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Copolymerization of carbon monoxide and aziridine†

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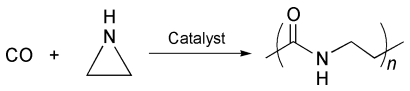
Alternating copolymerization of carbon monoxide with aziridine was realized, which serves as a prototype of a novel route for synthesis of poly-β-peptides.

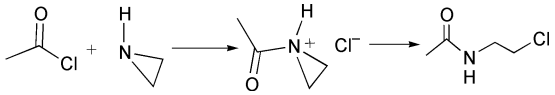
Rational discovery of new catalytic reactions is an important scientific challenge for synthetic chemists. We are interested in designing new catalytic polymerization reactions which involve reaction and incorporation of heteroatoms in the polymer chain to produce functional polymers. In light of the successful examples of carbonylation of aziridines and epoxides and alternating copolymerization of CO and alkenes,[1–4] we set out to develop metal-catalyzed alternating copolymerization of CO with aziridines [eqn. (1)].[5] This reaction in principle provides an



(1)

attractive route to poly-β-peptides, which have received considerable current attention as biomimetic materials.[7,8] Prior to this work, Sen and Arndtsen independently suggested the possibility of copolymerization of imines with CO to produce poly-α-peptides and demonstrated the first examples of imine insertion into Pd–acyl bonds.[9,10] We report here the initial identification of a catalyst for CO–aziridine copolymerization and that alternating polymerization can be achieved under carefully controlled experimental conditions.

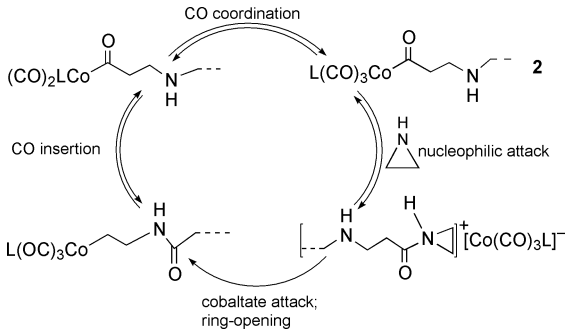
At the onset of this project, we conceived a catalytic cycle leading to the copolymerization. First of all, CO insertion and aziridine insertion into a metal–carbon bond are inevitable steps in any catalytic cycle that one might design for the copolymerization of CO and aziridine. Examples of the latter reaction are absent in organometallic chemistry to our knowledge. However, an interesting reaction of aziridine insertion into acetyl chloride was reported [eqn. (2)].[11] It is well established



(2)

that some metal–acyl species resemble organic acyl chlorides and undergo nucleophilic cleavage by alcohols and amines to afford esters and amides. By such analogy, insertion of aziridine into metal–acyl bonds might also occur. The aziridine insertion coupled with CO insertion into a metal–alkyl bond then forms a reasonable catalytic cycle leading to the alternating copolymerization (Scheme 1).

Under the above hypothesis, we screened a number of potential catalysts and arrived at Heck's complex $CH_3COCo(CO)_3PPh_3$ **1**. In the presence of 10 mol% of **1** under 1000 psi CO in THF solution, aziridine and CO was copolymerized to produce a crystalline, hot-water soluble polymer in good yield (entry 1, Table 1). The FT-IR and NMR spectra together confirm that the product is poly-β-alanine. In the IR spectrum, two prominent amide bands are present at 1645 and 1539 cm^{-1}.† The ^1H NMR spectrum reveals two triplet resonances (**a** and **b**) at δ 3.25 and 2.26 ppm (J = 6.5 Hz) (Fig. 1a), in agreement with the chemical shifts reported for poly-β-alanine prepared from acrylamide.[12] Additional fine features (labeled with asterisks) are present overlapping with or in close vicinities of **a** and **b**. The small differences in chemical shifts between them and the main peaks **a** and **b** lead us to believe that they belong to β-alanine units located at or close to the end of the chain. These resonances are not due to amine microstructures, which would possibly be present if repetitive aziridine insertions occurred (see below), because they do not move downfield in acid solutions in contrast to what should be expected for amines upon protonation. Work is in progress in our laboratory to positively identify these resonances. A resonance (**c**) at δ 1.80 ppm is observed due to the acetyl end group that originates from



Scheme 1 Working model for alternating copolymerization of CO with aziridine (L = PPh_3).

† Electronic supplementary information (ESI): NMR spectra, GPC summary, elemental analyses, experimental procedure of polymerization, and a scheme rationalizing the imperfect alternating enchainment. See http://www.rsc.org/suppdata/cc/b1/b103899k/

Table 1 Copolymerization of CO with aziridine using **1** as the catalyst[a]

Entry	[Cat]/mM	Aziridine/g	Aziridine–**1** (molar ratio)	CO pressure/psi	Reaction time/h	Yield/g	Amine units/mol%[b]	M_w[c]/10^3	PDI[c]
1	5.8	0.25	10	1000	12	0.25 (60%)	<2	14.1	4.85
2	5.8	0.25	10	500	12	0.25 (60%)	<2	—	—
3	5.8	0.25	10	250	12	0.17 (41%)	<2	—	—
4	5.8	0.75	30	1000	12	0.98 (79%)	~8	36.6	2.52
5	5.8	1.25	50	1000	12	1.84 (89%)	~12	57.8	11.56
6[d]	5.8	0.25 × 3	30	1000	12 × 3	1.06 (86%)	~2	36.6	5.67
7[d]	5.8	0.25 × 5	50	1000	12 × 5	1.92 (93%)	~2	63.3	9.32

[a] In 100 mL THF at 80 °C. [b] Amine defects estimated by ^1H NMR. [c] Determined by GPC in 1,1,1,3,3,3-hexafluoropropan-2-ol with 0.01 M sodium triflate, light scattering–viscometry–refractive index triple detector. [d] Aziridine was added in portions.

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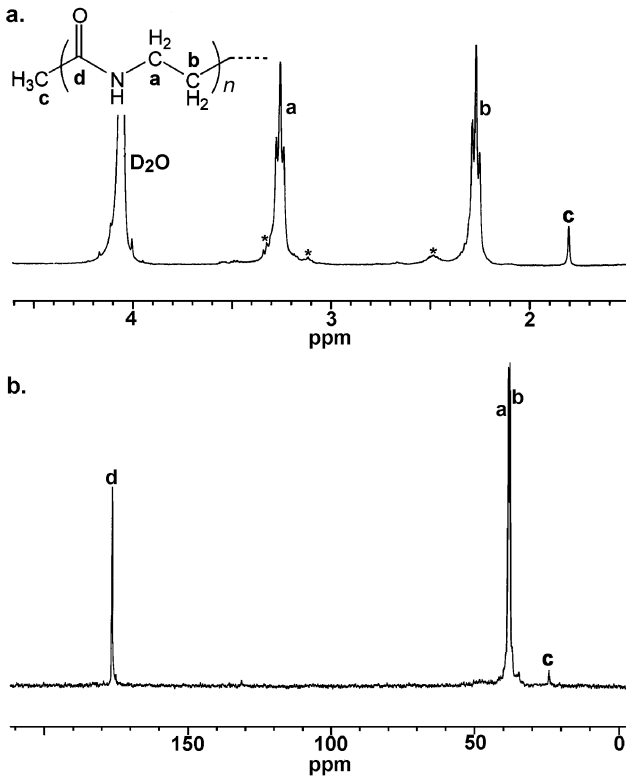

Fig. 1 a. ^{1}H NMR (360 MHz, D_2O, 95 °C) of poly-β-alanine produced from copolymerization of CO and aziridine (entry 1, Table 1). Integral ratio of **a**–**b**–**c** = 100:100:6. b. $^{13}C\{^1H\}$ NMR (90 MHz, D_2O, 95 °C, THF in D_2O as external standard) of the same sample.

1. Such assignment is consolidated by the observation that this peak disappeared when the methyl-deuterated **1** $CD_3COCo(CO)_3PPh_3$ was used for the copolymerization. In the ^{13}C spectrum (Fig. 1b), the amide carbonyl peak (**d**) is clearly shown at δ 176.2 ppm. The methylene ^{13}C resonances appear at δ 38.3 and 37.7 ppm. The peak at 24.2 ppm (**c**) in the ^{13}C spectrum is assigned to the methyl of the acetyl end group. All ^{13}C assignments are supported by ^1H–^{13}C HMQC and HMBC experiments.†

Varying CO pressure exerted little effect on the selectivity of the polymerization (entries 2 and 3, Table 1). However, the polymer yield decreased when the reaction was run under 250 psi of CO. The lower yield was likely caused by catalyst decomposition, not decrease of the reaction rate, as quadrupling the reaction time did not result in any alteration of yield.

When the initial aziridine concentration was increased (entries 4 and 5, Table 1), the selectivity of the reaction reduced, and additional peaks appeared in the ^1H spectrum.† The chemical shifts of these resonances and that they move downfield when the aqueous solution is acidified suggest that they belong to amines, which apparently arise from repetitive aziridine insertion. Extraction of the products using a wide range of solvents including methanol, ethanol, THF, and chloroform did not significantly change the relative amount of amine units, suggesting that the amine and β-alanine units are in the same chains. The problem of repetative aziridine insertion can be partially solved by slow addition of aziridine. When aziridine was added in portions under 1 atm of CO after the previously added aziridine was estimated to have been consumed, the selectivity was considerably improved without sacrifice of the yield (entries 6 and 7, Table 1).

The molecular weights and molecular weight distributions of the products are measured by gel-permeation chromatography (GPC) coupled with a light scattering-refractive index-viscometry triple detector (Table 1). The weight average molecular weights are determined with reproducibilities within 6%. The molecular weight distributions are complex and spread over a wide range, hampering accurate determination of the number average molecular weights. Thus, the polydispersities (PDI) listed in Table 1 should be taken as approximate values.

In regard to the mechanism of the polymerization, the complexity of molecular weight distribution profiles indicates that it is apparently not a simple one. However, the presence of the acetyl end group argues that complex **1** is indeed the catalyst.

The possibility that azetidin-2-one was the intermediate of the polymerization was ruled out by two parallel experiments. In the first experiment, equal molar amounts of azetidin-2-one and aziridine were subjected to the polymerization conditions. In the other experiment, only aziridine was added. The same amounts of polymer were produced in the two experiments. The requirement for high catalyst loading in order to achieve good selectivity for alternating enchainment indicates that the barriers for alternating enchainment and repetitive enchainment are not significantly different for the catalyst employed here. We are currently engaged in searching for catalyst systems that provide improved selectivity toward alternating enchainment and in elucidating the chain propagation/termination mechanisms.

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