polymerization increases. An increase in **B** content in

Table III. Nickel(0)-Catalyzed Ternary Copolymerization of Two Diynes B and E with CO_2 to Poly(2-pyrone) BE[a]

	BE					
time, h	yield,[b] %	M_n[c]	M_w/M_n[c]	[E]/[B][d]	[E][e]	[B][e]
1	36	1200	1.5	2.7	0.24	0.09
1.5	67	1500	1.6	2.0	0.42	0.21
2.5	80	1800	2.3	2.2	0.51[f]	0.23
4	76	2300	5.2	2.1	0.49	0.23

[a] B = E = 0.500 mmol; Ni/B + E = 0.10; tri-*n*-octylphosphine/Ni = 2; CO_2, 20 kg/cm^2 (initial pressure at room temperature); solvent, 5 mL, THF/MeCN = 1/1 (v/v); temperature, 80 °C. [b] Based on quantitative formation of **BE**. [c] Determined by GPC with polystyrene standards in chloroform. [d] Molar ratio of **E** and **B** components in **BE** determined by ^{1}H NMR. [e] Diyne incorporated into **BE**, mmol. [f] [E] value of 0.51 over 0.50 may be due to an error of copolymer composition analysis by ^{1}H NMR originating from indistinct separation of the key absorption and the other absorptions. See text.

the **A** + **B** feed favors formation of a copolymer having diyne **B** moieties at both ends after virtual consumption of the more reactive diyne **A** to slow down the copolymer growth and to produce the copolymer without further increase of its molecular weight. Thus the result of Figure 1 also demonstrates the lower copolymerizability of **B** than **A**.

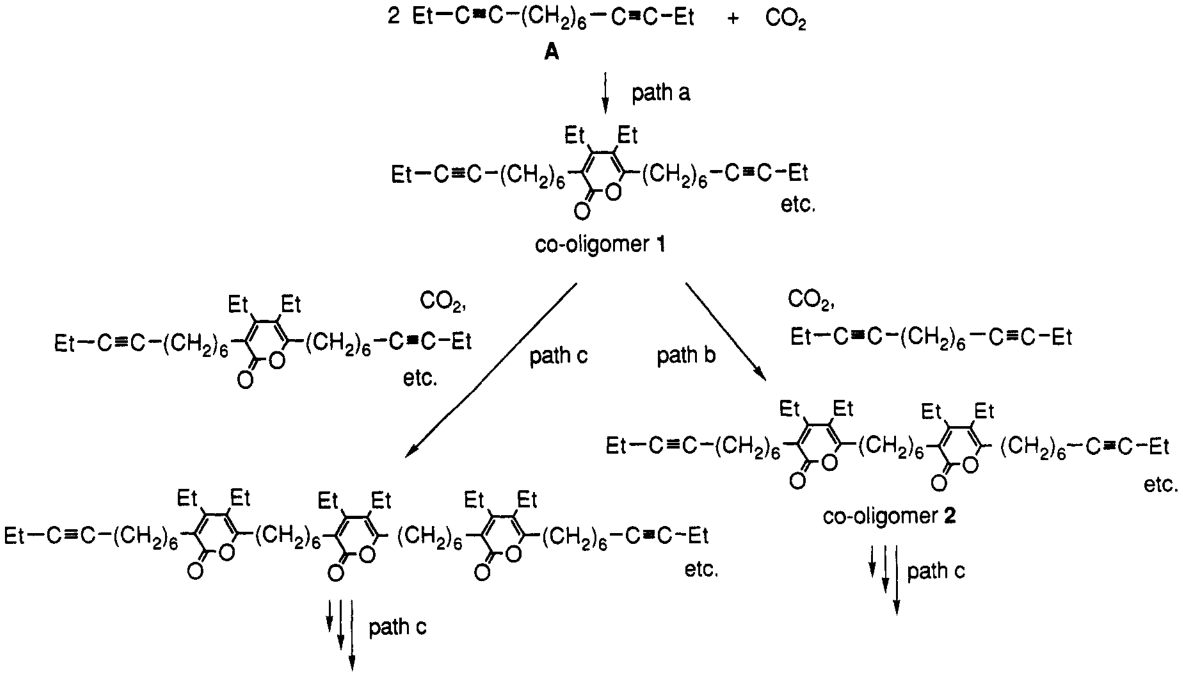
Increasing the diyne concentration by 4 times afforded a copolymer with a higher molecular weight (M_n = 11 400) together with a broader molecular weight distribution (M_w/M_n = 15) (Table II). This broad molecular weight distribution may be due to partial precipitation of the copolymer during the copolymerization, and not to increased branching and/or cross-linking originated from generation of diyne homopolymer units (eq 8) in the copolymer. This conclusion is supported by the finding that the copolymer exhibited a ^{13}C NMR spectrum similar to that of the copolymer obtained under the reaction conditions of footnote *h* in Table II, which shows only very small C=C absorptions of diyne homopolymer units.

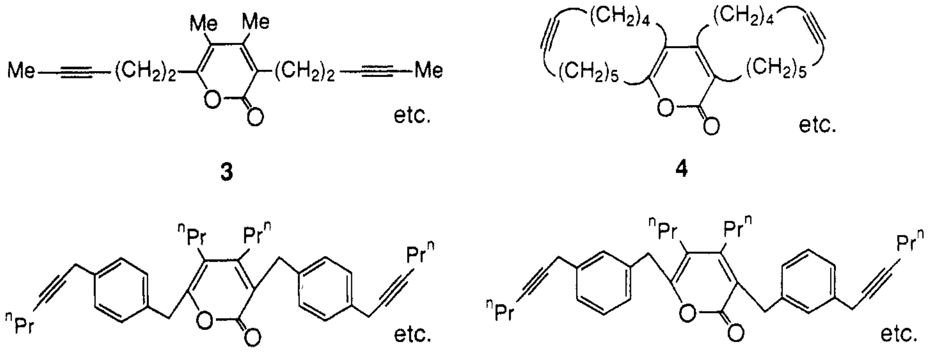
The relationship between the reaction time and the copolymer yield and molecular weight along with the copolymer composition in the copolymerization of **B**, **E**, and CO_2 was examined (Table III). The increase of copolymer yield and molecular weight with reaction time up to 2.5 h indicates that copolymer growth proceeds via stepwise polyaddition (vide post). Diyne **E** was quantitatively incorporated into **BE** after 2.5 h, and no further incorporation of **B** into the copolymer was observed. This copolymerization behavior of **B** is similar to that of **B** in the ternary copolymerization of **A**, **B**, and CO_2 shown in Figure 1.

The copolymer growth in the nickel(0)-catalyzed 1:1 cycloaddition copolymerization of the diyne with CO_2 is assumed to proceed as shown in Scheme I, taking the diyne **A**–CO_2 copolymerization as an example. This scheme is supported partly by isolation and characterization[1] of cooligomers **1** and **2** consisting of their regioisomers. The corresponding cooligomers **3**–**6** consisting of two diyne molecules and one CO_2 molecule shown in Figure 2 have been similarly isolated by shortening the reaction time of the copolymerization of diynes **B**, **E**, **C**, and **D**, respectively, with CO_2.[1-3] Cooligomers **1** and **4** consist of four regioisomers, while **3**, **5**, and **6** are composed of two predominant regioisomers. Orientation of the 2-pyrone ring in the copolymer seems to be random. The copolymerization involving two diynes may be reasonably considered to proceed similarly to Scheme I. Thus the so-called "initiation reaction" of the copolymerization is cooligomer formation involving the diyne comonomer (paths a and b, Scheme I), and its "propagation reaction" is cycloaddition of the terminal C≡C bond of the cooligomer or the copolymer (path c, Scheme I). Thus the copolymerizability of diyne should be discussed on the basis of the structure of the terminal C≡C bond of the cooligomer and the copolymer.

The structures of cooligomers **1** and **3**–**6** depicted in Scheme I and Figure 2, respectively, are useful for discussing the diyne copolymerizability. The structure of **3** suggests that the copolymerizability of the terminal C≡C bond of the cooligomer or the copolymer having the terminal diyne **B** moiety is reduced by the nearer presence of a sterically bulky 2-pyrone ring originated from the short methylene chain of **B**. This idea may explain the lower copolymerizability of **B** than **A**.[2] The C≡C bond of the copolymer having the terminal diyne **A** moiety does not suffer from such influence of the 2-pyrone ring owing to its longer methylene chain and therefore exhibits a high copolymerizability. Steric hindrance due to benzylic and

Scheme I. Mechanism of Copolymer Growth





3 4 5 6

Figure 2. Cooligomers **3**–**6** consisting of two diyne molecules and one CO_2 molecule.

Table IV. Evaluation of Cycloaddition Reactivity of the Diyne Comonomer with CO_2 in the Poly(2-pyrone) Formation[a]

diyne mixture	time, min	unreacted diyne,[e] %
A + **B** + **E**[b]	30	**A** (74%), **B** (49%), **E** (46%)
A + **B** + **C** + **D** + **E**[c]	45	**A** (58%), **D** (43%), **C** (40%), **B** (33%), **E** (27%)
A + **B** + **C** + **D** + **E**[d]	120	**A** (10%), **D** (4.0%), **C** (3.8%), **B** (0%), **E** (0%)

[a] Each diyne, 0.400 mmol; Ni/total diynes = 0.10; tri-*n*-octylphosphine/Ni = 2; CO_2, 20 kg/cm^2 (initial pressure at room temperature); solvent, 5 mL/mmol of total diynes; temperature, 80 °C. [b] Solvent, THF (3.2 mL) + MeCN (2.8 mL); *n*-tetradecane as a GC internal standard, 0.400 mmol. [c] Solvent, THF (5.9 mL) + MeCN (4.1 mL); *n*-tetradecane and *n*-nonadecane as GC internal standards, 0.400 mmol (each). [d] Solvent, THF (5.9 mL) + MeCN (4.1 mL); *n*-tetradecane and *n*-nonadecane as GC internal standards, 0.400 mmol (each). [e] Determined by GC and based on the diyne used.

n-propyl substituents to the cycloaddition reactivity of the C≡C bond of the terminal diyne **C** or **D** moiety of the cooligomer and the copolymer lowers the copolymerizability of **C** and **D**. The high copolymerizability of **E** is ascribed to the lower steric hindrance of the cyclic methylene substituents. Thus the copolymerizability order of **A** > **E** > **B** > **C** > **D** may be mainly and qualitatively explained in terms of steric hindrance caused by the substituent on the terminal C≡C group of the cooligomer and the copolymer to the copolymer growth reaction.

There are two kinds of cycloaddition reaction of the C≡C bond in the copolymerization of the diyne with CO_2 as depicted in Scheme I: one is cycloaddition involving the terminal C≡C bond of the cooligomer and/or the copolymer (path c) and the other is cycloaddition involving the diyne itself to form the cooligomer (paths a and b). The determined copolymerizability order of the diyne, **A** > **E** > **B** > **C** > **D**, may be mainly related to the former. The cycloaddition reactivity of the diyne comonomer relating to the latter was evaluated by measuring an amount of unreacted diyne in a copolymerization reaction mixture after a prescribed reaction time using gas chromatography. The results are shown in Table IV, which gives an order of the cycloaddition reactivity of the diyne comonomer for cooligomer formation, **E** > **B** > **C** > **D** > **A**. Although the partial order **E** > **B** > **C** > **D** may be understandable by the steric hindrance caused by the substituent on the C≡C bond (vide ante), the order **C** > **D** > **A** cannot be explained in terms of the steric effect. The higher cycloaddition reactivity of **C** and **D** than **A** might be ascribed to an electronic effect of the phenylene group of **C** and **D**.

The cycloaddition reactivity order of the diyne comonomer, **E** > **B** > **C** > **D** > **A**, differs from the copolymerizability order of the diyne, **A** > **E** > **B** > **C** > **D**. The partial order **E** > **B** > **C** > **D** is observed in two reactivity orders and may be explained in terms of the steric factor caused by substituents on the C≡C bond (vide ante). Noteworthy is the finding that **A** shows the highest copolymerizability while it is the diyne with the lowest cycloaddition reactivity. In addition to the above-mentioned steric factor, another factor may be important in the copolymerization of diyne **A**. One structural feature around the terminal C≡C bond of the cooligomer and the copolymer having the terminal diyne **E**, **B**, or **C** and **D** moiety is rigidity originating from the ladder structure, the short methylene chain, or the presence of the phenylene group, respectively, as shown in Figure 2. This rigidity may hinder the reacting terminal C≡C bond of the cooligomer and the copolymer from accommodating easily the nickel atom, the tri-*n*-octylphosphine ligand, and CO_2 for the 2-pyrone ring formation (eq 7) and accordingly may retard copolymer growth. This rigidity factor will be more serious as the molecular weight of the copolymer increases. On the contrary, the cooligomer and the copolymer with the terminal diyne **A** moiety have the mobile terminal C≡C bond moiety on a flexible long alkyl chain to effect easy 2-pyrone ring formation. This is one possible explanation for the highest copolymerizability of diyne **A**. Thus the copolymerizability of the diyne with CO_2 should be discussed on the basis of the structure of the terminal acetylenic moiety of the copolymer and the rigidity around it, which indicates one feature of the present copolymerization.

Thermogravimetric analysis (TGA) showed that the ternary copolymer obtained from two diynes and CO_2 generally has reduced thermal stability compared to that of the corresponding binary copolymer.

Acknowledgment. This work was sponsored by the New Energy and Industrial Technology Development Organization (NEDO)/Research Institute of Innovative Technology for the Earth (RITE).

References and Notes

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