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

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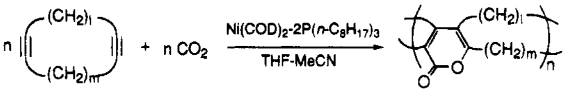
Introduction

Recently we developed the new polymerization reaction of transition metal-catalyzed 1:1 cycloaddition copolymerization of diynes,[1] which generates a new aspect of the transition metal-catalyzed cycloaddition reaction of alkynes,[2a] effects the diyne/CO_2 copolymerization[1a–d] as the first example of the efficient copolymerization of CO_2 with the unsaturated hydrocarbon, and provides a new synthetic method of the soluble ladder polymer.[1f]

Previously we reported briefly the nickel(0)-catalyzed cycloaddition copolymerization of 1,7-cyclotridecadiyne (**1a**) with CO_2 to the soluble ladder poly(2-pyrone) **2a** (eq 1).[1a] As the synthesis of the CO_2 copolymer[1a–d] and the development of the new synthetic method of the soluble ladder polymer[1f,3] are research subjects of considerable interest, we have examined further in this study the nickel(0)-catalyzed cycloaddition copolymerization of the cyclic diyne with CO_2 to clarify its feature by using three cyclic diynes **1** with different ring sizes, that is, **1a**, 1,7-cyclotetradecadiyne (**1b**), and 1,8-cyclopentadecadiyne (**1c**) (eq 1). Comparison of the ladder poly(2-pyrone) synthesis with the recently reported ladder poly(2-pyridone) synthesis[1f] has also been made.



(1)

1a: l, m = 4, 5
1b: l, m = 4, 6
1c: l, m = 5, 6

2a: l, m = 4, 5
2b: l, m = 4, 6
2c: l, m = 5, 6

Experimental Section

Instrumentation and general procedures are described in the previous reports[1b–d] unless otherwise stated. Cyclic diynes **1a–c** were commercial reagents and were distilled under nitrogen while cyclic diyne **1a** was used as purchased in the previous study.[1a] Carbon dioxide was a commercial reagent (assay, minimum 99.99 vol %) supplied by Teisan, Inc. and was used without further purification although carbon dioxide with minimum 99.9 vol % purity was used in the previous study.[1a]

Copolymerization of Cyclic Diynes 1a–c with 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), and **1a** (0.189 mL, 1.00 mmol) were placed in this order in a 50-mL stainless steel autoclave under magnetic stirring at ambient temperature. CO_2 gas was compressed, and the reaction mixture was heated at 60 °C for 20 h. After the reaction mixture was cooled by ice/water, the remaining CO_2 gas was purged off. Precipitation of white solids was observed. The resulting mixture was concentrated in vacuo. Addition of ether (20 mL) to the residue precipitated copolymer **2a**, which was purified by dissolving in CH_2Cl_2 (1.0 mL) and adding the CH_2Cl_2 solution to ether (20 mL). Drying in vacuo at room temperature gave **2a** as white solids (0.22 g, 99%). GPC analysis of **2a** showed $M_n = 6400$ and $M_w/M_n = 2.6$. **2a**: IR (KBr, cm^{-1}) 1702, 1620, 1538, 1065; ^1H NMR ($CDCl_3$) δ 1.10–2.10 (m, 10 H), 2.10–2.95 (m, 8 H); ^{13}C NMR ($CDCl_3$) δ 24.0–34.0 (m), 115.0–117.5 (m), 122.5–125.5 (m), 153.5–156.5 (m), 157.0–159.5 (m), 163.0–164.0 (m). Elemental analysis of copolymer **2a** did not give satisfactory results. For example, one sample of **2a** revealed the following analytical result: Anal. Calcd for $(C_{14}H_{18}O_2)_n$: C, 77.03; H, 8.31. Found: C, 73.80; H, 8.47. It was found that ashes were formed after combustion analysis of the copolymer. This finding suggests that nickel salts contaminate the copolymer. Copolymer **2a** was hygroscopic. The copolymerization of **1b** or **1c** with CO_2 was carried out similarly to the **1a**/CO_2 copolymerization, and the resulting reaction mixture containing the precipitated copolymer was treated as above. Addition of CH_2Cl_2 (10 mL) to the **2b** or **2c** obtained, removal of the supernatant solution, and drying in vacuo gave the insoluble part of **2b** or **2c**. CH_2Cl_2-insoluble **2b**: IR (KBr, cm^{-1}) 1704, 1624, 1541, 1063. CH_2Cl_2-insoluble **2c**: IR (KBr, cm^{-1}) 1700, 1624, 1541, 1049. The CH_2Cl_2 solution was evaporated to produce the soluble part of **2b** or **2c**. CH_2Cl_2-soluble **2b**: IR (film, cm^{-1}) 1696, 1624, 1543, 1071; ^1H NMR (CD_2Cl_2) δ 1.10–2.10 (m, 12 H), 2.10–2.95 (m, 8 H); ^{13}C NMR (CD_2Cl_2) δ 25.0–32.5 (m), 115.0–117.3 (m), 122.5–124.7 (m), 154.0–156.2 (m), 157.0–159.2 (m), 163.2–164.0 (m). CH_2Cl_2-soluble **2c**: IR (film, cm^{-1}) 1703, 1628, 1545, 1052; ^1H NMR (CD_2Cl_2) δ 1.10–2.00 (m, 14 H), 2.00–2.95 (m, 8 H); ^{13}C NMR (CD_2Cl_2) δ 24.5–33.0 (m), 115.8–117.4 (m), 123.5–125.1 (m), 154.5–156.5 (m), 158.6–160.3 (m), 163.2–164.9 (m).

Ternary Copolymerization of Cyclic Diynes 1a–c, 3,11-Tetradecadiyne (4), and CO_2. The reaction was carried out under nitrogen. In a 50-mL stainless steel autoclave were placed $Ni(COD)_2$ (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** (0.094 mL, 0.500 mmol), and **4** (0.115 mL, 0.50 mmol) in this order under magnetic stirring at ambient temperature. CO_2 gas was compressed to 20 kg/cm^2. The reaction mixture was heated at 90 °C for 2.5 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, which was purified by dissolving in CH_2Cl_2 (1.0 mL) and adding ether (20 mL). Drying in vacuo at room temperature gave copolymer **5a** as pale yellow solids (0.075 g, 33%). GPC analysis of the copolymer showed $M_n = 3900$ and $M_w/M_n = 1.4$. Copolymer **5a**: IR (KBr, cm^{-1}) 1706, 1629, 1546, 1048; ^1H NMR (CD_2Cl_2) δ 0.80–1.25 (m), 1.25–1.95 (m), 1.95–2.90 (m); ^{13}C NMR (CD_2Cl_2) δ 12.0–35.0 (m), 114.7–117.8 (m), 122.8–125.5 (m), 153.7–157.5 (m), 157.5–160.0 (m), 163.0–164.0 (m). In addition to these ^{13}C NMR absorptions, the absorptions of the terminal C≡C bond of the copolymer appeared at δ 79.3–82.8 (m). The ternary copolymerizations of cyclic diynes **1b** and **1c**, **4**, and CO_2 were carried out similarly to the **1a**/**4**/CO_2 copolymerization. Copolymer **5b**: IR (KBr, cm^{-1}) 1701, 1628, 1544, 1049; ^1H NMR (CD_2Cl_2) δ 0.80–1.23 (m), 1.23–2.00 (m), 2.00–2.90 (m); ^{13}C NMR (CD_2Cl_2) δ 12.0–32.5 (m), 114.8–117.5 (m), 122.6–125.5 (m), 153.9–156.7 (m), 156.7–160.0 (m), 163.2–164.2 (m). In addition to these ^{13}C NMR absorptions, the absorptions of the terminal C≡C bond of the copolymer appeared at δ 79.2–82.6 (m). Copolymer **5c**: IR (KBr, cm^{-1}) 1701, 1630, 1540, 1048; ^1H NMR (CD_2Cl_2) δ 0.80–1.25 (m), 1.25–2.00 (m), 2.00–2.90 (m); ^{13}C NMR (CD_2Cl_2) δ 12.0–32.5 (m), 114.8–117.5 (m), 123.0–125.2 (m), 154.0–156.5 (m), 157.5–159.8 (m), 163.2–164.0 (m). In addition to these ^{13}C NMR absorptions, the absorptions of the terminal C≡C bond of the copolymer appeared at δ 79.3–82.0 (m).

Preparation of Cooligomer 6 from 1,7-Cyclotridecadiyne (1a) with CO_2. The reaction was carried out under nitrogen. $Ni(COD)_2$ (0.0825 g, 0.300 mmol) in a THF (8.20 mL) solution, a benzene solution (0.509 mL) of PEt_3 (0.600

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mmol), MeCN (6.80 mL), and **1a** (0.566 mL, 3.00 mmol) were placed in this order in a 50-mL stainless steel autoclave under magnetic stirring at ambient temperature. CO_2 gas was compressed to 50 kg/cm^2. The reaction mixture was heated at 110 °C for 20 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 was purified by PLC (CH_2Cl_2/ether = 30/1 (v/v)) followed by MPLC (CH_2Cl_2/ether = 60/1 (v/v)) to give three fractions involving four regioisomeric cooligomers **6a–d**. Cooligomer **6a** (0.026 g, 4.4%) was isolated from the first fraction. Two unseparable cooligomers **6b** and **6c** (0.069 g, 12%) and one cooligomer **6d** (0.022 g, 3.8%) were obtained from the second and third fractions, respectively. Cooligomer **6a**: mp 195–198 °C; IR (KBr, cm^{-1}) 1700, 1632, 1550, 1058; ^{1}H NMR ($CDCl_3$) δ 1.50–1.80 (m, 18 H), 1.84–1.94 (m, 2 H), 2.18–2.26 (m, 4 H), 2.26–2.35 (m, 6 H), 2.41–2.49 (m, 2 H), 2.51–2.63 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 17.1, 17.3, 18.0, 18.1, 24.8, 25.3, 25.5, 26.5, 26.7, 27.1, 27.5, 27.7, 28.2, 28.4, 29.52, 29.54, 29.8, 30.9, 79.1, 79.3, 82.4, 82.6, 116.0, 124.1, 154.7, 158.8, 164.0. Anal. Calcd for $C_{27}H_{36}O_2$: C, 82.65; H, 9.18. Found: C, 82.36; H, 9.12. Although cooligomers **6b–d** did not give satisfactory elemental analysis results, the following spectroscopic data indicate that they are other three regioisomers **6b–d**. Cooligomers **6b** and **6c** were obtained as white powders from the second fraction (0.069 g, 12%): mp 154–158 °C; IR (KBr, cm^{-1}) 1698, 1630, 1546, 1064; ^{1}H NMR ($CDCl_3$) δ 1.47–1.81 (m), 1.81–2.03 (m), 2.14–2.41 (m), 2.41–2.67 (m); ^{13}C NMR ($CDCl_3$) δ 17.0, 17.06, 17.08, 17.3, 18.0, 18.05, 18.09, 24.75, 24.83, 25.0, 25.3, 25.4, 25.90, 25.92, 26.4, 26.5, 26.6, 26.7, 26.96, 27.03, 27.4, 27.6, 28.1, 28.5, 28.7, 29.1, 29.45, 29.48, 29.6, 29.7, 29.79, 29.84, 29.9, 30.9, 79.1, 79.2, 79.6, 80.3, 81.3, 81.7, 82.3, 82.5, 116.1, 116.2, 123.2, 124.1, 154.9, 155.3, 158.4, 158.9, 163.9, 164.0. Thus, eight C≡C absorptions (δ 79.1–82.5), eight C=C absorptions (δ 116.1–158.9), and two C=O absorptions (δ 163.9 and 164.0) demonstrate the existence of two regioisomers. Cooligomer **6d** was obtained as a white powder from the third fraction (0.022 g, 3.8%): mp 137–148 °C; IR (KBr, cm^{-1}) 1698, 1630, 1546, 1064; ^{1}H NMR ($CDCl_3$) δ 1.50–1.83 (m, 18 H), 1.83–1.97 (m, 2 H), 2.20–2.42 (m, 10 H), 2.42–2.60 (m, 6 H); ^{13}C NMR ($CDCl_3$) δ 17.0, 17.1, 18.06, 18.11, 24.9, 25.0, 25.9, 26.5, 26.55, 26.64, 27.0, 28.6, 29.3, 29.66, 29.73, 29.81, 29.83, 29.9, 79.7, 80.3, 81.3, 81.7, 116.3, 123.4, 155.5, 158.6, 164.0.

Results and Discussion

The results of the copolymerization of **1a–c** with CO_2 are summarized in Table 1. The **1a**/CO_2 copolymerization[1a] was improved by using purified **1a** and CO_2 gas with higher purity to afford ladder poly(2-pyrone)s **2a** with molecular weights of 6000–7500 quantitatively. These copolymers were white powders and soluble in CH_2Cl_2 and $CHCl_3$. During the copolymerization reaction, **2a** was precipitated because of its poor solubility in the reaction solvent of THF/MeCN. Therefore, it was not possible to prepare **2a** with the higher molecular weight.

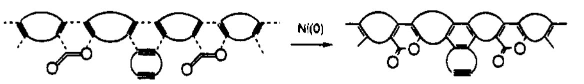
Cyclic diynes **1b** and **1c** also produced ladder poly(2-pyrone)s **2b** and **2c** in high yield. These copolymers, however, were not completely soluble in CH_2Cl_2 and $CHCl_3$. The yields of the CH_2Cl_2-soluble and CH_2Cl_2-insoluble parts of **2b** and **2c**, both of which showed the strong IR ν(C=O) absorptions characteristic of the 2-pyrone ring around 1700 cm^{-1}, are shown in Table 1. The effect of various conditions on the **1c**/CO_2 copolymerization was examined. Increase of the CO_2 pressure did not raise the yield of soluble **2c**. Lowering the comonomer concentration and the reaction temperature gave **2c** with an increased amount of the soluble part. Shortening the reaction time also gave a higher yield of soluble **2c**, but its molecular weight was lower. Under the conditions examined, however, completely soluble ladder poly(2-pyrone)s **2b** and **2c** could not be obtained. This result makes a sharp contrast with the formation of soluble ladder poly(2-pyrone) **2a** from **1a**.

Table 1. Synthesis of Ladder Poly(2-pyrone)s 2 by the Nickel(0)-Catalyzed Cycloaddition Copolymerization of Cyclic Diynes 1 with CO_2 (eq 1)[a]

				2			
1	CO_2, kg/cm^2	solvent, mL	temp, °C		yield,[b] %	M_n[c]	M_w/M_n[c]
a	50	5	110	**a**	100	7500	2.0
			60		99	6400	2.6
	20				100	6000	4.9
b	>50[f]	5	60	**b**	45 (55)	7700	1.1
	50				50 (50)	5800	1.2
c	>50[f]	10	60	**c**	24 (60)[d]	4800	1.4
					12 (88)	4800	1.5
	50				17 (83)	4800	1.4
		5			8 (92)	5500	1.5
					15 (85)[e]	4400	1.4
		10	40		29 (71)	4800	1.5
		5			50 (24)[e]	3500	1.6
	20	10	60		38 (62)	4400	1.4
		5			5 (95)	5900	1.3

[a] Conditions: **1**, 1 mmol; Ni(COD)$_2$/**1** = 0.1; P(n-C_8H_{17})$_3$/Ni = 2; CO_2, initial pressure at room temperature; solvent, THF/MeCN = 1/1 (v/v); time, 20 h. [b] Yield of CH_2Cl_2-soluble **2** based on the quantitative formation of **2**. The value in parentheses is the yield of CH_2Cl_2-insoluble **2**. [c] M_n of CH_2Cl_2-soluble **2** determined by GPC with polystyrene standards in chloroform. [d] P(n-C_8H_{17})$_3$/Ni = 4. [e] Time, 8.5 h. [f] The CO_2 pressure over 50 kg/cm^2 at room temperature was 70 kg/cm^2 at the reaction temperature.

A competing side reaction of the poly(2-pyrone) formation may be the diyne trimerization to produce benzenoid, cyclopentadienoid, and/or cyclooctatetraenoid repeating units in the copolymer (eq 2).[1b,2] Homopolymerization of **1a** gave methanol-insoluble homopolymer **3a** (22%, M_n = 840), the structure of which was not examined at the present time. ^{13}C NMR C=C absorptions of **3a** are shown in Figure 1. Formation of the insoluble ladder poly(2-pyrone) may be ascribed to contamination of the poly(2-pyrone) with the diyne trimerization units, which may result in branching and/or cross-linking of the copolymer in the progress of the copolymerization reaction to cause its insolubility. The results of Table 1 indicate that the cyclic diyne with the larger ring size produced the insoluble ladder poly(2-pyrone) more easily and suggest that it undergoes its trimerization more easily.



(2)

A similar effect of the ring size is also observed in the ladder poly(2-pyridone) synthesis by the nickel(0)-catalyzed cycloaddition copolymerization of cyclic diynes **1a–c** with isocyanates.[1f] For example, the copolymerization of **1a** with phenyl isocyanate afforded the soluble ladder poly(2-pyridone) while the copolymerization of **1b** and **1c** with phenyl isocyanate gave sparingly soluble and insoluble ladder poly(2-pyridone)s, respectively. It is possible to prepare, however, the soluble **1b**/isocyanate copolymer by changing the structure of the isocyanate from phenyl to n-octyl isocyanate. The addition of the excess phenyl isocyanate to **1c** suppressed the side reaction of the cyclic diyne trimerization and produced the soluble ladder poly(2-pyridone) from **1c**. This result contrasts to the ladder poly(2-pyrone) synthesis, where suppression of the cyclic diyne trimerization by increasing the CO_2 pressure was difficult (vide

Table 2. Ternary Copolymerization Involving 3,11-Tetradecadiyne (4), Cyclic Diynes 1, and CO_2 to Poly(2-pyrone)s 5[a]

			5			
1 + 4	time, h		yield,[b] %	M_n[c]	M_w/M_n[c]	[1]/[4][d]
1a + **4**	2.5	**a**	33	3900	1.4	0.31/1.0
1b + **4**	8	**b**	100	4800	1.5	
	4		100	3800	1.3	
	1.5		29	2500	1.1	0.99/1.0
1c + **4**	8	**c**	54	3700	1.5	1.2/1.0

[a] Conditions: **1** = **4** = 0.5 mmol; Ni/(**1** + **4**) = 0.1; $P(n\text{-}C_8H_{17})_3$/Ni = 2; CO_2, 20 kg/cm^2 (initial pressure at room temperature); solvent, 10 mL, THF/MeCN = 1/1 (v/v); temperature, 90 °C. [b] Based on the quantitative formation of **5**. [c] Determined by GPC with polystyrene standards in chloroform. [d] The relative copolymerizability: the molar ratio of **1** and **4** components in **5** determined by ^1H NMR spectroscopy.

ante). These findings differentiate the ladder poly(2-pyrone) synthesis from the ladder poly(2-pyridone) synthesis and indicate that CO_2 is a less reactive cycloaddition component than the isocyanate in the nickel(0)-catalyzed cycloaddition copolymerization of the diyne with the heterocumulene.

A copolymerizability order of three cyclic diynes **1a**–**c** in the **1**/CO_2 copolymerization was determined by the nickel(0)-catalyzed ternary copolymerization involving CO_2 and two equimolar diynes, that is, **1** and 3,11-tetradecadiyne $EtC{\equiv}C(CH_2)_6C{\equiv}CEt$ (**4**). The results of the ternary copolymerization are shown in Table 2. The composition of ternary copolymers **5a**–**c**, i.e., the molar ratio of two diyne components in **5a**–**c**, determined by ^1H NMR spectroscopy gave three relative copolymerizabilities of **1a**–**c** to **4**, which gave then the copolymerizability order of **1c** > **1b** = **4** > **1a**.

Previously we determined the copolymerizability order of four acyclic diynes and one cyclic diyne **1a** in the nickel(0)-catalyzed diyne/CO_2 copolymerization to the poly(2-pyrone): $EtC{\equiv}C(CH_2)_6C{\equiv}CEt$ > **1a** > $MeC{\equiv}C(CH_2)_2C{\equiv}CMe$ > 1,4-n-$PrC{\equiv}CCH_2C_6H_4CH_2C{\equiv}CPr$-$n$ > 1,3-n-$PrC{\equiv}CCH_2C_6H_4CH_2C{\equiv}CPr$-$n$ and proposed that the rigidity or the flexibility of the terminal diyne component involving the propagating C≡C bond moiety of the copolymer plays an important role in determining the copolymerizability of the diyne.[1c] Inversion of the copolymerizability of the cyclic diyne to the acyclic diyne $EtC{\equiv}C(CH_2)_6C{\equiv}CEt$ by increasing the ring size of the cyclic diyne is noteworthy. The copolymerizability order of **1c** > **1b** > **1a** suggests that the cyclic diyne with the larger ring is more flexible and accordingly is more reactive in the **1**/CO_2 copolymerization. These findings are compatible with the above-mentioned proposal and disclose one feature of the poly(2-pyrone) synthesis. The more reactive cyclic diyne may also generate the diyne trimerization unit in the copolymer more easily to produce the ladder poly(2-pyrone) with the poorer solubility. Thus, the copolymerizability order may be related to the solubility of three ladder poly(2-pyrone)s **2a**–**c**.

Ladder poly(2-pyrone)s **2a**–**c** and ternary copolymers **5a**–**c** were identified by IR, ^1H NMR, and ^{13}C NMR spectroscopies. The most decisive criterion is the ^{13}C NMR spectroscopy. Figure 1 summarizes the ^{13}C NMR C=O and C=C absorptions of **2a**, the soluble parts of **2b** and **2c**, and **5a**–**c**. They exhibited the ^{13}C NMR five groups of C=O and C=C absorptions characteristic of the 2-pyrone ring.[1a–d] To confirm further the repeating unit of the 2-pyridone ring of the copolymer, cooligomer **6** consisting of two **1a** molecules and one CO_2 molecule was prepared by shortening the reaction time to 20 min. Cooligomer **6** was composed of four regioisomers. MPLC purification of **6** gave two separable regioisomers **6a** and **6d** (4.4 and 3.8% yield) and a mixture of two unseparable regioisomers **6b** and **6c** (12% yield). Their ^{13}C NMR C=O and C=C absorptions are shown in Figure 2 where **6b** and **6c** in the mixture showed C=O and C=C absorptions with similar intensities. Thus, the four regioisomers were formed almost equally, which indicates the nonregioselective formation of **6**. It is not

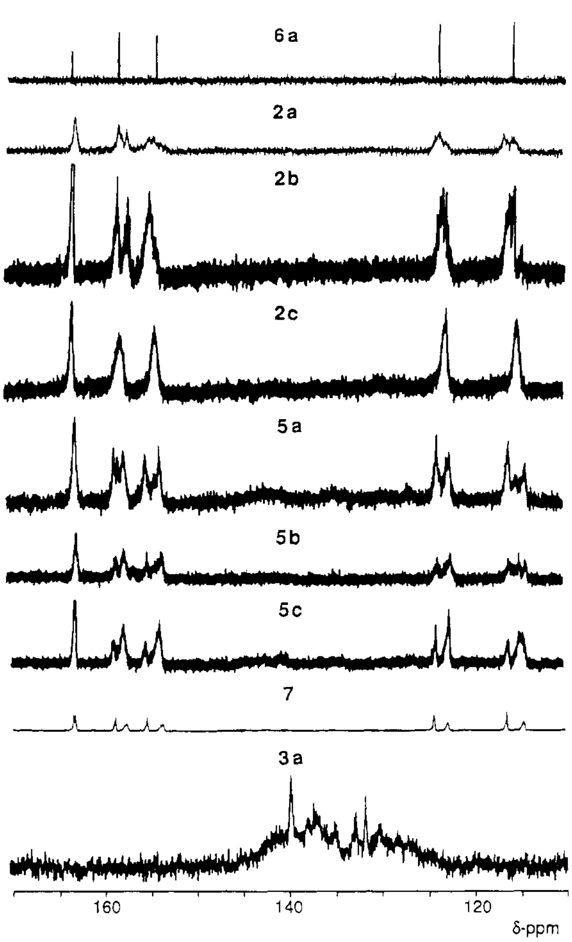


Figure 1. ^{13}C NMR C=O and C=C absorptions of **2b**, **2c**, and **5a**–**c** in CD_2Cl_2 and **2a**, **3a**, **6a**, and **7** in $CDCl_3$.

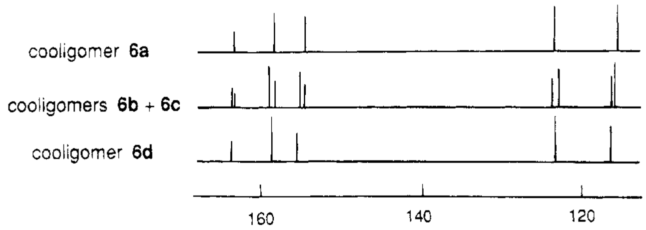
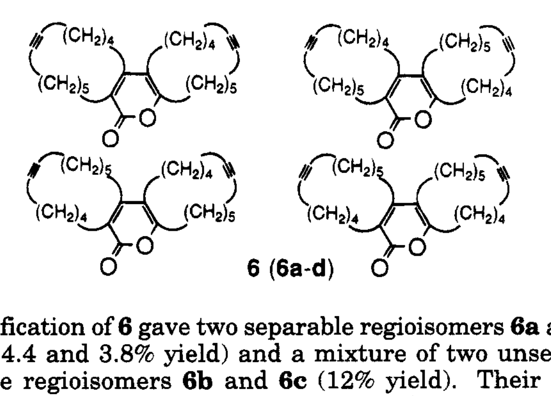


Figure 2. ^{13}C NMR C=O and C=C absorptions of cooligomer **6** (δ-ppm).



6 (**6a-d**)

possible at the present time, however, to assign four regioisomeric structures to **6a–d**, respectively.

^{13}C NMR C=O and C=C absorptions of cooligomer **6a**, which is the one among the four regioisomers, is shown in Figure 1. The good correspondence of the ^{13}C NMR C=O and C=C absorptions of **2a–c** with those of **6a** and the absence of the C=C absorptions of **3a** in their spectra demonstrate the formation of the 1:1 copolymer from **1** and CO_2, i.e., ladder poly(2-pyrone) **2**. The nonregioselective formation of **6** indicates that ladder poly(2-pyrone) **2** has four regioisomeric 2-pyrone rings. Determination of microstructures of **2** such as orientation of the 2-pyrone carbonyl group along the copolymer chain and its side position of the poly(2-pyrone) ladder is not possible at the present time although the ladder poly(2-pyrone) obtained seems to have these random microstructures. Ternary copolymers **5a–c** were identified by the finding that their ^{13}C NMR C=O and C=C absorptions along with their ^{1}H NMR absorptions were almost a superposition of those of the corresponding binary copolymer **2** and those of poly(2-pyrone) **7**[1a] obtained from **4** and CO_2 (Figure 1).

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