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Nickel(0)-Catalyzed Alternating Copolymerization of 2,6-Octadiyne with Carbon Dioxide to Poly(2-pyrone)

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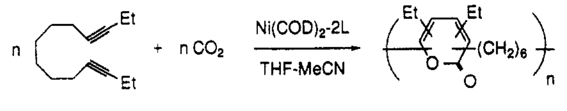
ABSTRACT: A nickel(0) catalyst generated from $Ni(COD)_2$ and tri-*n*-alkylphosphine effected efficient alternating copolymerization of 2,6-octadiyne (1) with CO_2 to a new class of polymer of poly(2-pyrone) 2. Various factors such as reaction temperature, CO_2 pressure, diyne concentration, and reaction solvent exerted influences on the alternating copolymerizability along with the copolymer yield and molecular weight. Under the reaction conditions, the reaction temperature of 60 °C, the CO_2 pressure of 20 kg/cm^2, and the THF/MeCN solvent, and using a $P(n\text{-}C_8H_{17})_3$ ligand and the higher diyne concentration, 2 with the molecular weight of ca. 7000 was obtained in excellent yield. The formation of the 1:1 alternating copolymer was demonstrated by the comparison of ^{13}C NMR C=O and/or C=C absorptions of 2 with those of a co-oligomer and a homopolymer.

Introduction

Use of CO_2 as a comonomer for polymer synthesis is an attractive approach to chemical utilization of CO_2, which is of great concern at the present time in relation to carbon resources and environmental problems. Until recently, however, only one example of CO_2 copolymerization has been known, which satisfies both alternating copolymerizability and degree of polymerization, that is, alternating copolymerization of CO_2 with epoxides[1] involving $C(CO_2)$–O(epoxide) bond formation.

Very recently we reported the efficient alternating copolymerization[2] of CO_2 with the acyclic diyne of 3,11-tetradecadiyne $EtC{\equiv}C(CH_2)_6C{\equiv}CEt$ (eq 1) together with the cyclic diyne of 1,7-cyclotridecadiyne to a new class of polymer of poly(2-pyrones) by the nickel(0)-catalyzed intermolecular cyclization of diynes involving CO_2. These are the first examples of alternating copolymerization of CO_2 with $C(CO_2)$–C(a comonomer) bond formation. Interestingly, the nickel(0)-catalyzed alternating copolymerization of CO_2 with the acyclic diyne was shown to be regulated by its relative reactivity of inter- to intramolecular[3] cyclization (eqs 1 and 2). This result suggests that acyclic diynes $RC{\equiv}C(CH_2)_mC{\equiv}CR$ with m = 2 undergo the nickel(0)-catalyzed alternating copolymerization with CO_2. Here we have studied the nickel(0)-catalyzed alternating copolymerization of CO_2 with 2,6-octadiyne (1).



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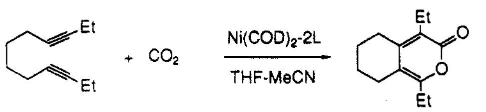

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Experimental Section

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. Chemical shifts are reported in ppm on the δ scale relative to tetramethylsilane as 0 ppm. Preparative layer chromatography (PLC) was carried out by using 20/20/0.2 cm plates prepared with Merck silica gel 60 PF-254. GPC was performed in chloroform using SHODEX AC-803 and 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. Tetrahydrofuran (THF) was distilled from $LiAlH_4$ under nitrogen. Acetonitrile (MeCN) was distilled from CaH_2 under nitrogen. 2,6-Octadiyne (1) was a commercial reagent and was distilled under nitrogen. Bis(1,5-cyclooctadiene)nickel(0) ($Ni(COD)_2$) was purchased from Kanto Chemical Co., Inc. Phosphorus ligands were commercial reagents and used without further purification. Carbon dioxide was a commercial reagent (assay; minimum 99.9 vol %) supplied by Sumitomo Seika Chemicals Co., Inc. and was used without further purification.

Copolymerization of 2,6-Octadiyne (1) with CO_2. The reaction was carried out under nitrogen. In a 50-mL stainless steel autoclave, $Ni(COD)_2$ (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 1 (0.256 mL, 2.00 mmol) were placed in this order under magnetic stirring at ambient temperature. CO_2 gas was compressed up to 20 kg/cm^2. The reaction mixture was heated at 60 °C for 20 h under magnetic stirring. After the reaction mixture was cooled by ice water, the remaining CO_2 gas was purged off and the reaction mixture was filtered. After washing a small amount of insoluble matters with THF, the combined solution was concentrated in vacuo. Addition of ether (30 mL) to a resulting residue precipitated copolymers, which were further purified by dissolution in methylene chloride (1 mL) and precipitation with ether (30 mL). Drying in vacuo at room temperature gave copolymers as pale yellow solids (0.27 g, 91% based on the formation of a 1:1 alternating copolymer of 1 with CO_2). Copolymer 2: IR (film, cm^{-1}) 1701, 1637, 1553, 1058; ^1H NMR 1.00–2.40 (m), 2.40–3.20 (m); ^{13}C NMR 112.0–113.0 (m), 114.2–115.7 (m), 119.3–121.0 (m), 121.0–123.5 (m), 150.1–154.0 (m), 154.0–156.9 (m), 162.3–164.5 (m). In addition to these ^{13}C NMR C=C and C=O absorptions, CH_2 and CH_3 absorptions are observed between 12.6 and 31.8 ppm and very weak absorptions assignable to a repeating unit without a CO_2 component appear around 133.5 and 142.0 ppm (Figure 1d). Copolymer 2 did not show a satisfactory result of elemental analysis. For example, copolymer 2 with yield 87% and M_n = 1700 in Table III revealed the following analytical results. Anal. Calcd for $(C_9H_{10}O_2)_n$: C, 71.98; H, 6.71. Found: C, 63.78; H, 6.76. It was found that ashes were formed after combustion analysis of the copolymer. This finding suggests that nickel salts contaminate the copolymer.

Homopolymerization of 2,6-Octadiyne (1). 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 (2.38 mL), $P(n\text{-}C_8H_{17})_3$ (0.0893 mL, 0.200 mmol), MeCN (2.62 mL), and 1 (0.128 mL, 1.00 mmol) were placed in this order under magnetic stirring at ambient temperature. The reaction mixture

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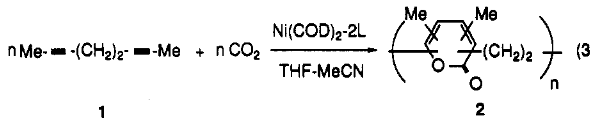
was heated at 110 °C for 20 h under magnetic stirring. After cooling by ice water, the reaction mixture was filtered. After a small amount of insoluble matter was washed with THF, the combined solution was concentrated in vacuo. Addition of methanol (30 mL) to a resulting residue precipitated homopolymers, which were further purified by dissolution in methylene chloride (1 mL) and precipitation with methanol (30 mL). Drying in vacuo at room temperature gave homopolymers as pale yellow solids (0.45 g, 42%, M_n(GPC) = 1900). Homopolymer: IR (film, cm^{-1}) 2230, 1426, 737; ^{13}C NMR 126.9–128.2 (m), 130.3–133.5 (m), 133.5–137.3 (m), 140.1–141.2 (m). In addition to these ^{13}C NMR C═C absorptions (Figure 1f), CH_2 and CH_3 absorptions are observed between 2.5 and 30.8 ppm and C≡C absorptions appear at 74.5–75.2 (m) and 77.6–78.4 (m).

Preparation of the Co-oligomer A from 2,6-Octadiyne (1) and CO_2. The reaction was carried out under nitrogen. In a 50-mL stainless steel autoclave, $Ni(COD)_2$ (0.0825 g, 0.300 mmol) in a THF solution (7.13 mL), $P(n\text{-}C_8H_{17})_3$ (0.268 mL, 0.60 mmol), MeCN (7.87 mL), and 1 (0.385 mL, 3.00 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 12 min under magnetic stirring. After the reaction mixture was cooled by ice water, the remaining CO_2 gas was purged off and the reaction mixture was filtered. The filtrate was concentrated under vacuum to give a residue, which precipitated copolymers by addition of ether. The copolymers were isolated by filtration and were dried in vacuo at ambient temperature (0.082 g, 18% based on the formation of a 1:1 alternating copolymer of 1 with CO_2, M_n(GPC) = 550). The filtrate was evaporated in vacuo to give a residue, which was purified by PLC (hexane/ethyl acetate = 4/1 (v/v)) to afford the co-oligomer A (0.068 g, 18%). Co-oligomer A: IR (neat, cm^{-1}) 2228, 1703, 1625, 1541, 1043; ^1H NMR 1.74 (t, J = 2.6 Hz, 3 H), 1.747 (t, J = 2.6 Hz, 3 H), 1.752 (t, J = 2.6 Hz, 3 H), 1.76 (t, J = 2.6 Hz, 3 H), 1.99 (s, 3 H), 2.17 (s, 3 H), 2.20 (s, 3 H), 2.25 (tq, J = 7.3 Hz, 2.5, 2 H), 2.28 (s, 3 H), 2.35 (tq, J = 7.3, 2.5 Hz, 4 H), 2.46 (tq, J = 7.3, 2.5 Hz, 2 H), 2.57 (t, J = 7.5 Hz, 2 H), 2.71 (t, J = 7.9 Hz, 2 H), 2.72 (t, J = 7.3, 2 H), 2.73 (t, J = 7.8, 2 H); ^{13}C NMR 3.34, 13.2, 16.1, 16.7, 17.2, 17.4, 17.49, 17.52, 19.0, 26.9, 30.7, 76.0, 76.7, 76.9, 77.2, 77.4, 78.38, 78.41, 112.4, 114.8, 121.8, 121.9, 151.6, 152.3, 155.4, 155.5, 162.9, 163.0. In addition to these ^{13}C NMR major absorptions of the co-oligomer A, ^{13}C NMR C═C and C═O minor absorptions were observed at 111.4, 114.0, 119.8, 120.1, 152.3, 152.7, 155.4, 155.5, 163.76, and 163.79 (Figure 1b). These ^1H and ^{13}C NMR data indicate that the co-oligomer A mainly consists of two regioisomers shown in Figure 2, whose structures were determined by a ^1H NMR NOE technique. Anal. Calcd for $C_{17}H_{20}O_2$: C, 79.65; H, 7.86. Found: C, 79.37; H, 8.11.

Results and Discussion

When 1 was treated with CO_2 under initial pressure of 50 kg/cm^2 in a mixed solvent of THF/MeCN at 60 °C in the presence of a nickel(0) catalyst (10 mol %) generated from $Ni(COD)_2$ and 2 equiv of a tertiary phosphine ligand, copolymers 2 were obtained by concentration of the reaction mixture under vacuum followed by precipitation with ether (eq 3). The copolymers were purified by dissolving in a small amount of methylene chloride and subsequent addition of ether. Molecular weights of 2 were determined by GPC with polystyrene standards in chloroform. The copolymers are pale yellow solids. They are soluble in methylene chloride and chloroform but are insoluble in ether, benzene, and hexane. The copolymers show IR and ^1H NMR absorptions assignable to a 2-pyrone ring. Thus, an IR ν(C═O) absorption appears around 1700 cm^{-1} and ^1H NMR absorptions of methyl and methylene groups directly attached to the 2-pyrone ring are observed as multiplets at δ 1.00–2.40 and 2.40–3.20 ppm, respectively. The most useful diagnosis of the 2-pyrone ring is by ^{13}C NMR spectroscopy.[4] The copolymers exhibit five groups of ^{13}C NMR C═C and C═O absorptions characteristic of the 2-pyrone ring (Figure 1d).



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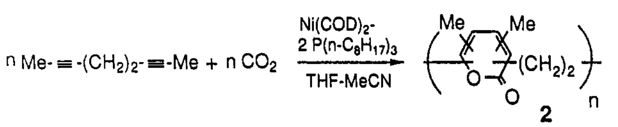


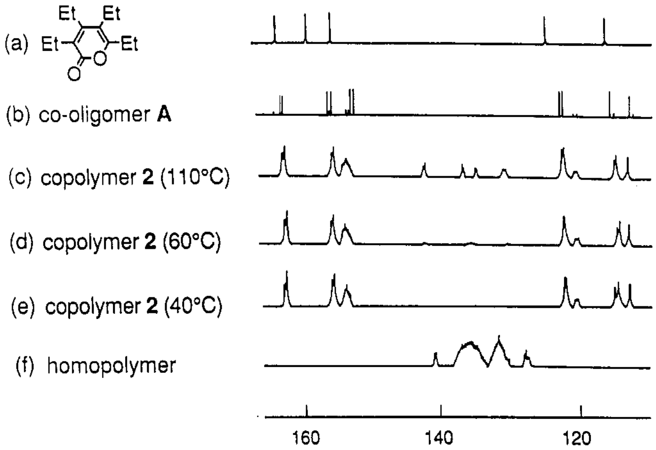


Figure 1. ^{13}C NMR C═C and C═O absorptions of copolymers 2 prepared at various temperatures and of related compounds (δ, ppm).

Table I
Nickel(0)-Catalyzed Alternating Copolymerization of Diyne 1 with CO_2 to Poly(2-pyrone) 2[a]

amt of 1, mmol	ligand (L)	temp, °C	2: yield, %[b]	2: M_n[c]	2: M_w/M_n
1	PEt_3	110	51	2000	1.7
	$P(n\text{-}C_8H_{17})_3$		65	2000	1.7
			64[e]	1900	1.8
2			60	2000	2.0
1		60	78	1700 (2100)[d]	2.0
2			64	1900	2.2
1		40	46	1300	1.4
		room temp	17	700	1.4
	$P(i\text{-}Bu)_3$	60	7		
	PMe_3		10		

[a] Ni/1 = 0.10; L/Ni = 2; CO_2, 50 kg/cm^2 (initial pressure at room temperature); solvent, 5 mL, THF/MeCN = 1/2 (v/v); time, 20 h. [b] Based on the formation of a 1:1 alternating copolymer of 1 with CO_2. [c] Determined by GPC with polystyrene standards in chloroform. [d] Determined by VPO in chloroform. [e] L/Ni = 3.

Yields and molecular weights of 2 obtained under various reaction conditions are summarized in Table I. Similarly to the previous result[2] of the effect of the phosphine ligand on the alternating copolymerization of 3,11-tetradecadiyne with CO_2 (eq 1), trialkylphosphines having an *n*-alkyl group such as triethyl- and tri-*n*-octylphosphines were effective ligands. On the contrary, triisobutyl- and trimethylphosphines were much less efficient. 1,2-Bis(diphenylphosphino)ethane, a chelating ligand, was almost ineffective. The reaction temperature around 60 °C was sufficient to afford copolymers in good yields. Molecular weights of 2, however, are not high.

Table II shows a relationship of the copolymer yields and molecular weights to the polymerization time; further polymer growth almost did not take place after 5 h. Addition of more new catalyst (10 mol %) to the reaction mixture after 5 h and further copolymerization at 60 °C for 15 h under CO_2 pressure of 20 kg/cm^2 gave the copolymer with higher yield (90%), but with unchanged molecular weight (M_n = 1700, M_w/M_n = 1.6). This finding suggests that further propagation reaction of the copolymer

Table II
Alternating Copolymerization of Diyne 1 with CO_2 to Poly(2-pyrone) 2 Catalyzed by $Ni(COD)_2$–$2P(n\text{-}C_8H_{17})_3$[a]

time, h	2 yield, %[b]	M_n[c]	M_w/M_n
1	12		
2	22		
3	39	1100	1.4
4	63	1300	1.7
5	78	1500 (1900)[d]	1.5
7	80	1500	2.2
20	78	1700	2.0

[a] 1, 1 mmol; Ni/1 = 0.10; L/Ni = 2; CO_2, 50 kg/cm^2 (initial pressure at room temperature); solvent, 5 mL, THF/MeCN = 1/1.5 (v/v); temperature 60 °C. [b] Based on the formation of a 1:1 alternating copolymer of 1 with CO_2. [c] Determined by GPC with polystyrene standards in chloroform. [d] Determined by VPO in chloroform.

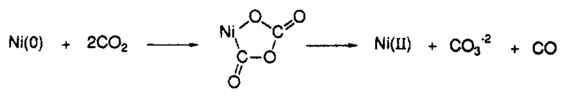
Table III
Alternating Copolymerization of Diyne 1 with CO_2 to Poly(2-pyrone) 2 Catalyzed by $Ni(COD)_2$–$2P(n\text{-}C_8H_{17})_3$[a]

amt of 1, mmol	CO_2 pressure,[b] kg/cm^2	temp, °C	2 yield, %[c]	M_n[d]	M_w/M_n
2	50	60	64[e]	1900	2.2
1			78	1700 (2100)[f]	2.0
	30		70	1700	1.9
4	20		95	7300	4.6
3			93	6700 (5300)[f]	5.8
2			91	3000 (3500)[f]	5.4
			86[g]	2200	3.3
		50	92	2500	6.0
1		60	88	2100 (2700)[f]	2.7
		50	87	1700	1.8
	10	60	75	1700	1.8
	5		37	1200	1.7

[a] Ni/1 = 0.10; L/Ni = 2; time, 20 h; solvent, 5 mL, THF/MeCN = 1/1.5 (v/v). [b] Initial pressure at room temperature. [c] Based on the formation of a 1:1 alternating copolymer of 1 with CO_2. [d] Determined by GPC with polystyrene standards in chloroform. [e] Time, 40 h. [f] Determined by VPO in chloroform. [g] Time, 5 h.

with the molecular weight of ca. 1500 almost stops under the reaction conditions of Table II and deactivation of the nickel(0) catalyst (vide post) also takes place. Therefore, effects of CO_2 pressure and diyne concentration upon the copolymerization were examined.

The CO_2 pressure and the diyne concentration have influences on the copolymerization, as is shown in Table III. A decrease of the CO_2 pressure from 50 to 20 kg/cm^2 and an increase of the diyne concentration gave higher copolymer yields and molecular weights. The copolymerization under the CO_2 pressure of 20 kg/cm^2 necessitated a reaction time of more than 5 h to obtain the copolymer with the higher molecular weight. The influence of the CO_2 pressure may be related to deactivation of the nickel(0) catalyst according to disproportionation of CO_2,[5] shown in eq 4. An accepted mechanism[6] of the nickel(0)-catalyzed 2-pyrone formation from acetylenes and CO_2 is depicted in eq 5. Too high a CO_2 pressure presumably favors the deactivation of the nickel(0) catalyst over the formation of a five-membered nickelacycle intermediate, and the higher diyne concentration promotes the nickel(0)-catalyzed intermolecular 2-pyrone ring formation. In the copolymerization reaction using the higher diyne concentration under the CO_2 pressure around 20 kg/cm^2, the lifetime of the nickel(0) catalyst becomes longer to effect the 2-pyrone ring formation from two propagating polymer molecules and CO_2, affording the copolymer with the higher molecular weight and accordingly a broader molecular weight distribution. Molecular weights of a few copolymers were determined by VPO. The results indicate that their evaluation by GPC is reasonable.



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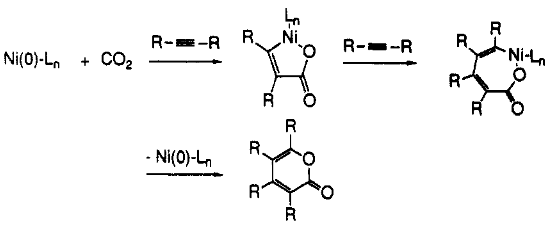

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To define a copolymer structure, preparation of a co-oligomer and a homopolymer of 1 were carried out. An ether-soluble co-oligomer A was obtained in 18% yield by shortening the reaction time. Spectroscopic (IR, ^{1}H NMR, and ^{13}C NMR) data and elemental analysis demonstrate that the co-oligomer A consists of one CO_2 molecule plus two diyne molecules. The co-oligomer A exhibits eight strong ^{13}C NMR absorptions with almost equal intensities (Figure 1b) assignable to the C=C bonds of the 2-pyrone ring, which indicates that the co-oligomer A is composed of nearly equal amounts of two regioisomers. The structure of the regioisomer, as shown in Figure 2, was determined by ^{1}H NMR NOE measurements. With regard to the additional eight very weak ^{13}C NMR C=C absorptions of the co-oligomer A, formation of the other two regioisomers is not significant. Identification of the co-oligomer A suggests that its formation and subsequent reaction produce the copolymer and its repeating unit corresponds to the structure of the 2-pyrone ring of the co-oligomer A.

Homopolymerization of 1 without CO_2 at 110 °C gave methanol-insoluble polymers (42%, M_n = 1900). On the other hand, homopolymerization at 60 °C did not produce a methanol-insoluble polymer. The structure of the homopolymer has not been determined at the present time, but it may be assumed to contain benzenoid, cyclopentadienoid, and/or cyclooctatetraenoid repeating units[7,8a] on the basis of the results of nickel(0)-catalyzed oligomerization of acetylenes. The homopolymer exhibits ^{13}C NMR C=C absorptions (Figure 1f) different from those of the copolymer.

Although the copolymer (Figure 1c) prepared at 110 °C shows small but distinct C=C absorptions of the homopolymer, the copolymers (Figure 1d) obtained at 60 and 50 °C exhibit negligible absorptions. The ^{13}C NMR C=C absorptions of the homopolymer were not observed in the copolymer (Figure 1e) obtained at 40 °C. Thus, lowering the reaction temperature decreases the homopolymer unit in the copolymer and favors the alternating copolymerization. This finding indicates that the copolymerization occurs much more readily than the diyne homopolymerization, which is in accord with the result that no methanol-insoluble homopolymer was obtained at 60 °C (vide ante).

The copolymerization under the CO_2 pressure of 20 kg/cm^2 at 60 °C in THF alone without MeCN gave the copolymer with the lower molecular weight in a little decreased yield compared with the copolymers obtained in THF/MeCN. Hence, it is better to use the MeCN[8] cosolvent for the alternating copolymerization. The $Ni(COD)_2/2P(n\text{-}C_8H_{17})_3$ catalyst, however, was decomposed in MeCN without THF.

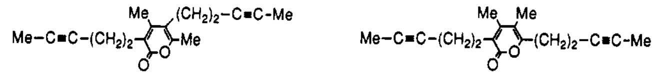

Figure 2. Two regioisomers of the co-oligomer A.

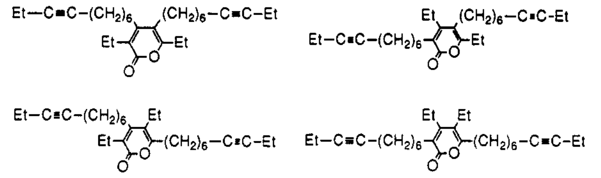

Figure 3. Four regioisomers of the co-oligomer from 3,11-tetradecadiyne and CO_2.

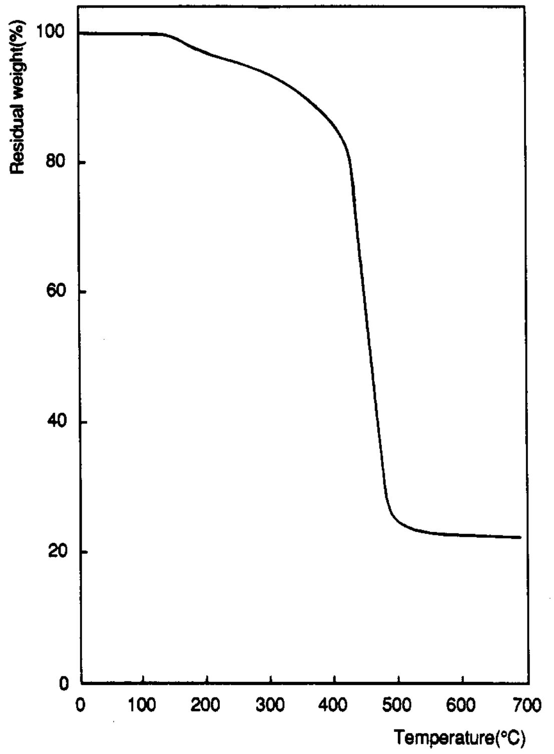

Figure 4. TGA curve of poly(2-pyrone) 2.

A pattern (Figure 1d) of the ^{13}C NMR C=O and C=C absorptions of the copolymer almost free from the C=C absorptions of the homopolymer acords with that of the co-oligomer A. This finding indicates that the efficient alternating copolymerization of 1 with CO_2 occurs to produce poly(2-pyrone) 2 and its repeating unit corresponds to the structure of 2-pyrone ring of the co-oligomer A. The orientation of 2-pyrone rings along the polymer chain is reasonably assumed to be random.

There are two noteworthy results in the nickel(0)-catalyzed oligomerization and copolymerization of 1 with CO_2 in comparison with those of 3,11-tetradecadiyne with CO_2.[2] One is better regioselectivity in the formation of the co-oligomer A. 3,11-Tetradecadiyne produces the co-oligomer consisting of all four possible regioisomers in nearly equal amounts (Figure 3),[2] while the diyne 1 forms the co-oligomer A consisting of two regioisomers (Figure 2). Accordingly, copolymer 2 has a more regulated structure than that of the alternating copolymer from 3,11-tetradecadiyne and CO_2. Another is formation of copolymer 2 with the lower molecular weight. A $MeC{\equiv}C(CH_2)_2$ substituent is more rigid than an $EtC{\equiv}C(CH_2)_6$ substituent and exerts greater steric hidrance on generation of five- and seven-membered nickelacycle intermediates (eq 5) to give the better regioselectivity to the formation of the co-oligomer A. The structure of co-oligomer A suggests that the intermolecular cycloaddition reactivity of its C≡C bond is lowered by the near presence of a sterically bulky 2-pyrone ring. Thus, the steric hindrance due to both the 2-pyrone ring and the $MeC{\equiv}C(CH_2)_2$ substituent, which originates from the short methylene chain of 1, reduced the reactivity of the terminal C≡C bond of the propagating polymer to promote the deactivation of the nickel(0) catalyst (eq 4) and to give the copolymer 2 with the lower molecular weight compared with that of the copolymer from 3,11-tetradecadiyne and CO_2.

A thermogravimetric analysis (TGA) curve of copolymer 2 obtained at 110 °C with 65% yield in Table I shows a rapid weight loss around 420 °C under nitrogen (Figure 4).

We have previously reported the alternating copolymerization of 3,11-tetradecadiyne and 1,7-cyclotridecadiyne with CO_2 to form a new class of polymer of poly(2-pyrones)[2] as the first example of the alternating copolymerization of an unsaturated hydrocarbon with CO_2 and accordingly the first example of the alternating copolymerization of CO_2 involving $C(CO_2)$–C(a comonomer) bond formation. Therefore, the present copolymerization is the third example of the nickel(0)-catalyzed alternating copolymerization of the diyne with CO_2. These results suggest that various poly(2-pyrones) can be prepared by changing the structure of the diyne. Exploration of their physical properties and chemical reactions is an interesting further research subject.

Synthesis of poly(2-pyrone) by the nickel(0)-catalyzed alternating copolymerization of the diyne with CO_2 provides a novel polymerization method, i.e., the transition-metal-complex-catalyzed alternating intermolecular cycloaddition copolymerization of the diyne with a cycloaddition component. In place of CO_2, there are many other candidates for the cycloaddition component, for example, nitriles, isocyanates, carbodiimides, carbon monoxide, and isonitriles.[7] Synthesis of new polymers using diynes and these comonomers is also an intriguing problem.

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Registry No. $Ni(COD)_2$, 1295-35-8; (carbon dioxide)(2,6-octadiyne) (copolymer), 143495-44-7.