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New Synthesis of Poly(2-pyridone)s and Copoly(2-pyridone/2-pyrone)s by the Reaction of Ammonia and Primary Amines with the Poly(2-pyrone) Prepared from Diyne and Carbon Dioxide

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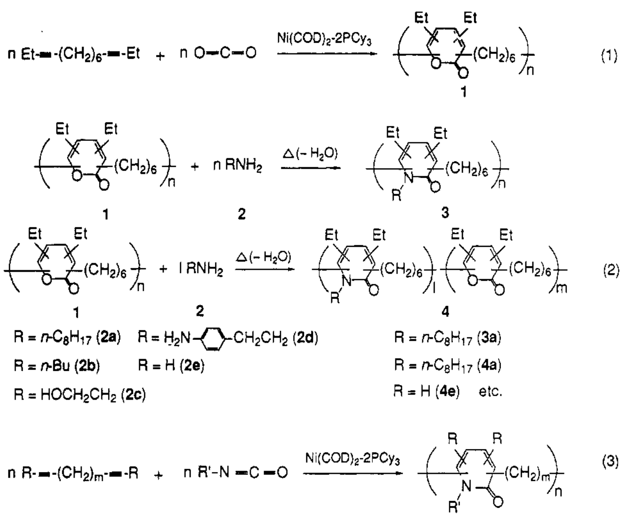
Synthesis of a CO_2 copolymer and development of its uses are interesting research subjects. Recently we reported the synthesis of unprecedented poly(2-pyrone)s by the nickel(0)-catalyzed 1:1 cycloaddition copolymerization of diynes with CO_2 (for example, eq 1).[1,2] Exploration of the polymer reaction of the poly(2-pyrone) is important in relation to the development of its uses. A 2-pyrone ring exhibits a variety of chemical reactivities.[3] As an example of the reaction with a nucleophile, the 2-pyrone ring is known to be converted into a 2-pyridone ring by the reaction with ammonia and primary amines.[3,4] We communicate here a new synthesis of poly(2-pyridone)s **3** and copoly(2-pyridone/2-pyrone)s **4** by the reaction of poly(2-pyrone) (**1**) with ammonia and primary amines **2** (eq 2).[2] Recently we reported the poly(2-pyridone) synthesis by the nickel(0)-catalyzed 1:1 cycloaddition copolymerization of diynes with isocyanates (eq 3).[2,5] One feature of the present poly(2-pyridone) synthesis is that it can afford the N-unsubstituted poly(2-pyridone) and the poly(2-pyridone)s with hydroxy and amino functional groups, which cannot be prepared by the above-mentioned cycloaddition copolymerization method. The copoly(2-pyridone/2-pyrone) corresponds to a ternary cycloaddition copolymer[1,5] from the diyne, the isocyanate, and CO_2. The present study is interesting as the new synthesis of the poly(2-pyridone) and the copoly(2-pyridone/2-pyrone) using CO_2 via the poly(2-pyrone).



Poly(2-pyrone) (**1**)[1a] prepared from 3,11-tetradecadiyne and CO_2 (eq 1) was efficiently converted into poly(2-pyridone) (**3a**) by reaction with an excess amount of *n*-octylamine (**2a**), which was used as a solvent, at 180 °C for 20 h (eq 2 and Table 1). No reaction was observed at 120 °C. It is noteworthy that 3,4,5,6-tetraethyl-2-pyrone, a model compound, was converted only partly into 3,4,5,6-tetraethyl-2-pyridone under reaction conditions similar to those at 180 °C.[6] Poly(2-pyridone) **3a** was identified by the agreement of its IR, ^1H NMR, and ^{13}C NMR (Figure 1) spectra with those of authentic **3a**[5a] prepared by the nickel(0)-catalyzed cycloaddition copolymerization of 3,11-tetradecadiyne with *n*-octyl isocyanate (eq 3).

Table 1. Reaction of Poly(2-pyrone) (1) with *n*-Octylamine (2a) to Poly(2-pyridone) 3a or Copoly(2-pyridone/2-pyrone)s 4a[a]

				3a or 4a				
temp (°C)	time (h)	**2a/1**[b]	solvent (mL)		yield (%)[c]	M_n[d]	M_w/M_n[d]	l:m[e]
180	20	30		**3a**	61	13 700	1.9	100:0
170	20	30		**4a**	71	14 400	2.0	82:18
150					92	13 900	2.3	45:55
170	10				78	12 400	1.9	67:33
	20	3	THF(1)		80[f]	14 800	2.0	51:49
		10			83	15 100	1.8	80:20

[a] The reaction was carried out in a 50-mL stainless steel autoclave using 0.2 mmol of the 2-pyrone ring of **1** (M_n, 9600; M_w/M_n, 2.2). [b] The molar ratio of **2a** to the 2-pyrone ring of **1**. [c] Based on the quantitative formation of **3a** or **4a** with the determined composition from **1** used. [d] Determined by GPC with polystyrene standards in chloroform. [e] Determined by IR. [f] The ^{13}C NMR spectrum is shown in Figure 1.

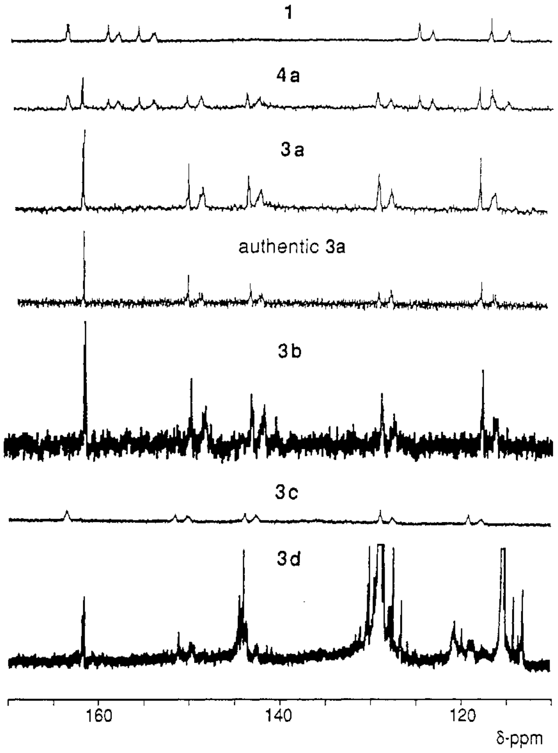


Figure 1. ^{13}C NMR C=O and C=C absorptions in $CDCl_3$ except those of **3d** in $CDCl_3/CD_3OD$.

Lowering the reaction temperature, shortening the reaction time, reducing the amount of the amine, and using a THF solvent effected incomplete conversions to produce copoly(2-pyridone/2-pyrone)s **4a** with various compositions (eq 2). The results are summarized in Table 1. The composition of **4a**, that is, the ratio of the 2-pyridone ring to the 2-pyrone ring in **4a**, was determined by IR spectroscopy using $\nu_{C=O}$ absorptions of **1** (1703 cm^{-1})[1a] and authentic **3a** (1635 cm^{-1})[5a] as IR standards. Formation of copoly(2-pyridone/2-pyrone) **4a** was demonstrated by the finding that its ^{13}C NMR C=O and C=C absorptions

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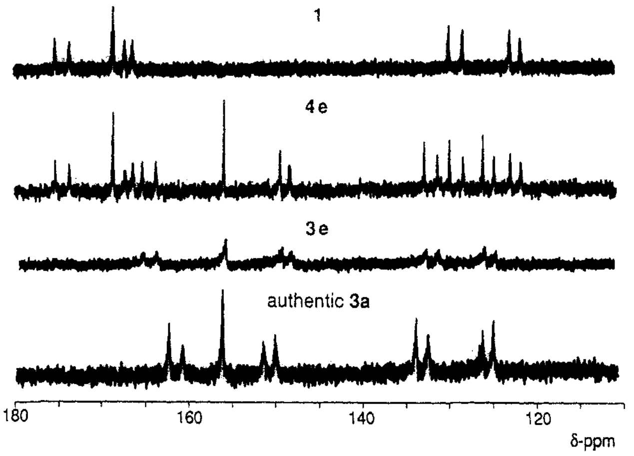

Figure 2. ^{13}C NMR C═O and C═C absorptions in $MeSO_3H$.

are superpositions of those of poly(2-pyrone) (1) and authentic poly(2-pyridone) **3a** (Figure 1).

Other primary amines could be used at 170–180 °C for the poly(2-pyridone) formation reaction. *n*-Butylamine effected the reaction to give **3b** (80%, $M_n = 3700$, $M_w/M_n = 3.9$), but no reaction was observed with cyclohexylamine and aniline. Ethanolamine (**2c**) and 2-(4-aminophenyl)ethylamine (**2d**), that is, bifunctional primary amines having hydroxyl and additional nonreactive amino groups, afforded **3c** (93%) and **3d** (87%) having hydroxyl and amino functional groups. The GPC molecular weight of **3c** in chloroform was only $M_n = 800$ ($M_w/M_n = 3.0$). This unusual low M_n value may be due to its inadequate compatibility with the polystyrene GPC column because the formation of **3c** was confirmed by the finding that **3c** exhibits only five groups of ^{13}C NMR C═O and C═C absorptions corresponding to the 2-pyridone ring in the C═O and C═C region (vide infra). **3d** was insoluble in chloroform and its GPC molecular weight was not determined, while it was soluble in a mixed solvent of chloroform/methanol = 7/3. The formation of **3b–d** was indicated by their characteristic ^{13}C NMR C═O and C═C absorptions of the corresponding 2-pyridone rings (Figure 1). The two strong absorptions of **3d** at δ 115.4 and 129.1 are assigned to two kinds of carbon atoms bound to the hydrogen of the 4-aminophenyl group.

Ammonia (**2e**) reacted with **1** in a 50-mL stainless steel autoclave at 170 °C for 20 h under a pressure of ca. 100 kg/cm^2 to afford N-unsubstituted poly(2-pyridone) **3e**. Under the reduced pressure of 50 kg/cm^2, copoly(2-pyridone/2-pyrone) **4e** with nearly equal amounts of 2-pyridone and 2-pyrone rings was obtained. Formation of **3e** is noteworthy because no reaction was observed between 3,4,5,6-tetraethyl-2-pyrone and **2e** under the reaction condition affording **3e**.[6] Poly(2-pyridone) **3e** and copoly(2-pyridone/2-pyrone) **4e** were insoluble in chloroform and methylene chloride, which are good solvents for *N*-alkyl- and aryl-substituted poly(2-pyridone)s[5] and for poly(2-pyrone)s,[1] but were soluble in acetic acid, trifluoroacetic acid, and methanesulfonic acid. Poly(2-pyridone) **3e** and copoly(2-pyridone/2-pyrone) **4e** were identified by IR, ^1H NMR, and ^{13}C NMR spectroscopies. The most decisive evidence of the formation of **3e** and **4e** was their ^{13}C NMR C═O and C═C absorptions in methanesulfonic acid (Figure 2): five groups of C═O and C═C absorptions characteristic of the 2-pyridone ring of **3e** were similar to those of authentic **3a**,[5a] and two sets of five groups of C═O and C═C absorptions of the 2-pyridone and 2-pyrone rings of **4e** were superpositions of those of **1** and **3e**, respectively.

N-Unsubstituted poly(2-pyridone) **3e** and poly(2-pyridone)s **3c,d** with hydroxy and amino functional groups cannot be prepared by the nickel(0)-catalyzed 1:1 cycloaddition copolymerization of diynes with isocyanates (eq 3)[5] because of nonavailability of the corresponding isocyanates. Thus, the preparation of **3c–e** indicates one advantage of the present poly(2-pyridone) synthesis. The preparation of **3e** and **4e** may be interesting in relation to the recently developed chemistry[7] of the intermolecular hydrogen-bond formation of the 2-pyridone ring. The copoly(2-pyridone/2-pyrone) corresponds to a ternary cycloaddition copolymer from the diyne, the isocyanate, and CO_2, but its synthesis by the cycloaddition copolymerization method[1,5] using the nickel(0) catalyst is unsuccessful at the present time.[8]

The reaction of the poly(2-pyrone) with ammonia and primary amines depended upon the structure of the poly(2-pyrone). The polymer produced by the reaction of **2a** or **2e** with poly(2-pyrone)[1b] obtained from 2,6-octadiyne and CO_2 showed a different IR $\nu_{C=O}$ absorption from that of the poly(2-pyrone), but it did not exhibit ^{13}C NMR C═O and C═C absorptions characteristic of the 2-pyridone ring. The ladder poly(2-pyrone)[1a] prepared from 1,7-cyclotridecadiyne and CO_2 did not react with **2b** or **2e** at 170 °C, which indicates its high stability toward the amine.

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References and Notes

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(2) The expression of the repeating units of **1**, **3**, and **4** in eqs 1 and 2 is based on the result that the formation of the 2-pyrone ring of **1** is not regioselective; that is, for example, one ethyl substituent takes the 3- or 4-position of the 2-pyrone ring and the methylene chain exists at its 4- or 3-position, respectively.[1a] The 2-pyridone ring formation of the diyne–isocyanate copolymerization (eq 3) is also not regioselective.[5a]

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(6) Explanation of this finding is not clear at the present time. A tentative one without experimental evidence is the concentration of the nucleophile of *n*-octylamine or ammonia near the 2-pyrone ring of **1** by the generated 2-pyridone ring through the hydrogen-bond formation. The different spatial structure of the 2-pyrone ring of **1** from that of the model compound, which may produce the reactive electrophilic carbonyl or C═C bond, is another possibility. This is not probable, however, because **1** and the model compound had similar IR and ^{13}C NMR absorptions of the 2-pyrone ring.

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(8) Tsuda, T.; Yasukawa, H., unpublished results.