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Nickel(0)-Catalyzed 1:1 Cycloaddition Copolymerization of 1,3- and 1,4-Di(2-hexynyl)benzenes with Carbon Dioxide to Poly(2-pyrone)s

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ABSTRACT: A nickel(0) catalyst generated from Ni(COD)$_2$ and triethyl- or tri-*n*-octylphosphine effected efficient 1:1 cycloaddition copolymerization of 1,3- and 1,4-di(2-hexynyl)benzenes (**1** and **2**) with CO$_2$ to poly(2-pyrone)s **3** and **4**, respectively. Copolymerization of **1** with CO$_2$ at 80 °C in THF/MeCN for 20 h under a CO$_2$ pressure of 10–50 kg/cm^2 afforded **3** with molecular weights of 6000–7000 in ca. 50% yield, and copolymerization of **2** with CO$_2$ at 70 °C in THF/MeCN for 20 h under a CO$_2$ pressure of 20–50 kg/cm^2 afforded **4** with molecular weights of 9000–12 000 in ca. 60% yield. Formation of the poly(2-pyrone) was demonstrated by IR, ^{1}H NMR, and ^{13}C NMR spectroscopies and by measuring the content of the 2-pyrone ring in the copolymer by IR spectroscopy using a cooligomer as an IR standard.

Introduction

Utilization of CO$_2$ in polymer synthesis to prepare an alternating copolymer of CO$_2$ is a research subject of great interest. Until recently, however, only one example of CO$_2$ copolymerization was known which satisfied both alternating copolymerizability and degree of polymerization. It is the alternating copolymerization of CO$_2$ with epoxides.[1] We recently reported the nickel(0)-catalyzed 1:1 cycloaddition copolymerization of diynes with CO$_2$ via intermolecular cyclization to the novel poly(2-pyrone)s (Chart I, eqs 1–3).[2,3] This is a new polymerization reaction of transition metal-catalyzed cycloaddition copolymerization of diynes. If diynes with various structures are available, this poly(2-pyrone) synthesis can become quite useful.

Recently, we reported tricyclic 2-pyrone synthesis by the nickel(0)-catalyzed intramolecular cycloaddition of 1,2-di(2-hexynyl)benzene involving CO$_2$ (eq 4).[4] On the other hand, 1,3- and 1,4-di(2-hexynyl)benzenes (**1** and **2**) are expected to undergo nickel(0)-catalyzed intermolecular cycloaddition involving CO$_2$ to poly(2-pyrone)s because of their reduced intramolecular cycloaddition reactivity. In this report we describe the nickel(0)-catalyzed 1:1 cycloaddition copolymerization of **1** and **2** with CO$_2$ to poly(2-pyrone)s **3** and **4**, respectively, which have a phenylene functional group in a methylene chain connecting the 2-pyrone rings (eqs 5 and 6).

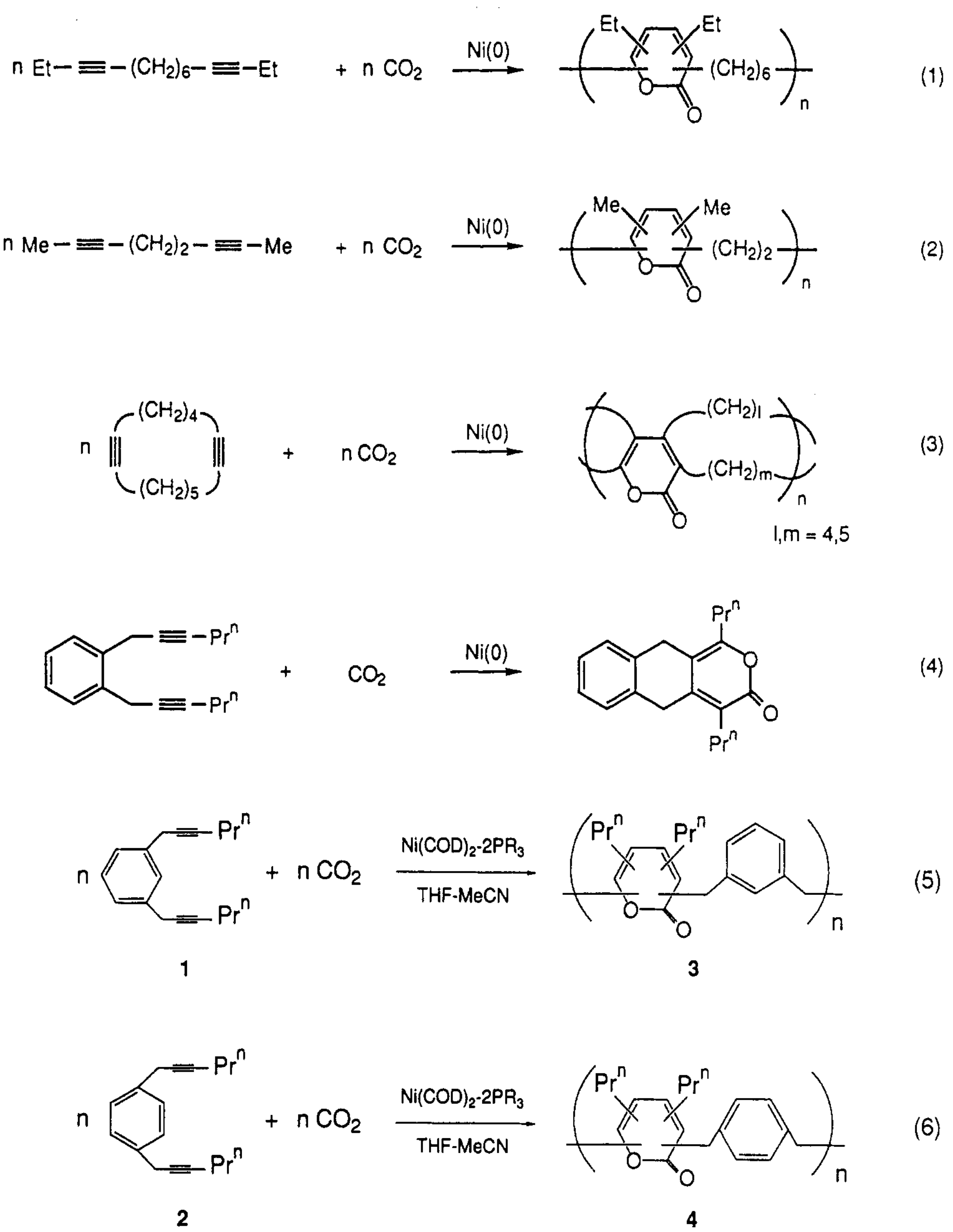
Experimental Section

General Procedures. IR spectra were determined on a Perkin-Elmer 1600 spectrophotometer. IR solution spectra were obtained in a 0.01-cm cell. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were taken in CDCl$_3$ on a JEOL JNM-JX-400 instrument. ^{1}H 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. MASS spectra were obtained on a JEOL DX-300 instrument. Preparative layer chromatography (PLC) was carried out by using 20 × 20 × 0.2 cm plates prepared with Merck silica gel 60 PF-254. Medium-pressure liquid chromatography (MPLC) was carried out on a Yamazen 700E instrument. 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. 1-Pentyne, *n*-butyllithium hexane solution, and *m*- and *p*-xylylene dibromides were commercial reagents and were used directly. 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. Phosphorus ligands were commercial reagents and were used without further purification. Carbon dioxide was a commercial reagent (assay: minimum 99.9 vol %) supplied by Sumitomo Seika, Inc., and was used without further purification.

Preparation of 1,3- and 1,4-Di(2-hexynyl)benzenes (1 and 2). The reaction was carried out under nitrogen. Lithium 1-pentylide was prepared from 1-pentyne (4.10 mL, 41.7 mmol) and a hexane solution of *n*-butyllithium (41.7 mmol) in THF (30 mL). The resulting solution of lithium 1-pentylide was added dropwise with magnetic stirring to a THF solution (30 mL) of *m*-xylylene dibromide (5.00 g, 18.9 mmol) cooled at 0 °C. The reaction mixture was allowed to react at ambient temperature for 3 days. Addition of a saturated sodium chloride aqueous solution (20 mL), extraction with hexane (200 mL), drying with anhydrous magnesium sulfate, and subsequent evaporation of volatile matter under vacuum gave a yellow liquid, which was purified by MPLC (silica gel, hexane/ethyl acetate = 20/1 (v/v)) to afford **1** (3.16 g, 13.3 mmol, 70%). **1**: IR (neat, cm^{-1}) 3058, 3027, 2230, 1608, 1489, 771; ^{1}H NMR (200 MHz) 1.00 (t, $J = 7.4$, 6 H), 1.56 (sext, $J = 7.0$, 4 H), 2.20 (tt, $J = 6.8$, 2.4, 4 H), 3.58 (t, $J = 2.1$, 4 H), 6.90–7.45 (m, 4 H); ^{13}C NMR 13.6, 20.9, 22.5, 25.1, 77.7, 82.5, 125.9, 127.4, 128.5, 137.8; HRMS (*m/e*) 238.1743, calcd for C$_{18}$H$_{22}$ 238.1721. Diyne **2** was similarly prepared in 63% yield. **2**: IR (neat, cm^{-1}) 3052, 3024, 2230, 1512, 1463, 793; ^{1}H NMR 0.96 (t, $J = 7.3$, 6 H), 1.51 (sext, $J = 7.3$, 4 H), 2.15 (tt, $J = 7.1$, 1.2, 4 H), 3.52 (t, $J = 2.4$, 4 H), 7.03–7.36 (m, 4 H); ^{13}C NMR 13.6, 20.9, 22.5, 24.8, 77.8, 82.4, 127.9, 135.7; HRMS (*m/e*) 238.1747, calcd for C$_{18}$H$_{22}$ 238.1721.

Copolymerization of 1,3-Di(2-hexynyl)benzene (1) with CO$_2$. The reaction was carried out under nitrogen. Ni(COD)$_2$ (0.0275 g, 0.100 mmol) in a THF solution (2.60 mL), P(n-C$_8$H$_{17}$)$_3$ (0.0893 mL, 0.200 mmol), MeCN (2.40 mL), and **1** (0.246 mL, 1.00 mmol) were mixed in this order in a 50-mL stainless steel autoclave with magnetic stirring at ambient temperature. CO$_2$ gas was compressed up to 50 kg/cm^2. The reaction mixture was heated at 80 °C for 20 h with magnetic stirring. After the reaction mixture was cooled with ice water, the remaining CO$_2$ gas was purged off and the reaction mixture was filtered. After a small amount of insoluble matter was washed with chloroform, the combined solution was concentrated in vacuo. Addition of methanol (30 mL) to the resulting residue precipitated a copolymer. Removing the supernatant solution over the copolymer by suction and drying in vacuo at room temperature gave the copolymer (0.22 g, 82% based on the formation of a 1:1 copolymer of **1** with CO$_2$). GPC analysis of the copolymer showed $M_n = 2500$ and $M_w/M_n = 5.9$. This copolymer was further purified by dissolving in chloroform (0.5 mL) and adding the chloroform solution dropwise to methanol (25 mL). Removing the super-

Chart I



natant solution over the precipitated copolymer by suction and drying in vacuo at room temperature gave copolymer 3 as pale yellow solids (0.13 g, 46%). GPC analysis of the copolymer showed M_n = 6700 and M_w/M_n = 3.0. Copolymer 3: IR (KBr, cm^{-1}) 1709, 1630, 1604, 1544, 1063, 760; ^{1}H NMR 0.60–1.10 (m), 1.10–1.18 (m), 2.00–2.60 (m), 3.40–4.10 (m), 6.70–7.50 (m); ^{13}C NMR (CD_2Cl_2) 113.0–114.0 (m), 116.2–117.5 (m), 121.6–122.9 (m), 150.9–152.3 (m), 155.7–157.5 (m), 159.3–161.2 (m), 162.6–164.3 (m). The ^{13}C NMR C=C absorptions of the phenyl groups appear at δ 124.4–130.6 (m) and 136.0–142.0 (m). In addition to these ^{13}C NMR C=C and C=O absorptions, CH_2 and CH_3 absorptions are observed between δ 13.3 and 37.4. No ^{13}C NMR C≡C absorption is observed. Copolymer 3 did not show a satisfactory elemental analysis. For example, 3 with M_n = 6700 in Table I revealed the following analytical result: Anal. Calcd for $(C_{19}H_{22}O_2)_n$: H, 7.85; C, 80.82. Found: H, 7.58; C, 76.64. It was found that ashes were formed after combustion analysis of the copolymer. This finding suggests that nickel salts contaminate the copolymer.

Copolymerization of 1,4-Di(2-hexynyl)benzene (2) with CO_2. The reaction was exactly the same as that described for 1 and CO_2 except the reaction temperature was 70 °C. The copolymer yield was 0.25 g (88% based on the formation of a 1:1 copolymer of 2 with CO_2). GPC analysis of the copolymer showed M_n = 6500 and M_w/M_n = 3.8. This copolymer was further purified by dissolving in chloroform (0.5 mL) and adding the chloroform solution dropwise to methanol (25 mL). Removing the supernatant solution over the precipitated copolymer by suction and drying in vacuo at room temperature gave copolymer 4 as pale yellow solids (0.17 g, 62%). GPC analysis of the copolymer showed M_n = 9000 and M_w/M_n = 2.7. Copolymer 4: IR (film, cm^{-1}) 1708, 1630, 1543, 1510, 1055, 792; ^{1}H NMR 0.60–1.10 (m), 1.10–1.80 (m), 2.10–2.60 (m), 3.40–4.10 (m), 6.80–7.40 (m); ^{13}C NMR (CD_2Cl_2) 113.3–114.0 (m), 116.3–117.3 (m), 121.7–123.0 (m), 125.4–126.3 (m), 151.3–152.3 (m), 156.0–157.4 (m), 159.8–160.9 (m), 163.1–164.2 (m). In addition to these ^{13}C NMR C=C and C=O absorptions, CH_2 and CH_3 absorptions are observed between δ 13.8 and 37.0 and phenyl absorptions appear at δ 127.2–130.5 (m) and 134.2–138.3 (m). No ^{13}C NMR C≡C absorption is observed.

Homopolymerization of 1,3-Di(2-hexynyl)benzene (1) and 1,4-Di(2-hexynyl)benzene (2). The reaction was carried out under nitrogen. Ni(COD)$_2$ (0.0275 g, 0.100 mmol) in a THF solution (2.40 mL), $P(n\text{-}C_8H_{17})_3$ (0.0893 mL, 0.200 mmol), MeCN (2.60 mL), and 1 (0.246 mL, 1.00 mmol) were mixed in this order in a 50-mL stainless steel autoclave with magnetic stirring at ambient temperature. The reaction mixture was heated at 80 °C for 20 h with magnetic stirring. The reaction mixture was cooled with ice water and then filtered. After a small amount of insoluble matter was washed with chloroform, the combined solution was concentrated in vacuo. Addition of methanol (25 mL) to the resulting residue precipitated a homopolymer. Removing the supernatant solution over the homopolymer by suction and drying in vacuo at room temperature gave the homopolymer as pale yellow solids (0.019 g, 7.9%). IR (KBr, cm^{-1}) 3067, 3021, 2205, 1647, 1602, 802; ^{1}H NMR 0.50–1.10 (m), 1.10–1.70 (m), 1.80–2.40 (m), 3.00–4.10 (m), 6.50–7.40 (m); ^{13}C NMR 12.4–44.8 (m) (CH_2 and CH_3 groups), 76.8 (m), 81.3 (m) (unreacted C≡C groups of diyne moieties in the homopolymer), 123.5–143.0 (m) (C=C and phenyl groups). Homopolymerization of **2** without CO_2 was carried out at 90 °C similarly to **1** but gave a chloroform-insoluble homopolymer in 29% yield.

Preparation of Cooligomer A from 1,3-Di(2-hexynyl)-benzene (1) and CO$_2$. The reaction was carried out under nitrogen. Ni(COD)$_2$ (0.0550 g, 0.200 mmol) in a THF solution (5.60 mL), P(n-C_8H_{17})$_3$ (0.178 mL, 0.400 mmol), MeCN (4.40 mL), and **1** (0.492 mL, 2.00 mmol) were mixed in this order in a 50-mL stainless steel autoclave with magnetic stirring at ambient temperature. CO_2 gas was compressed up to 50 kg/cm^2. The reaction mixture was heated at 80 °C for 2 h with magnetic stirring. After the reaction mixture was cooled with ice water, the remaining CO_2 gas was purged off and the reaction mixture was filtered. The filtrate was evaporated in vacuo to give a residue, which was purified twice by PLC (hexane/ethyl acetate = 5/1 (v/v)) to afford cooligomer **A** (0.095 g, 18%). Cooligomer **A**: IR (neat, cm^{-1}) 3064, 3032, 2228, 1706, 1637, 1561, 1536, 1076, 1047, 778; ^{1}H NMR (200 MHz, CD_2Cl_2) 0.70–1.10 (m, 12 H), 1.15–1.80 (m, 8 H), 2.05–2.55 (m, 8 H), 3.45–3.64 (m, 4 H), 3.64–3.95 (m, 4 H), 6.75–7.35 (m, 8 H); ^{13}C NMR (CD_2Cl_2) 13.9–37.6 (CH_2 and CH_3 absorptions), 77.9, 78.0, 78.1, 78.2, 82.9, 83.08, 83.14 (C≡C absorptions), 126.2–129.6 (C=C absorptions of the 2-pyrone ring and phenyl groups), 137.7–140.5 (phenyl absorptions), 113.9, 114.1, 117.2, 117.5, 122.4, 122.7, 152.0, 152.2, 156.7, 156.8, 157.0, 157.3, 160.5, 161.1, 163.5, 163.8, 163.9, 164.1 (C=O and C=C absorptions of the 2-pyrone rings); MS (m/e, relative intensity) 520 (M$^+$, 100), 492 (90), 338 (69), 171 (>100), 141 (85), 129 (85), 105 (71); HRMS (m/e) 520.3319, calcd for $C_{37}H_{44}O_2$ 520.3341. The two ^{13}C NMR C=C absorptions of the four regioisomeric 2-pyrone rings mix with the C=C absorptions of the phenyl groups, which appear at δ 126.2–129.6. Among the four C=O absorptions, the intensities of the two absorptions at δ 163.8 and 164.1 are similar and were about half those of the other two absorptions at δ 163.5 and 163.9 with similar intensities. Anal. Calcd for $C_{37}H_{44}O_2$: C, 85.34; H, 8.52. Found: C, 84.47; H, 8.44. The result of the carbon elemental analysis is not satisfactory. The purity of cooligomer **A** was found to be ca. 92% on the basis of its ^{1}H NMR spectrum (200 MHz, CD_2Cl_2), which is included in the Supplementary Material. Further purification of cooligomer **A** by high-pressure liquid chromatography did not improve its purity.

Preparation of Cooligomer B from 1,4-Di(2-hexynyl)-benzene (2) and CO$_2$. Cooligomer **B** was prepared similarly to cooligomer **A** in 16% yield. Cooligomer **B**: IR (neat, cm^{-1}) 3053, 3029, 2288, 1640, 1551, 1516, 1061, 1024, 793; ^{1}H NMR (200 MHz) 0.70–1.10 (m, 12 H), 1.15–1.80 (m, 8 H), 2.05–2.55 (m, 8 H), 3.45–3.63 (m, 4 H), 3.63–3.95 (m, 4 H), 6.85–7.40 (m, 8 H); ^{13}C NMR (CD_2Cl_2) 13.9–37.6 (CH_2 and CH_3 absorptions), 78.04, 78.06, 78.12, 78.3, 82.8, 82.97, 83.00 (C≡C absorptions), 128.0–130.3, 135.6–138.4 (phenyl absorptions), 114.0, 114.1, 117.1, 117.3, 122.5, 122.7, 126.2, 126.3, 152.1, 152.4, 156.7, 156.90, 156.91, 157.4, 160.5, 161.1, 163.6, 163.90, 163.93, 164.1 (C=O and C=C absorptions of the 2-pyrone rings); MS (m/e, relative intensity) 520 (M$^+$, 75), 492 (45), 338 (31), 171 (100); HRMS (m/e) 520.3369, calcd for $C_{37}H_{44}O_2$ 520.3341. Among the four C=O absorptions, the intensities of the two absorptions at δ 163.90 and 164.1 are similar and were about half those of the other two absorptions at δ 163.6 and 163.93 with similar intensities. Anal. Calcd for $C_{37}H_{44}O_2$: C, 85.34; H, 8.52. Found: C, 84.38; H, 8.44. The result of the carbon elemental analysis is not satisfactory. The purity of cooligomer **B** was found to be ca. 93% on the basis of its ^{1}H NMR spectrum (200 MHz, $CDCl_3$), which is included in the Supplementary Material.

Results and Discussion

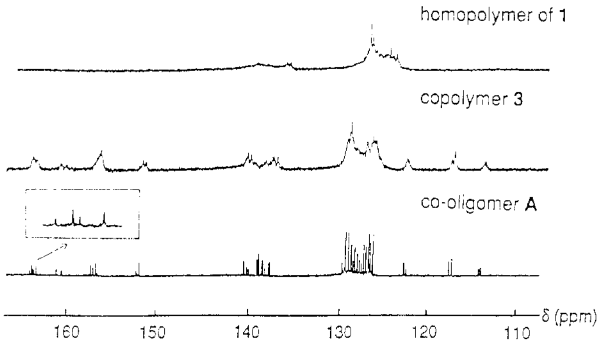


Figure 1. ^{13}C NMR C=C and/or C=O absorptions of copolymer **3** and related compounds (δ, ppm).

When **1** was treated with CO_2 under pressure in a mixed THF/MeCN solvent in the presence of a nickel(0) catalyst (10 mol %) generated from Ni(COD)$_2$ and 2 equiv of a triethyl- or tri-n-octylphosphine ligand, copolymer **3** was obtained by concentration of the reaction mixture under vacuum followed by precipitation with methanol (eq 5). Copolymer yield and molecular weight were determined after the copolymer was dried in vacuo at room temperature. This copolymer was further purified by dissolving it in a small amount of chloroform and adding the chloroform solution into methanol, which decreased the copolymer yield and increased the molecular weight of the copolymer by fractionation.

The copolymer is pale yellow solids. It is soluble in methylene chloride, chloroform, THF, and benzene but insoluble in methanol and hexane. It shows IR ν(C=O) absorption at 1700 cm^{-1} and ^{1}H NMR absorptions of the methylene groups directly attached to the 2-pyrone ring at δ 2.00–2.60 and 3.40–4.10. The ^{13}C NMR spectrum of the copolymer shows five groups of C=C and C=O absorptions characteristic of the 2-pyrone ring at δ 113.0–117.5 (C=C), 121.6–122.9 (C=C), 150.9–161.2 (two C=C groups), and 162.6–164.3 (C=O) (Figure 1).[2,3] Each group of the ^{13}C NMR C=C and C=O absorptions appears as a multiplet due to regioisomeric 2-pyrone rings (vide post).

The yields and molecular weights of **3** obtained under various reaction conditions are summarized in Table I. Trialkylphosphines having an n-alkyl group such as triethyl- and tri-n-octylphosphines were effective ligands. Copolymerization at 80 °C in THF/MeCN for 20 h under a CO_2 pressure of 10–50 kg/cm^2 afforded copolymers with molecular weights of 6000–7000 in ca. 50% yield after the purification with $CHCl_3$–MeOH (vide ante). On the other hand, tricyclohexylphosphine was ineffective for the copolymerization and gave a homopolymer of **1**. Homopolymerization of **1** without CO_2 using the tri-n-octylphosphine ligand at 80 °C gave a methanol-insoluble homopolymer but only with 8% yield. Its ^{13}C NMR spectrum is shown in Figure 1. The structure of the homopolymer has not yet been determined, but it may be assumed to contain benzenoid, cyclopentadienoid, and/or cyclooctatetraenoid repeating units on the basis of the results of nickel(0)-catalyzed oligomerization of acetylenes.[5]

Copolymerization in THF/MeCN at 80 °C for 20 h using the tri-n-octylphosphine ligand under a CO_2 pressure of 10, 20, and 50 kg/cm^2 gave copolymers precipitated with MeOH in high yield (ca. 90%) but with low molecular weight. This finding suggests that copolymer growth is not fast owing to steric hindrance by n-propyl and benzylic substituents to cycloaddition reaction of a terminal C≡C bond of the cooligomer and the copolymer.[3]

Formation of the poly(2-pyrone) with 1:1 copolymerizability (eqs 1–3) is readily demonstrated by the absence of C=C absorptions of the corresponding homopolymer in its ^{13}C NMR spectrum.[2,3] This evaluation method,

Table I. Nickel(0)-Catalyzed Copolymerization of 1,3-Di(2-hexynyl)benzene (1) with CO_2 to Poly(2-pyrone) 3[a]

					3 obtained by precipitation with MeOH			3 obtained by further purification with $CHCl_3$–MeOH			
ligand (L)	CO_2 pressure, kg/cm^2	solvent	temp, °C	time, h	yield,[b] %	M_n[c]	M_w/M_n[c]	yield,[b] %	M_n[c]	M_w/M_n[c]	copolymerizability,[e] mol %
$P(c\text{-}C_6H_{11})_3$	50	THF–MeCN	80	20	49	1300	5.2	24	2300	4.8	0
PEt_3					74	2400	5.5	46	6100 (5300)[d]	3.8	95
$P(n\text{-}C_8H_{17})_3$					82[f]	2500	5.9	46	6700	3.0	92
	20				93	2500	4.6	56	7000	3.0	94
				5	48	3200	2.8	22	6600	1.5	84
		THF		20	40	1500	2.0	15	3500	3.3	34
		THF–MeCN	60		37	1500	1.6				
	10		80		88	2700	3.2	44	6900 (7200)[d]	2.2	97
	5				56	3400	3.6	28	7200	1.8	79

[a] Diyne 1, 1 mmol; $Ni(COD)_2/1 = 0.10$; $L/Ni(COD)_2 = 2$; CO_2 pressure, initial pressure at room temperature; solvent, 5 mL, THF:MeCN = ca. 1:1 (v/v). [b] Based on the formation of a 1:1 copolymer of 1 with CO_2. [c] Determined by GPC with polystyrene standards in chloroform. [d] Determined by VPO in chloroform. [e] Diyne 1 utilized in the formation of the 2-pyrone ring in the copolymer. [f] Copolymerizability, 93%.

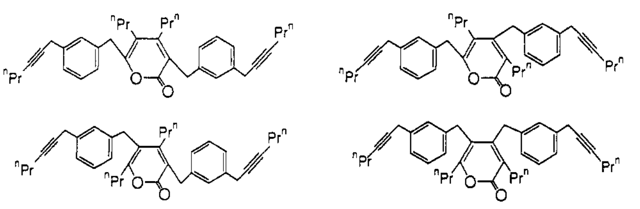


Figure 2. Four regioisomers of cooligomer A.

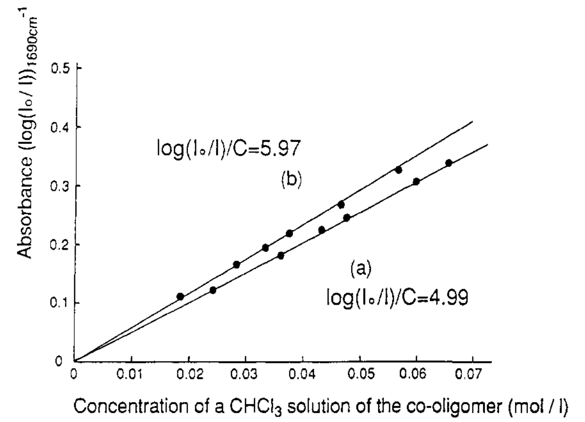


Figure 3. IR calibration curves for determining the content of the 2-pyrone ring in copolymers 3 and 4: (a) cooligomer A; (b) cooligomer B.

however, cannot be applied to copolymer 3 because comonomer 1 has a phenylene group and the ^{13}C NMR C═C absorptions of 3 partly overlap those of the homopolymer (Figure 1). Therefore the copolymerizability of 3, i.e., the mole percent of diyne 1 utilized in the formation of the 2-pyrone ring in the copolymer, was determined by IR spectroscopy using the ν(C═O) absorption of cooligomer A consisting of two diyne molecules and one CO_2 molecule as an IR standard.

Shortening the reaction time of the copolymerization at 80 °C in THF/MeCN under a CO_2 pressure of 50 kg/cm^2 using the tri-*n*-octylphosphine ligand from 20 to 2 h gave cooligomer A in 18% yield. Cooligomer A exhibits four ^{13}C NMR C═O absorptions with different intensities; the intensities of the two absorptions at δ 163.8 and 164.1 are similar and are about half those of the other two absorptions at δ 163.5 and 163.9 with similar intensities (Figure 1). Eight and six ^{13}C NMR C═C absorptions of the 2-pyrone ring are observed down- and upfield, respectively (Figure 1 and Experimental Section). Two other C═C absorptions are considered to be mixed with the phenyl absorptions. Thus cooligomer A consists of four regioisomeric 2-pyrones depicted in Figure 2, among which two regioisomers predominate. Agreement of the pattern of the ^{13}C NMR C═O and C═C absorptions of the copolymer having 46% yield and M_n = 6700 in Table I with those of cooligomer A (Figure 1) indicates that the copolymer has a poly(2-pyrone) structure.

An IR calibration curve for determining the content of the 2-pyrone ring in the copolymer was constructed as shown in Figure 3a using the IR ν(C═O) absorption of a chloroform solution of cooligomer A near 1690 cm^{-1}. The copolymerizability of copolymer 3, i.e., the mole percent of the diyne 1 utilized in the formation of the 2-pyrone ring in the copolymer, determined by the calibration curve is summarized in Table I. Copolymers obtained at 80 °C in THF/MeCN under a CO_2 pressure of 10–50 kg/cm^2 using triethyl- and tri-*n*-octylphosphine ligands show a high copolymerizability around 95%. The poly(2-pyrone) 3 obtained by the first precipitation with methanol (vide ante), which had the higher yield but the lower molecular weight, also has a high copolymerizability (footnote *f* in Table I). Therefore it may be concluded that efficient 1:1 cycloaddition copolymerization of diyne 1 with CO_2 takes

Table II. Nickel(0)-Catalyzed Copolymerization of 1,4-Di(2-hexynyl)benzene (2) with CO_2 to Poly(2-pyrone) 4[a]

			4 obtained by precipitation with MeOH			4 obtained by further purification with $CHCl_3$–MeOH			
CO_2 pressure, kg/cm^2	temp, °C	time, h	yield,[b] %	M_n[c]	M_w/M_n[c]	yield,[b] %	M_n[c]	M_w/M_n[c]	copolymerizability,[e] mol %
50	70	20	88	6500	3.8	62	9000 (8700)[d]	2.7	99
		5	63	2700	3.9	45	3900	3.4	86
20		20	83	8200	4.6	59	11500	3.5	91
	60		76[f]	3300	2.6	53	5000 (4800)[d]	2.3	94

[a] 2, 1 mmol; $Ni(COD)_2/2 = 0.10$; $P(n\text{-}C_8H_{17})_3/Ni(COD)_2 = 2.$; CO_2 pressure, initial pressure at room temperature; solvent, 5 mL, THF:MeCN = ca. 1:1 (v/v). [b] Based on the formation of a 1:1 copolymer of 2 with CO_2. [c] Determined by GPC with polystyrene standards in chloroform. [d] Determined by VPO in chloroform. [e] Diyne 2 utilized in the formation of the 2-pyrone ring in the copolymer. [f] Copolymerizability, 89%.

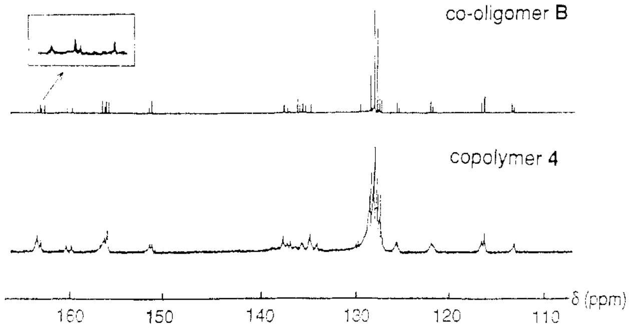


Figure 4. ^{13}C NMR C=C and C=O absorptions of copolymer 4 and cooligomer **B** (δ, ppm).

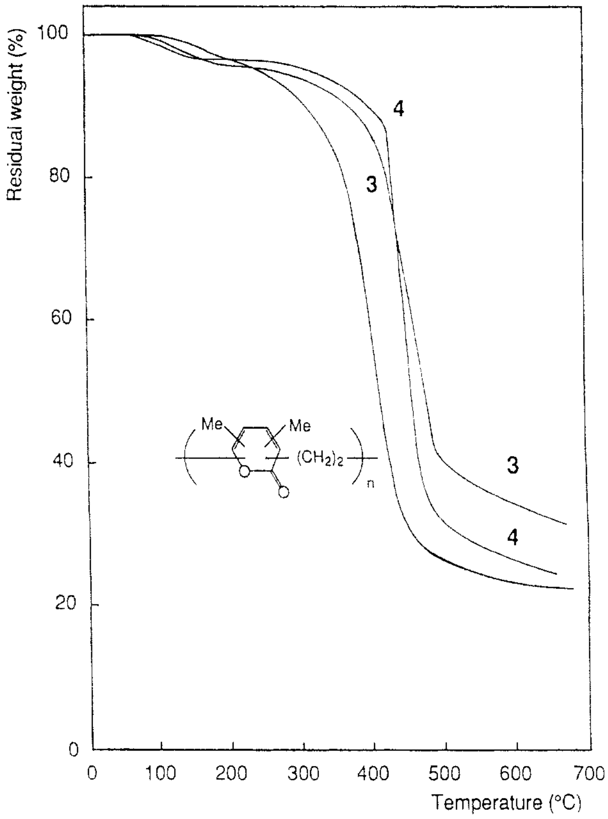


Figure 5. TGA curve of poly(2-pyrone)s **3** and **4**.

place to afford poly(2-pyrone) **3** having a phenylene group in the copolymer main chain.

Diyne **2** also underwent 1:1 cycloaddition copolymerization with CO_2 to poly(2-pyrone) **4** (eq 6). The copolymerization results are summarized in Table II. Cooligomer **B** corresponding to cooligomer **A** was prepared similarly, and the copolymerizability of copolymer **4** was determined on the basis of the calibration curve b in Figure 3 constructed by the use of cooligomer **B** as an IR standard. Copolymerization at 70 °C in THF/MeCN for 20 h under a CO_2 pressure of 20–50 kg/cm^2 using the tri-*n*-octylphosphine ligand afforded copolymers with molecular weights of 9000–12 000 and a high copolymerizability over 90% in ca. 60% yield. As shown in Tables I and II, comonomer **2** afforded copolymers with higher molecular weights than comonomer **1**. This result indicates that **2** has a higher copolymerization reactivity than **1**.[6] Formation of poly(2-pyrone) **4** is also indicated by agreement of the pattern of ^{13}C NMR C=O and C=C absorptions of the copolymer having 62% yield and M_n = 9000 in Table II with those of cooligomer **B** (Figure 4). Cooligomer **B** exhibits 20 ^{13}C NMR C=O and C=C absorptions of the 2-pyrone ring (Figure 4 and Experimental Section), which indicates that cooligomer **B** consists of four regioisomers like cooligomer **A**.

Thermogravimetric analysis (TGA) indicated that both copolymer **3** obtained using the triethylphosphine ligand in Table I and copolymer **4** obtained at 70 °C for 20 h under a CO_2 pressure of 50 kg/cm^2 in Table II had a thermal stability similar to that of the poly(2-pyrone) from 3,11-tetradecadiyne[2,7] and a higher thermal stability than that of the poly(2-pyrone) from 2,6-octadiyne[3,7] to show a rapid weight loss around 420 °C under nitrogen (Figure 5).

Thus two new poly(2-pyrone)s **3** and **4** have been prepared (eqs 5 and 6). Considering together the previous synthesis of three poly(2-pyrone)s (eqs 1–3),[2,3] this finding indicates the usability of various diynes in the nickel(0)-catalyzed 1:1 cycloaddition copolymerization of diynes with CO_2 to poly(2-pyrone)s and accordingly demonstrates the usefulness of this new polymerization reaction.

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Supplementary Material Available: ^{1}H NMR spectra showing the purity of cooligomers **A** and **B** (2 pages). Ordering information is given on any current masthead page.

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(7) The TGA curve of the poly(2-pyrone) from 3,11-tetradecadiyne was depicted by mistake in Figure 4 of ref 3. The TGA curve of the poly(2-pyrone) from 2,6-octadiyne is shown in Figure 5 along with poly(2-pyrone)s 3 and 4.