Communications to the Editor

New Synthesis of Soluble Ladder Polymers by Nickel(0)-Catalyzed Cycloaddition Copolymerization of Cyclic Diynes

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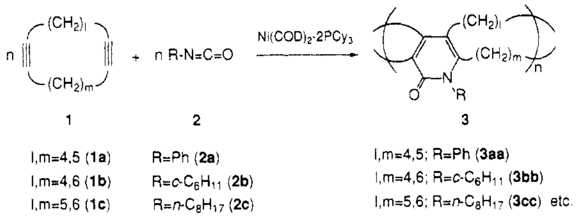
Ladder polymer synthesis has a long history, but insolubility of the ladder polymers prepared has prevented the development of this attractive research field.[1a] A new generation of the ladder polymer, however, has been brought forth by the synthesis of soluble ladder polymers using two new approaches, i.e., repetitive Diels-Alder reaction[1b] and polymer-analogous cyclization of linear precursors.[1c,d] This successful synthesis of soluble ladder polymers is stimulating further interest in the exploitation of the new synthesis of soluble ladder polymers and/or their application to electronic and optical materials.[1] Recently we have developed the nickel(0)-catalyzed cycloaddition copolymerization of acyclic diynes with heterocumulenes of CO_2[2] and isocyanates.[3] The efficient synthesis of the 1:1 copolymer of CO_2, that is, the poly(2-pyrone), by the cycloaddition copolymerization of the diyne is highly noteworthy.[2]

We communicate here nickel(0)-catalyzed facile and efficient synthesis of soluble ladder poly(2-pyridone)s (**3**) from cyclic diynes (**1**) and isocyanates (**2**) (eq 1), which provides a new synthetic method of the soluble ladder polymer and also indicates a new aspect of the cycloaddition copolymerization of the diyne. The present synthetic method of the soluble ladder polymers is characterized by transition-metal-catalyzed facile one-step cycloaddition[4] of the acetylene with the heterocumulene as an elementary reaction.



(1)

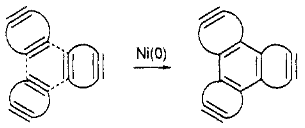
Nine ladder poly(2-pyridone)s **3aa–cc** were prepared using three commercially available cyclic diynes, i.e., 1,7-cyclotridecadiyne (**1a**), 1,7-cyclotetradecadiyne (**1b**), and 1,8-cyclopentadecadiyne (**1c**), and three isocyanates, i.e., phenyl (**2a**), cyclohexyl (**2b**), and *n*-octyl (**2c**) isocyanates (eq 1). The copolymerization was carried out in THF at 60 °C in the presence of a nickel(0) catalyst generated from $Ni(COD)_2$ (10 mol %) and 2 equiv of a tricyclohexylphosphine ligand according to the standard condition of the copolymerization of acyclic diynes with isocyanates.[3]

Table I. Nickel(0)-Catalyzed 1:1 Cycloaddition Copolymerization of Cyclic Diynes 1 with Isocyanates 2 to Ladder Poly(2-pyridone)s 3[a]

		3			
1	2		yield,[b] %	M_n[c]	M_w/M_n[c]
a	**a**	**aa**	80	36 800	4.6
	b	**ab**	92[7]	17 900	3.9
	c	**ac**	94	26 200	4.9
	b[e,f]	**ab**	99	43 600	4.2
b	**a**[d]	**ba**	81	63 100	3.5
	b	**bb**	93	16 400	6.0
	c	**bc**	98	26 000	6.9
c	**a**[e]	**ca**	90	39 800	1.9
	b[e]	**cb**	91	23 800	5.4
	c[e]	**cc**	89	19 100	2.0

[a] **1**, 1.00 mmol; **2**, 1.00 mmol; $Ni(COD)_2/1 = 0.10$; $PCy_3/Ni(COD)_2 = 2$; solvent, THF, 5 mL; temp, 60 °C; time, 20 h. [b] Based on the formation of a 1:1 copolymer of **1** with **2**. [c] Determined by GPC with polystyrene standards in chloroform. [d] **2**, 5.00 mmol. [e] **2**, 2.00 mmol. [f] $Ni(COD)_2$/**1a** = 0.02; solvent, THF, 2.5 mL; temp, 90 °C.

The results of the copolymerization are summarized in Table I. The ladder poly(2-pyridone)s (**3**) with molecular weights of ca. 15 000–65 000 were obtained in high yield by purification with CH_2Cl_2/Et_2O or $CH_2Cl_2/MeOH$. They were soluble in methylene chloride, chloroform, and acetic acid. The copolymerization of **1c** with an equimolar amount of **2a–c** gave insoluble copolymers on account of probable formation of branched and/or cross-linked ladder poly(2-pyridone)s originating from the generation of diyne trimerization units[5] (for example, eq 2) in the copolymers.



(2)

Use of a 2-fold excess of **2a–c** to **1c** suppressed the diyne trimerization to afford soluble ladder poly(2-pyridone)s **3ca–cc**. The equimolar **1b**/**2a** copolymerization also produced sparingly soluble poly(2-pyridone) **3ba**. Thus the feed ratio of **2** to **1** controls 1:1 copolymerizability of the copolymerization to affect the solubility of the ladder poly(2-pyridone). Films of **3aa**, **3ba**, **3ca**, and **3cc** could be made from their chloroform solutions. Poly(2-pyridone) **3ca** had a thermal stability similar to that of the poly(2-pyridone)[3] prepared from 3,11-tetradecadiyne and **2a** to show a rapid weight loss around 420 °C under nitrogen.

Formation of ladder poly(2-pyridone)s **3** was demonstrated by IR, ^1H NMR, and ^{13}C NMR spectroscopies.[3] For example, poly(2-pyridone) **3aa** showed its IR ν(C=O) absorption at 1627 cm^{-1}. Its ^{13}C NMR spectrum exhibited C=C and C=O absorptions at δ 116.2–119.0 (m), 143.0–146.0 (m), 150.0–153.0 (m), 163.0–164.0 (m) (C=C and C=O absorptions of 2-pyridone rings), 128.0–131.0 (m) (C=C absorptions of 2-pyridone rings and C_6H_5 groups), and 140.2–141.4 (m) (C_6H_5 group absorptions) (Figure 1a). ^1H NMR peaks were observed at δ 0.80–2.10 (m, 10H), 2.10–3.20 (m, 8H), 7.00–7.30 (m, 2H), and 7.30–7.70 (m, 3H) with satisfactory relative peak areas.

Homopolymerization of **1a–c** under the copolymerization condition gave methanol-insoluble homopolymers with molecular weights of ca. M_n = 500–1400 in ca. 50–100% yield. Their ^{13}C NMR major C=C absorptions of diyne trimerization units[5] (for example, eq 2) appeared at

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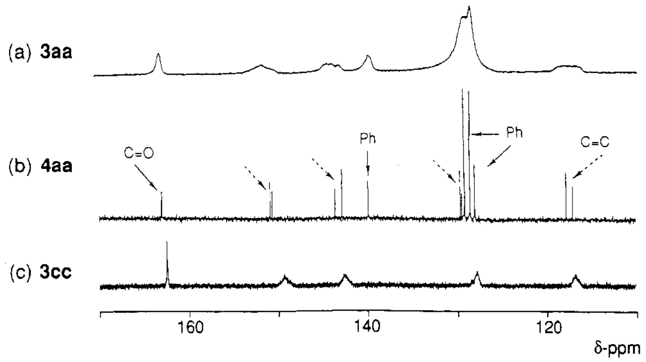
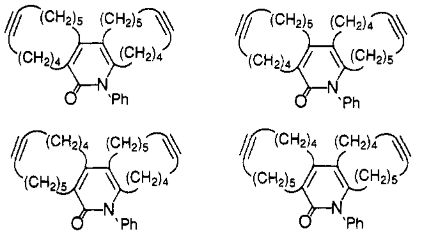


Figure 1. ^{13}C NMR C═C and C═O absorptions of (a) poly(2-pyridone) **3aa**, (b) the fraction I of cooligomer **4aa** involving its two regioisomers, and (c) poly(2-pyridone) **3cc**.

δ 136.0–138.6 (m) ppm with or without minor ones at δ 128.1–129.5 (m) ppm. Homopolymerization of **2a** under the copolymerization condition produced unidentified products with the low molecular weight of M_n = ca. 400. Poly(2-pyridone)s **3ab**, **3ac**, **3bb**, **3bc**, **3cb**, and **3cc** (Figure 1c) without the phenyl isocyanate component showed the five characteristic ^{13}C NMR C═C and C═O absorptions without the above-mentioned C═C absorptions of diyne homopolymers. This finding indicates that efficient 1:1 cycloaddition copolymerization of cyclic diynes **1** with **2b** and **2c** occurs to produce corresponding ladder poly(2-pyridone)s.

To confirm further the ladder poly(2-pyridone) structure, cooligomer **4aa** consisting of two molecules of diyne **1a** and one molecule of isocyanate **2a** was prepared in 80% yield by the short-time reaction using a 2-fold excess of **1a** to **2a**. Cooligomer **4aa** was a mixture of four regioisomers (eq 3). HPLC purification of **4aa** afforded



(3)

two fractions I and II, each of which contained two regioisomers. Fraction I exhibited 10 ^{13}C NMR C═C and C═O absorptions of two kinds of 2-pyridone rings at δ 117.0, 117.7, 129.5, 129.7, 142.9, 143.6, 150.7, 150.9, 162.9, and 163.0 along with other absorptions at δ 14.2–30.5 (CH_2 absorptions), 79.29, 79.31, 79.9, 80.1, 81.6, 81.7, 82.5 (C≡C absorptions), 127.97, 128.01, 128.51, 128.60, 129.17, 129.14, 139.86, and 139.89 (C_6H_5 group absorptions) (Figure 1b). Excellent correspondence (Figure 1) of the ^{13}C NMR C═C and C═O absorptions of **3aa** and **3cc** with those of regioisomers of **4aa** indicates that efficient 1:1 cycloaddition copolymerization of **1a** with **2a** and **1c** with **2c** occurs to produce ladder poly(2-pyridone)s **3aa** and **3cc**. Thus, the primary structure of the copolymer of the ladder poly(2-pyridone) was demonstrated, but its microstructures such as orientation of the 2-pyridone carbonyl group along the copolymer chain and its side position of the poly(2-pyridone) ladder were not determined at the present time although the ladder poly(2-pyridone) obtained seems to have these random microstructures.

The relationship of the reaction time with the copolymer yield and molecular weight in the **1a**/**2b** copolymerization is shown in Figure 2. It reveals a characteristic nature of copolymer growth in the ladder poly(2-pyridone) formation: comonomers are rapidly consumed to form cooligomers and copolymers, which then react each other via stepwise polyaddition to grow to the ladder poly(2-pyridone)s with higher molecular weights.

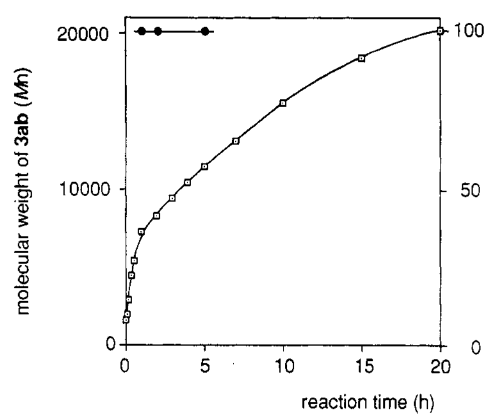


Figure 2. Relationship of the reaction time with the yield (●) and the molecular weight (▣) of **3ab** in the copolymerization of **1a** with **2b**.

Previously we reported briefly the preparation of the soluble ladder poly(2-pyrone) by the nickel(0)-catalyzed cycloaddition copolymerization of **1a** with CO_2.[2a] The copolymerization of **1c** with CO_2, however, produces an insoluble ladder poly(2-pyrone).[6] The present ladder poly(2-pyridone) synthesis has a significant advantage over the ladder poly(2-pyrone) synthesis, that is, (1) synthesis of a variety of ladder poly(2-pyridone)s by changing the structure of the isocyanate cycloaddition component and (2) control of the 1:1 copolymerizability of the copolymerization, which is related to the solubility of the poly(2-pyridone), by changing the feed ratio of the isocyanate to the cyclic diyne. Synthesis of a variety of ladder polymers may be possible by changing the structure of the cyclic diyne and the kind of the cycloaddition component.

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References and Notes

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(7) The result of the elemental analysis of poly(2-pyridone) **3ab** was not satisfactory. Anal. Calcd for $(C_{20}H_{29}NO)_n$: C, 80.22; H, 9.76; N, 4.68. Found: C, 75.14; H, 9.59; N, 4.23. It was found that ashes were formed after combustion analysis. This finding indicates that nickel salts contaminate **3ab**, which was confirmed by X-ray fluorescence analysis.