Articles

Cobalt-Catalyzed Carbonylative Polymerization of Azetidines

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ABSTRACT: We provide a full account on our study of the cobalt-catalyzed carbonylative polymerization of *N*-alkylazetidines involving three representative monomers. The individual *N*-alkylazetidine monomers display different characteristics in the polymerization, allowing the incorporation of amine and ester units into the amide-based polymers. We will first present the synthesis and characterization of poly(amide-*co*-amine) with a gradient amine distribution. Then, we will describe how to control the ester distribution in poly(amide-co-ester)s. Poly(amide-co-ester)s containing multiple segments, within which the ester units distribute in a gradient fashion, will be compared with multiblock poly(amide-co-ester)s. Finally, we report our discovery of a novel chain transfer pathway via *N*-benzyl abstraction.

Introduction

The role of transition metal catalysis in polymer synthesis has substantially expanded in the last one to two decades. The control over the molecular weight and molecular architecture has reached a level unimaginable not long ago and imparted completely new materials properties and applications to the classical polyolefins.[1,2] Diverse types of organometallic reactions have now been exploited for the synthesis of a wide variety of functional polymers with applications ranging from green plastics, biomedicine, and solar energy conversion.[3−8] A common feature of the important advances is that single catalytically active species operating under well-defined mechanisms or mechanistic hypotheses are responsible for the polymerization.

We and a few other groups have endeavored to develop the carbonylative polymerization of heterocycles and heteroalkenes for the synthesis of aliphatic polyamides and polyesters.[9−17] Among the many interesting developments under the broad topic, we have reported that the cobalt-catalyzed carbonylative polymerizations of *N*-alkylaziridines and *N*-alkylazetidines display the characters of living polymerizations.[11bdfg] To the best of our knowledge, no other known chain polymerization can produce poly(tertiary amide)s, let alone in a living fashion. Particularly, the chain propagation mechanism of the well-known anionic polymerization of lactams involves reaction of the deprotonated lactam monomer with the *N*-acyllactam chain end and, therefore, is not suitable for *N*-alkyllactam monomers.[18] Although linear polymers are often obtained from the polymerization of β-lactams, this mechanistic characteristic also causes branching in the polymerization of lactams with larger ring sizes because the acidities of the N−H groups in the polymers and the monomers are similar. The living ring-opening polymerization of β-lactams catalyzed by transition metals also appears to involve either the deprotonation of the N−H moiety of the lactam monomers or a proton transfer step.[19]

In our preliminary communication on the carbonylative copolymerization of *N*-alkylazetidines and tetrahydrofuran, we highlighted the effect of LiI as the cocatalyst for the synthesis and characterization of multiblock poly(amide-co-ester)s and for elimination of the γ-lacatm byproduct.[11g] Here we give a full report on the cobalt-catalyzed polymerization involving three representative azetidine monomers. Our discussions are subsequently organized based on the differentiating characteristics of the individual monomers to illustrate the control of molecular weights, molecular weight distribution, and functional group incorporation and distribution in the polymerization. When appropriate, comparisons will be made among the azetidine monomers and the aziridine monomers.

Experimental Section

Materials. All operations were conducted with Schlenk line and dry box techniques under a nitrogen atmosphere, except where carbon monoxide was used as specified. Anhydrous THF and dioxane were purchased from Aldrich and used without further purification. *N*-*n*-Butylazetidine (**1**) and *N*-benzylazetidine (**3**) were synthesized as described in the literature.[20,21] *N*-*iso*-Butylazetidine (**2**) was synthesized using a method similar to that of **3**. Monomers **1** and **2** were dried and stored over a Na/K alloy, and **3** was dried and stored over dibutylmagnesium. All monomers were freshly vacuum-transferred before polymerization. The catalyst, $CH_3COCo(CO)_3P(o\text{-}Tol)_3$ (**4**), was prepared according to the established procedure.[6]

Measurements. NMR experiments were performed on either Varian Mercury 300 MHz or Varian Inova 400 MHz instruments. Chemical shifts were determined using solvent peaks as the references. Gel permeation chromatography of the polymer products were performed using a Waters 150C system or a Waters Breeze system equipped with a refractive index detector. The relative molecular weight was determined using monodisperse polystyrene standards as the references. $CHCl_3$ was used as the eluent. The flow rate was 1 mL/min, and the column temperature was set at 35 °C.

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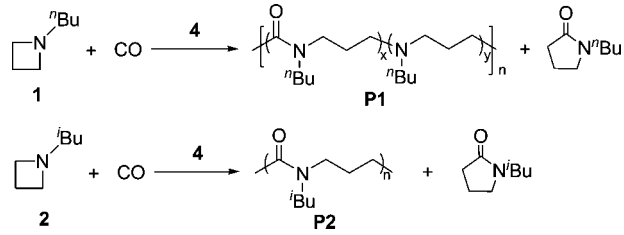
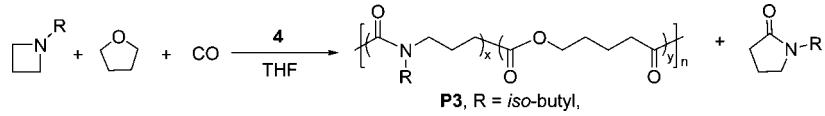
Table 1. Carbonylative Polymerization of 1 and 2 in Dioxane[a]



entry	monomer	solvent amount (mL)	monomer **4** (molar ratio)	polymer yield (%)	amine content (mol %)	lactam yield (%)	$M_n \times 10^{-3}$ /PDI [d]
1	**1**	20	48:1	75	30[b]	7[b]	0.98/1.55
2	**1**	20	32:1	92	17[b]	8[b]	4.10/1.45
3	**1**	20	16:1	93	8.6[b]	7[b]	3.18/1.31
4	**1**	30	32:1	92	6.5[b]	8[b]	4.44/1.28
5	**1**	50	48:1	92	7.6[b]	8[b]	6.39/1.31
6	**1**	70	64:1	90	8.9[b]	10[b]	8.59/1.29
7	**2**	10	16:1	86	<1%	14[c]	2.56/1.20
8	**2**	20	32:1	85	<1%	15[c]	4.64/1.19
9	**2**	30	48:1	87	<1%	13[c]	7.31/1.23
11	**2**	45	80:1	80	<1%	18[c]	12.7/1.20

[a] Reaction conditions: 0.12 mmol of catalyst **4** at 70 °C for 48 h. [b] Estimated by ^{1}H NMR in toluene-d_8 at 100 °C. [c] Estimated by ^{1}H NMR in dioxane-d_8 at 90 °C. [d] Determined by GPC calibrated with monodisperse polystyrene samples.

Table 2. Carbonylative Copolymerization of Azetidines with THF Catalyzed by 4[a]



entry	monomer	THF (mL)	monomer/**4** (molar ratio)	polymer yield	ester content [g] (%)	γ-LA yield (%) [g]	$M_n \times 10^{-3}$ (PDI) [h]
1[b,c]	**1**	20	16/1	92[d]	4.7	8	3.78(1.55)
2[b,c]	**2**	20	16/1	82	9.4	18	2.68(1.20)
3[b,c]	**3**	20	16/1	76	15	24	2.29(1.68)
4[e]	**2**	60	(9 × 1):1	75	14	25	1.50(1.28)
5[e]	**2**	65	(9 × 2):1	72	12	28	2.77(1.30)
6[e]	**2**	70	(9 × 3):1	70	11	30	3.90(1.32)
7[e]	**2**	75	(9 × 4):1	69	9.9	31	4.96(1.35)
8[f]	**2**	60	(18 × 1):1	85	8.3	85	3.39(1.22)
9[f]	**2**	65	(18 × 2):1	83	7.7	83	6.69(1.26)
10[f]	**2**	70	(18 × 3):1	82	6.6	82	9.89(1.29)
11[f]	**2**	75	(18 × 4):1	81	5.9	81	12.7(1.30)

[a] Catalyst **4** (0.12 mmol) was used in all runs. [b] Oil bath temperature = 70 °C, reaction time = 48 h. [c] Data from ref 11g. [d] Approximately 10 mol % of amine units present in the polymer chain. [e] Autoclave interior temp = 70 °C, 9 equiv of **2** added in every 5 h. [f] Autoclave interior temp = 62 °C, 18 equiv of **2** added in every 12 h. [g] Determined by ^{1}H NMR. [h] Determined by GPC calibrated with monodisperse polystyrene samples.

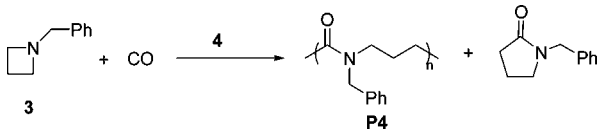
MALDI-TOF measurements were performed on a Bruker Reflex III mass spectrometer. Dithranol was used as the matrix compound. Sodium trifluoroacetate was used as the cationization agent. The sample, matrix and cationization agent were mixed in a 2:10:1 ratio and dissolved in THF (10 mg/mL). Approximately 0.5 μL of this mixture was deposited onto the sample holder and allowed to dry before insertion into the vacuum system. All quoted mass-to-charge (*m*/*z*) ratios are monoisotopic, containing the most abundant isotopes of the elements present.

Synthesis of *N*-*iso*-Butylazetidine (2). The procedure described in the literature for **1** was used.[20] Yield: 65%. ^{1}H NMR ($CDCl_3$): δ 0.86 (d, J = 6.4 Hz, $(CH_3)_2CH$), 1.57 (m, J = 6.38, $(CH_3)_2CH$), 2.04 (m, J = 7.02 Hz, NCH_2CH_2), 2.18 (d, J = 6.89 Hz, $NCH_2CH(CH_3)_2$), 3.15 (t, J = 6.98 Hz, NCH_2CH_2). ^{13}C NMR ($CDCl_3$): δ 18.03, 21.26, 27.19, 56.03, 68.93. IR (KBr disk): 2965 (S), 2924 (m), 2873 (m), 2818 (s), 2710 (w), 1464 (m), 1387 (w), 1366 (w), 1296 (w), 1271 (w), 1235 (w), 1201 (m), 1132 (w), 1028 (m), 986 9w), 918 (w), 769 (w), 679 (w). Anal. Calcd. for $C_7H_{15}N$ (113.12): C, 74.27; H, 13.36; N, 12.37. Found: C, 74.18; H, 13.49; N, 12.08.

Polymerization Procedure for Monomer Addition All at Once. A solution of catalyst **4** prepared under 1 atm of CO and a solution of freshly dried *N*-alkylazetidine were injected under a gentle CO flow into a 300 mL Parr high-pressure reactor at room temperature. Additional solvent was added to make the total volume reach the amount specified in Tables 1−3 (see Results and Discussion). The reactor was closed, and the pressure of CO was increased to 1000 psi. The reactor was then placed in an oil bath at 70 °C and stirred with a magnetic stir for a period of time specified in Tables 1−3. After the reactor was cooled to room temperature, CO was released into a ventilated hood. The reaction mixture was transferred into a round-bottom flask, and the solvent was removed under vacuum. The crude product was weighed to determine the overall monomer conversion, and ^{1}H NMR was measured to determine the polymer-to-lactam ratio in the product based on the integrations of the characteristic ^{1}H NMR peaks. The mixture was then washed with hexane to remove the lactam byproduct and isolate the solid polymer product.

Polymerization Procedure Involving Multiple Monomer Additions. The polymerizations were run in a 300-mL autoclave (Autoclave Engineers) with a stainless steel tube at the top as the reservoir for the subsequent additions of **2**. The tube was connected with the reactor via a stainless steel ball-valve fitting. First, a solution of **4** prepared under 1 atm of CO and a solution of freshly dried **2** were injected under a gentle CO flow into the autoclave at room temperature. Additional solvent was added to make the total

Table 3. Carbonylative Polymerization of 3 in Dioxane Catalyzed by 4[a]



entry	**4**:**3** ratio	product ratio **P4**/ lactam[b]	M_n/PDI[c]
1	32:1	85/15	2370/1.50
2	48:1	80/20	2490/1.61
3	64:1	82/18	2430/1.71

[a] Reaction condition: 0.12 mmol of catalyst **4** at 70 °C for 48 h. [b] Determined by ^{1}H NMR in tetrachloroethane-d_2 at 100 °C. [c] Determined by GPC calibrated with monodisperse polystyrene samples.

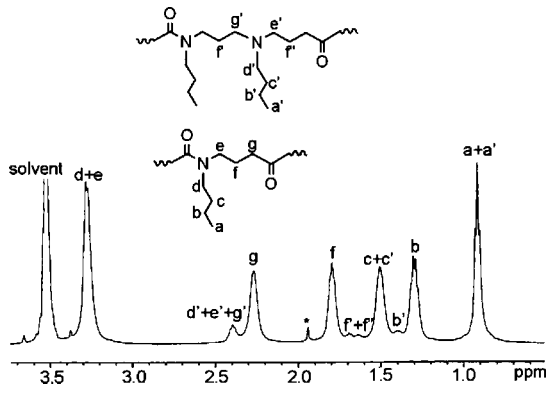


Figure 1. ^{1}H NMR spectrum of **P1**. The spectrum was recorded at 90 °C in dioxane-d_4. The peak labeled with an asterisk is assigned to the acetyl end group, which originates from the catalyst **4**.

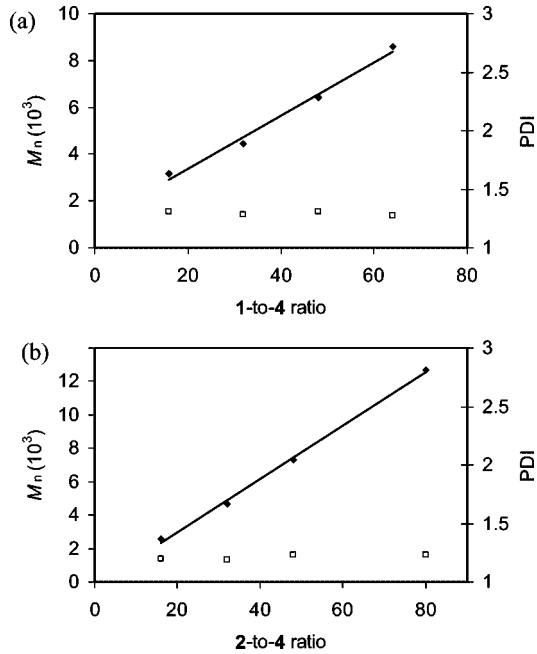


Figure 2. Linear increase of M_n with increase of monomer-to-catalyst ratio. (a) Poly(amide-*co*-amine)s (**P1**) from entries 3−6, Table 1. (b) Polyamides (**P2**) from entries 7−10, Table 1. Also included in the plot are the PDI values indicated by the open squares.

volume reach the amount specified in Table 2. After being pressurized with 1000 psi of CO, the reactor was closed, stirred with a mechanical stirred, and heated with a heating jacket to the desired temperature. The internal temperature of the autoclave was measured through a thermocouple. The reservoir, isolated from the autoclave by the ball valve, was at this time charged with the second

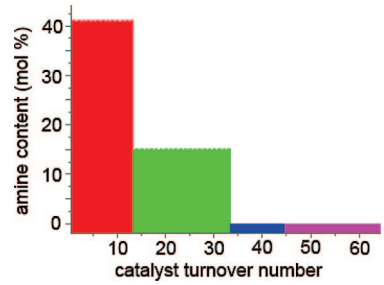
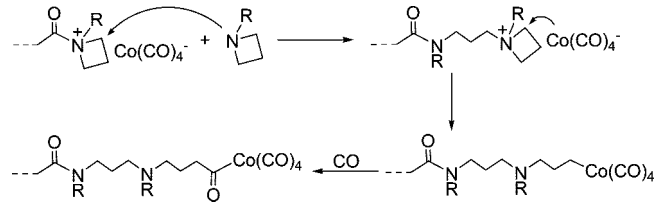


Figure 3. Distribution of amine units in **P1** prepared according to the conditions specified in entry 6, Table 1.

Scheme 1. Proposed Mechanism for Formation of Amine Units



aliquot of **2** and slightly over- pressurized. By turning the ball valve open, **2** was added into the reaction at the time specified in Table 2. The addition was repeated as it was necessary. After the reaction was done, the reactor was cooled to room temperature, and CO pressure was released into a ventilated hood. The reaction mixture was transferred into a round-bottom flask, and the solvent was removed under vacuum. The crude product was weighed to determine the overall yield, and ^{1}H NMR was measured to determine the product ratio based on the integrations of the characteristic peaks of the polymer product and the γ-lactam byproduct. The mixture was then washed with diethyl ether to allow the isolation of the solid polymer product.

Methanolysis of Poly(ester-*co*-amide). The poly(amide-*co*-ester) product (0.5 g) was dissolved in methanol (30 mL). Hydrogen chloride in anhydrous ether (2 mL, 2.0 M) was added. The mixture was stirred at room temperature for 24 h. The solvent was removed under vacuum. The residue was washed by a mixture of ether and hexane (v/v 1/1). The insoluble fraction was dried under high vacuum and characterized by GPC and NMR. The residual oil in the soluble fraction after removal of the solvent was characterized by NMR to be γ-valerolactone.

Results and Discussion

Poly(amide-*co*-amine) versus Polyamide and Amine Distribution. The carbonylative polymerization of **1** catalyzed by **4** in dioxane produces poly(amide-*co*-amine) **P1** as the major product accompanied by a few percent of *N*-*n*-butyl-γ-lactam byproduct (Table 1). The presence of the amine repeat units in **P1** is evident from the ^{1}H NMR (Figure 1), and the amine

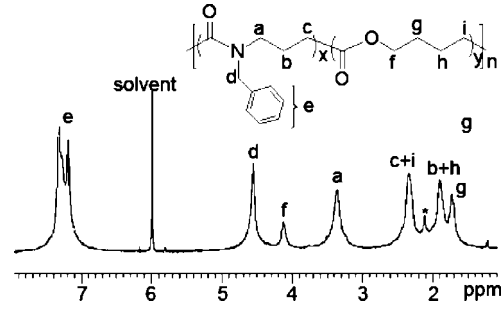
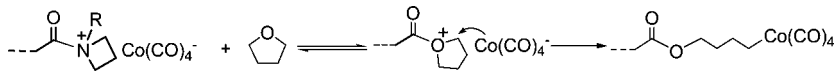


Figure 4. ^{1}H NMR spectrum of poly(amide-*co*-ester) produced by carbonylative copolymerization of **3** and THF. The peak labeled with an asterisk is assigned to the acetyl end group. The spectrum was recorded at 120 °C in tetrachloroethane-d_2.

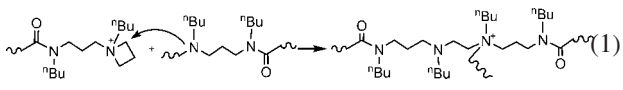
Scheme 2. Proposed Mechanism of Azetidine-Assisted THF Enchainment



content can be estimated using the integrations of two ^{1}H resonances at δ 3.28 ppm and 0.91 ppm, well-separated from the other peaks, and corresponding to the methylene groups d+e and the methyl groups a+a′, respectively. The only variable that causes obvious change of the amine contents in the products is the concentration of **1**. Higher initial concentration of **1** resulted in higher amine content (entries 1−3). To reach quantitative conversion of **1**, the amine content in the product must be kept below a certain level (entries 2−6); otherwise, chain termination occurs (entry 1). Under the presently adopted conditions and when <10 mol% of amine units are present in the final product (entries 3−6), the number-average molecular weight (M_n) of **P1** increases with the increase of **1**:**4** ratio (Figure 2a). The PDI values are also reasonably low. In comparison to **1**, the carbonylative polymerization of **2** under similar conditions produces polyamide **P2** without any ^{1}H NMR-detectable amount of amine unit in the polymer chain (entries 7−11, Table 1). The linear increase of M_n with the increase of **2**:**4** ratio is also observed (Figure 2b). The polydispersities of polyamides **P2** appear slightly narrower than those of poly(amide-*co*-amine)s **P1**. It should be noted that if the carbonylative polymerization of **2** were run in more concentrated solutions, a small amount of amine units can still be observed in the product. We did not further explore in that direction because the amount of amine units incorporated into the polymer is too small.

The controllable M_n and relatively narrow polydispersity of **P1** along with the observation that a higher azetidine concentration results in a higher amine content suggest that the amine units should distribute in a dampening gradient in the polymer chain. To further verify the gradient distribution, we stopped the polymerization at various stages of monomer consumption and analyzed the amine content at each stage in the polymer. The result of the analysis demonstrates that the amine content is rather high at the head of the **P1** chain, decreases as the chain propagates, and falls to approximately zero in the second half of the polymerization (Figure 3).

The formation of the amine units was encountered in the carbonylative polymerization of unsubstituted aziridines but not *N*-alkylaziridines.[11] Similar to the aziridine case, we propose that the repetitive enchainment is due to the nucleophilic addition of the azetidine monomer to the acylazetidinium intermediate (Scheme 1). In moderately polar solvents such as dioxane, the cobaltate anion and the cationic chain end should be an ion pair. Nucleophilic addition of the cobaltate to the azetidinium chain end would resume the carbonylative polymerization. The aforementioned change of amine content as a function of monomer concentration and monomer structure (i.e., **1** vs **2**) can all be rationalized on the basis of this proposed mechanism. The termination of the polymerization, which occurs when a high amine concentration is reached during the polymerization, can be explained by the nucleophilic attack of the amine units on the azetidinium chain end (eq 1). The resulting quaternary



(1)

ammonium groups are points of chain branching or intramolecular cyclization. Both structures are expected to cause the apparent molecular weights to be abnormally low if determined by GPC calibrated with linear standards in agreement with our experimental observation (entry 1, Table 1). Similar chain termination occurs in the cationic polymerization of *N*-alkylazetidines.[22]

To make the discussion complete, we note that the formation of γ-lactam is a common side reaction for the cobalt-catalyzed carbonylative polymerization of *N*-alkylazetidines. The backbiting mechanism proposed in our preliminary communication is consistent with all observations so far.[23] The side reaction can be suppressed by the addition of LiI into the polymerization.[11g] If the polymerization is run in dioxane, however, the addition of LiI causes a broadening of the molecular weight distribution, although the formation of γ-lactam is indeed eliminated. The low solubility of LiI in dioxane, which may or may not explain the broadening of the molecular weight distribution, also adds a practical hurdle for using it for reactions carried out in dioxane. As a result, we did not further explore the use of LiI for the polymerizations carried out in dioxane.

Synthesis of and Control of Ester Distribution in Poly(amide-*co*-ester). When the carbonylative polymerization catalyzed by **4** is carried out in THF instead of dioxane, THF is carbonylated and incorporated into the polymer chain as δ-valeroate ester units. This was observed for the polymerization of all three monomers **1**−**3**, but the degree of ester incorporation varies in each case (entries 1−3, Table 2). Under identical polymerization conditions, the ester contents in the product follow the order of **3** > **2** > **1**, which can be straightforwardly estimated by ^{1}H NMR integrations of the resonances at δ ~4.07 ppm and ~3.36 ppm characteristic for the ester and amide linkages (Figure 4). In the absence of an azetidine monomer, THF carbonylative polymerization does not happen. This suggests that the azetidines monomers promote the THF enchainment, and the sterically bulky azetidines are more effective in this regard. The mechanism of the azetidine-promoted THF enchainment likely involves the acylazetidinium intermediate in equilibrium with the acyloxonium (Scheme 2). The bulky azetidines such as **2** and **3** possibly shift the equilibrium in favor of acyloxonium.

Our investigation on the synthesis of poly(amide-co-ester) utilizing the novel carbonylative enchainment of THF has focused on **2** as the azetidine monomer because of the living characters of the polymerization and the good ability of **2** to promote the THF carbonylative enchainment. Monomer **3** was not explored because of the presence of a chain transfer process, which will be discussed later. As demonstrated in our preliminary communication,[11g] the ester units distribute in a gradient fashion when the polymerization was carried out in the absence of LiI, but form a short block at the end of the polymerization in the presence of LiI. By utilizing the latter scenario, we reported the synthesis of poly(amide-*co*-ester) containing multiple blocks of amide units and ester units (**P3-MB**) by multiple addition of aliquots of **2** into the polymerization mixture at certain time intervals.

Here, we have carried out the multiple addition experiments in the absence of LiI to synthesize poly(amide-co-ester)s containing multiple segments, within which the ester units distribute in a gradient fashion (**P3-MSG**). In other words, we expect that when all additions are done, the ester abundance in the poly(amide-*co*-ester) product goes through several minimums and maximums from the head to the tail of the polymer chain. Two series of such experiments were carried out. The amount of each addition is varied in the two series (entries 4−7 and 8−11, Table 2) with the aim to control the length of each individual segment. In both cases, the addition of additional aliquots of **2** resulted in linear increase of the M_n values of the

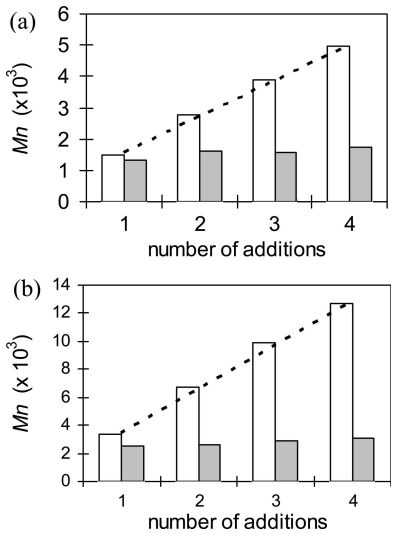


Figure 5. Linear increase of M_n of **P3-MSG** with the increase of number of additions of **2**. The M_n values before (open bar) and after methanolysis (shaded bar) are also compared. (a) **P3-MSG** made by the addition of 9 equiv of **2** for each addition, from entries 4−7, Table 2. The PDI values of the methanolysis products are 1.41, 1.54, 1.65, and 1.70. (b) **P3-MSG** made by the addition of 18 equiv of **2** for each addition, from entries 8−11, Table 2. The PDI values of the methanolysis products are 1.48, 1.61, 1.75, and 1.78.

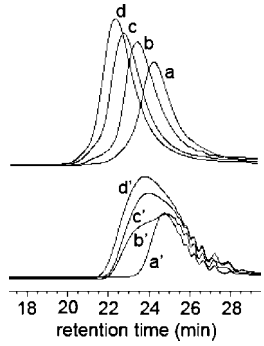


Figure 6. GPC traces of **P3-MSG** (top, a−d) and their respective methanolysis products (bottom, a′−d′). The **P3-MSG** samples are synthesized as described in entries 4−7, Table 2.

P3-MSGs (Figure 5). The ester distribution of the resulting **P3-MGS**s was investigated by analyzing the products of their H^+-catalyzed methanolysis at room temperature, where only ester linkages were cleaved. The methanolysis product was extracted with a 1:1 mixture of diethyl ether and hexane. Only a diminutive amount of δ-valerolactone was found in the diethyl ether/hexane mixture. This is in contrast to the observation of an appreciable amount of δ-valerolactone in the methanolysis product of **P3-MB**, indicating the absence of ester blocks. The remaining solid is a polyamide without any observable ester content except the methyl ester end group. Discrete peaks can be observed in the GPC trace near the end of elution (Figure 6), corresponding to the short oligoamides sandwiched between two ester units in the original **P3-MSG** before methanolysis. The molecular weight of the polyamide is significantly reduced, and the molecular weight distribution is substantially broadened compared to the original **P3-MSG**s. In contrast, the molecular weight distribution of the methanolyzed **P3-MB** remains relatively narrow in the range of PDI = 1.11−1.28.[11g] Further, the M_n values of the methanolyzed **P3-MSG** can be controlled by the amount of **2** added each time. When 9 and 18 equiv of **2** were added, the M_n values of the methanolyzed polymer reside in the range of 1320−1750 and 2550−3110 g/mol, respectively. All the above observations are consistent with the anticipated

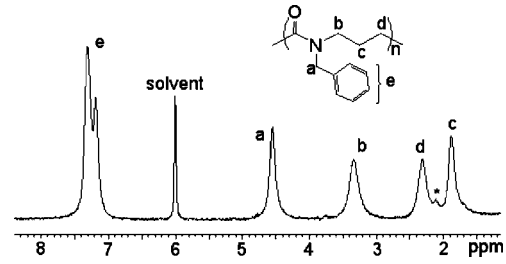
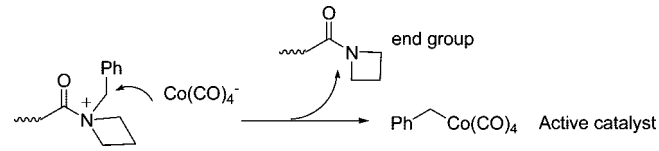


Figure 7. ^{1}H NMR spectrum of **P4**. The peak labeled with an asterisk is assigned to the acetyl end group. The spectrum was recorded at 120 °C in tetrachloroethane-d_2.

Scheme 3. Proposed Chain Transfer by Benzyl Abstraction



segmental, gradient distributions of the ester units along the polymer chain. Therefore, two types of poly(amide-*co*-ester)s with controllable ester distribution and degradation properties can be synthesized via the carbonylative copolymerization of **2** and THF either in the presence of LiI or in the absence of LiI.

Chain Transfer in Carbonylative Polymerization of 3. The carbonylative polymerization of *N*-benzylazetidine **3** catalyzed by **4** carried out under the typical polymerization conditions (i.e., 60−70 °C under 1000 psi of CO pressure) did not show the living characters that we customarily observe in the carbonylative polymerization of azetidines **1** and **2** and *N*-alkylaziridines. The M_n values of the products remained approximately same at 2370−2500 g/mol despite a 2-fold change of catalyst-to-monomer molar ratio (Table 3). The PDI values are substantially higher than what is usually obtained when **1** and **2** were used as the monomers. The chemical structure of the expected polyamide **P4** was confirmed by NMR (Figure 7). *N*-Benzyl-γ-lactame was obtained as a byproduct as usual. The total conversions to the polymer and γ-LA product were quantitative, and the product ratio did not vary with the change of the catalyst loading. The same relatively large PDI and lower than expected M_n value were observed for the polymerization carried out in THF (entry 3, Table 2). The data appear to suggest the existence of a viable chain transfer pathway during the polymerization.

Upon inspection of the structure of **3** and the possible reaction mechanism, it appears likely that cobaltate may nucleophilically attack the benzyl group in the acylazetidium intermediate of the catalytic process (Scheme 3), resulting in an *N*-acylazetidine end group and tetracarbonyl benzylcobalt. The latter can initiate the growth of a new chain.[11b] The NMR spectra of **P4** prove rather uninformative for the characterization of the end groups. The characteristic peaks corresponding to the *N*-acylazetidine[24] and phenylacety[11b] end groups can be expected to overlap with the peaks corresponding to the repeat units. We therefore turned to matrix-assisted laser desorption mass spectrometry (MALDI MS) for evidence of the anticipated end groups. Two major series **A** and **B** were observed in the MALDI mass spectrum (Figure 8). Their mass/charge ratios can be expressed by the following formulas: $m/z = 23 + 99 + 175n$ and $23 + 175 + 175n$, respectively, where n is the degree of polymerization. The two series can be assigned to the sodium complexes of structures **A** and **B**. The minor series **C** with $m/z = 23 + 60 + 175n$ can be assigned to the sodium complexes of structure **C**, in which the carboxylic acid end group arose from the hydrolysis or oxidation of the acyl-Co bond during workup.

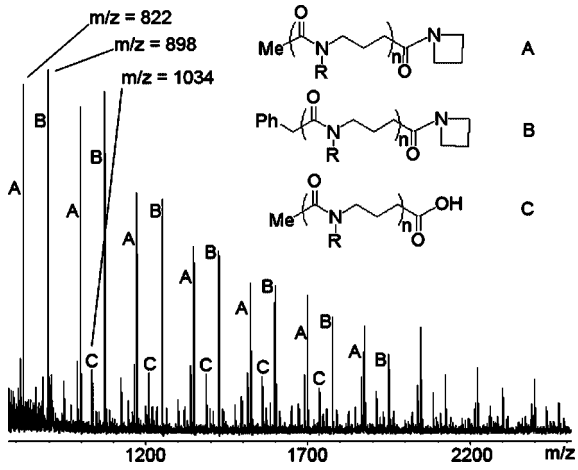


Figure 8. MALDI mass spectrum of **P4**.

It should be noted that although the abstraction of the *N*-benzyl group from a cyclic tertiary amine is common for five- and six-membered rings, ring-opening reactions generally happen for three- and four-membered rings. For example, no chain transfer reaction was reported in the cationic polymerization of *N*-benzylazetidine.[25] Neither have we observed such benzyl abstraction in our study of the carbonylative polymerization of aziridines. Further, it was recently reported that the reaction between an *N*-benzylazetidine and its derivatives with chloroformate afforded the ring-opening addition product in quantitative yield.[26] The abstraction of the benzyl group by the cobaltate observed here is therefore rather unique.

Summary

We have described the cobalt-catalyzed carbonylative polymerization of three representative *N*-alkylazetidines and their carbonylative copolymerization with THF. By choosing the appropriate monomer and polymerization conditions, polyamides, poly(amide-*co*-amine)s, and poly(amide-*co*-ester) can be obtained. The distributions of the amine and ester units are not even in the polymer chain. Poly(amide-*co*-ester) containing multiple segments with block or gradient ester distributions can be synthesized by multiple additions of *N*-isobutylazetidine into the reaction mixture in the presence of LiI or in the absence of LiI. The interesting distributions may prove useful for the development of potential applications (e.g., gene delivery and controlled release) in the future. *N*-Benyzlazetidine is different from the other two monomers in that a chain transfer pathway is presented via the nucleophilic abstraction of the *N*-benzyl group. The remaining acyl-azetidine at the chain end can be utilized for further chemical modifications or polymerization.

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