

ortho-Aromatic Polyamides by Ring-opening Polymerization of *N*-carboxyanhydrides

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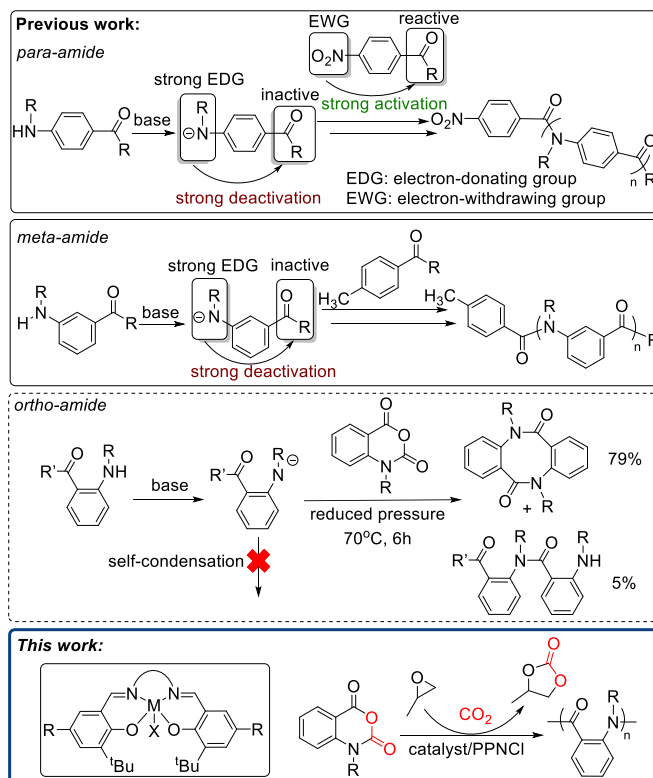
ABSTRACT

We report the ring-opening polymerization of *N*-alkylated aromatic six-membered ring *N*-carboxyanhydrides (6-NCA-R) catalyzed by transition metal Schiff base complexes in the presence of a base. This system allows the facile synthesis of ortho-aromatic polyamides with high molecular weights via chain-growth polymerization. A mechanism is proposed based on the results of polymerizations performed under various reaction conditions. Copolymerization of 6-NCA-R with heterocyclic monomers is performed to prepare heteroatom (N, O, and S) containing copolymers. The thermal properties of the polymers with different *N*-alkyl side chains were investigated by thermogravimetric analysis, differential scanning calorimetry, and powder X-ray diffraction.

INTRODUCTION

Aromatic polyamides are extra tough and flame-resistant materials that have a wide range of applications.¹⁻³ The introduction of alkyl groups to the nitrogen atoms in the backbone significantly expands the range of chemical variations that can be achieved in aromatic poly- and oligoamides, making them an important group of abiotic foldamers.⁴⁻⁶ While para and meta substrates have been investigated, examples of ortho-aromatic polyamides remain rare. Hamilton and coworkers reported that the presence of intramolecular hydrogen bonds in ortho-benzamide oligomers leads to a planar arrangement of substituents and promotes the formation of linear strand structures.⁷ Alkylation of the nitrogen atom would disrupt these hydrogen bonds, allowing an increased chemical diversity and the possibility of tuning cis/trans isomerization based on steric and electronic interactions.

The synthesis of aromatic polyamides (Scheme 1), however, is generally limited to polycondensation reactions that lead to polymers with low molecular weight and broad dispersity.⁸ In 2000, Yokozawa and coworkers reported a strategy that used a base to deactivate monomers and a reactive initiator to optimize the condensation reaction.⁹ Similarly, in 2021, Kiblinger and coworkers reported another activation strategy that showed good control over the polycondensation reaction.¹⁴ However, these methods were only effective for para and meta-aromatic polyamides. Furthermore, while Yokozawa and coworkers showed the formation of ortho-amides from the reaction of deprotonated *N*-alkylanthranilic acid ester and *N*-alkylisatoic anhydride in the presence of a base, the polymerization reaction to form polyamides did not occur,¹⁵ and the synthesis of ortho-aromatic polyamides remains challenging.



Scheme 1. Synthesis of aromatic polyamides. Chain-growth polymerization for the synthesis of para¹¹ and meta¹² aromatic polyamides was reported by Yokozawa and coworkers, but the same strategy does not apply to ortho-aromatic polyamides.¹⁵

Although the ring-opening polymerization of *N*-carboxyanhydrides (NCAs) has been investigated in polyamide synthesis as an alternative route to polycondensation reactions,¹⁶⁻²¹ aromatic β -NCAs, such as isatoic anhydride and its derivatives, have not been employed before. Thus, the synthesis of polyamides via the ring-opening polymerization of aromatic β -NCAs is an unexplored synthetic route due to the absence of a suitable catalytic system.

Given our previous success with using metal complexes for the ring-opening polymerization of cyclic esters and ethers,²²⁻³⁷ we decided to apply a similar system to NCA polymerization. Herein, we report the first example of successful ring-opening polymerization of aromatic β -NCAs to prepare ortho-aromatic polyamides using Schiff base metal complexes, [PPN]Cl ([PPN]⁺ = bis(triphenylphosphoranylidene)iminium), and propylene oxide. High molecular weight ortho-aromatic polyamides were obtained from β -NCA monomers with different *N*-alkyl side chains, allowing the further characterization of a new class of polyamides. We also propose a mechanism for the ring-opening polymerization of aromatic β -NCAs. Similar systems were previously exploited in the ring-opening copolymerization of epoxides and anhydrides,^{38, 39} ring-opening copolymerization of epoxides and dihydrocoumarin,⁴⁰ coupling reactions between CO₂ and epoxides,^{41, 42} as well as the ring-opening polymerization of *S*-carboxyanhydrides.⁴³ The homopolymerization of α -NCAs by Schiff base metal complexes for polypeptide synthesis was also reported.⁴⁴

RESULTS AND DISCUSSION

The polymerization of 5-membered-ring NCAs can be initiated by primary amines, whereas the aromatic 6-membered-ring NCAs exhibit significantly lower reactivity. Our attempts to use an aromatic primary amine, *p*-phenylenediamine,^{45, 46} as an initiator for 6-NCA-R polymerization led

to no reaction (Table S4, entry 1). Consequently, the polymerization of aromatic 6-membered-ring NCAs necessitates the development of a suitable catalytic system.

We started by adapting reaction conditions from reported five-membered-ring NCA polymerizations⁴⁴ using a ferrocene-based aluminum complex.²⁴ An equivalent of (salfen)AlOⁱPr (**Al-1**, salfen = *N,N'*-bis(2,4-di-*tert*-butylphenoxy)-1,1'-ferrocenediimine), 2 equivalents of [PPN]Cl, 50 equivalents of 6-NCA-Bn (Bn = benzyl), and propylene oxide (PO) as the solvent were used (Table 1, entry 1). The reaction mixture was heated at 80 °C for 2 hours, resulting in the formation of an off-white precipitate. Notably, the resulting solid was only slightly soluble in trifluoroacetic acid (TFA), while being insoluble in solvents such as tetrahydrofuran (THF), methylene chloride, dimethylformamide, or dimethyl sulfoxide. We speculated that the product obtained was a polymer, but our characterization was limited due to its low solubility. To address this issue, we attempted to increase the polymer solubility by using monomers with longer *N*-alkyl side chains. Therefore, we synthesized 6-NCA-C₈H₁₇ (NCA-8), an analogue with an *N*-octyl group, and used it as a monomer (Table 1, entry 2). Using the same reaction conditions as described above, we obtained poly(NCA-8) with a significantly improved solubility, allowing us to acquire its ¹H and ¹³C NMR spectra in CDCl₃ (Figure 1A). The integration of peaks in the ¹H NMR spectrum is consistent with the structure of poly(NCA-8).

The polymer peaks in the ¹H NMR spectrum appeared broader compared to those of the corresponding NCA monomer (Figure 1A). Particularly, the broad and multiple -NCH₂- peaks of the polymer, which are labeled “e” in Figure 1A, were observed in the range of 3.15 to 5.10 ppm due to the presence of both *cis* and *trans* conformations of the amide bond in the polymer backbone.^{47,48} A variable temperature ¹H NMR study of the polymer showed the peak interchange within that range as the temperature increased from 30 to 110 °C (Figure S23). Additionally, during

the course of the NCA-8 polymerization, the formation of propylene carbonate was observed by ^1H NMR spectroscopy (Figure S24). As the conversion of monomer increased over time, the yield of propylene carbonate increased accordingly, and eventually an almost quantitative yield (94.2%) for propylene carbonate was observed in 2 hours. This suggests that as soon as CO_2 is generated from the NCA polymerization process, the transformation of released CO_2 into propylene carbonate takes place simultaneously. A mechanism is proposed below (Scheme 2). The formation of cyclic carbonate was also observed when Schiff base metal compounds together with $[\text{PPN}]\text{Cl}$ and PO were employed in the 5-membered ring NCA polymerization.⁴⁴

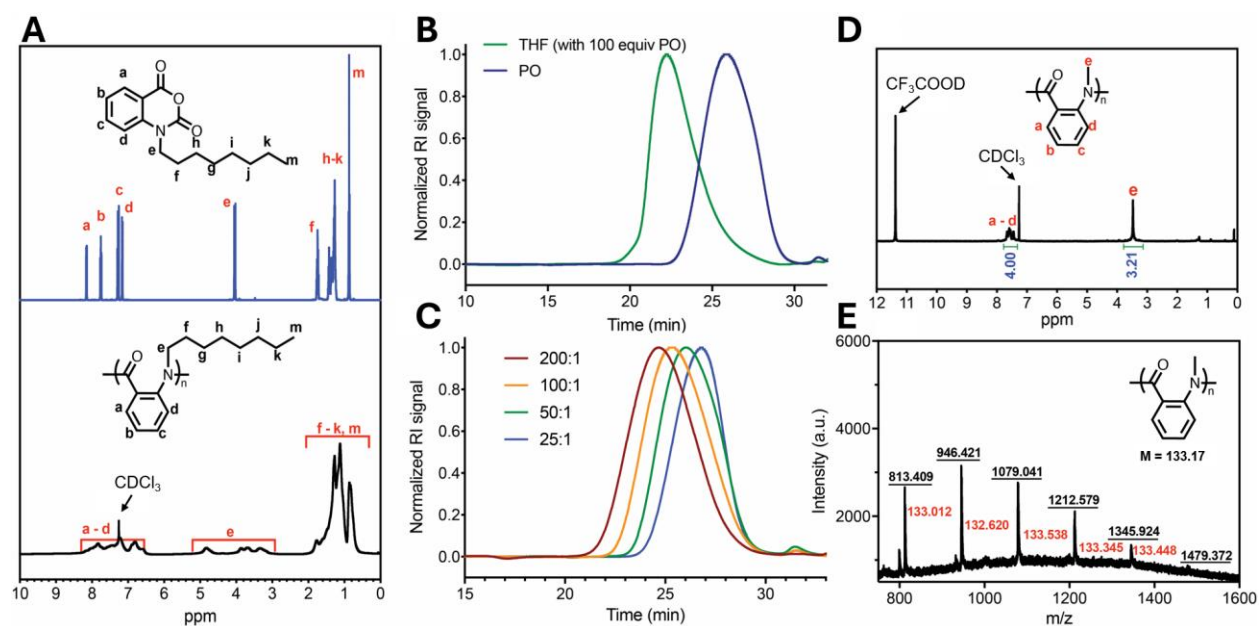
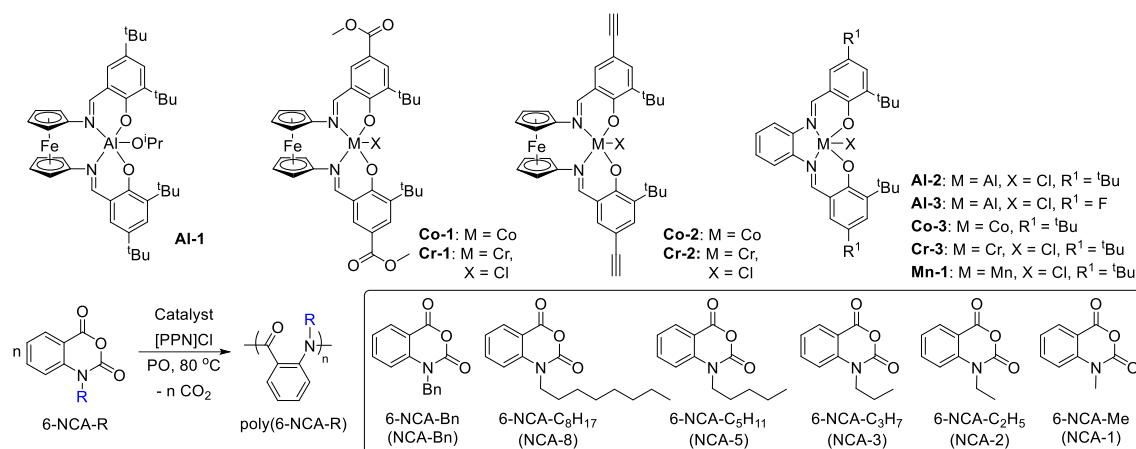


Figure 1. (A) ^1H NMR (500 MHz, 25 °C) spectra of NCA-8 (top) and poly(NCA-8) (bottom) in CDCl_3 . (B) SEC traces of polymer obtained from using THF as the solvent with 100 equiv of PO added (green; Table 1, entry 15) and using neat PO (blue; Table 1, entry 7). (C) SEC traces of the polymers obtained with varying the $[\text{NCA-8}]:[\text{cat}]$ feed ratio (Table 1, entries 7, 25-27). (D) ^1H NMR (500 MHz, 25 °C) spectrum of poly(NCA-1) (Table 1, entry 32) in $\text{CDCl}_3:\text{CF}_3\text{COOD} = 5:1$. (E) MALDI-TOF-MS of poly(NCA-1) (Table 1, entry 32).

Table 1. Ring-opening polymerization of 6-NCA-R.^a



	Cat.	6-NCA-R	[cat]:[PPNCl]:[M]	Solv.	Temp. (°C)	Time (h)	Yield (%) ^b	M _{n,theo} (kDa) ^c	M _{n,SEC} (kDa) ^d	Đ ^d	I (%) ^e
1	Al-1	NCA-Bn	1:2:50	PO	80	2	86	-	- ⁱ	- ⁱ	-
2	Al-1	NCA-8	1:2:50	PO	80	2	74	8.7	38.1	1.33	22.8
3	Co-1	NCA-8	1:2:50	PO	80	2	92	10.7	16.8	1.33	63.7
4	Cr-1	NCA-8	1:2:50	PO	80	2	85	10.2	29.2	1.45	34.9
5	Co-2	NCA-8	1:2:50	PO	80	2	99	12.2	24.4	1.48	50
6	Cr-2	NCA-8	1:2:50	PO	80	2	96	11.4	24.7	1.56	46.2
7	Al-2	NCA-8	1:2:50	PO	80	2	83	9.6	25.3	1.33	37.9
8	Co-3	NCA-8	1:2:50	PO	80	2	60	7.0	22.4	1.29	31.3
9	Cr-3	NCA-8	1:2:50	PO	80	2	30	3.5	8.4	1.26	41.7
10	Mn-1	NCA-8	1:2:50	PO	80	2	60	7.0	17.6	1.22	39.8
11	Al-2	NCA-8	1:0:50	PO	80	24	0	-	-	-	-
12	Al-2	NCA-8	0:2:50	PO	80	2	49	5.7	38.6	1.65	14.8
13	Al-2	NCA-8	1:1:50	PO	80	2	70	8.8	25.9	1.38	34
14	Al-2	NCA-8	1:5:50	PO	80	2	74	8.6	18.5	1.23	46.5
15 ^f	Al-2	NCA-8	1:2:50	THF	80	2	89	10.3	105	1.57	9.8
16 ^g	Al-2	NCA-8	1:2:50	THF	80	2	18	2.2	31.2	1.47	7.1
17 ^h	Al-2	NCA-8	1:2:50	THF	80	43	0	-	-	-	-
18 ^f	Al-2	NCA-8	1:2:100	THF	80	4	64	14.8	125	1.61	11.8
19 ^f	Al-2	NCA-8	1:2:200	THF	80	7	29	13.4	206	1.64	6.5
20	Al-2	NCA-8	1:2:50	CHO	80	2	0	-	-	-	-
21	Al-2	NCA-8	1:2:50	CHO	80	24	90	10.4	34.6	1.40	30.1
22	Al-2	NCA-8	1:2:50	PO	50	4	65	7.5	22.0	1.25	34.9
23	Al-2	NCA-8	1:2:50	PO	25	24	11	1.3	12.7	1.16	10.2
24	Al-3	NCA-8	1:1:50	PO	80	22	79	9.1	28.0	1.33	32.5
25	Al-2	NCA-8	1:2:25	PO	80	1	65	3.8	20.8	1.21	18.3
26	Al-2	NCA-8	1:2:100	PO	80	4	90	20.8	32.2	1.35	64.6
27	Al-2	NCA-8	1:2:200	PO	80	7	86	39.8	44.5	1.41	89.4
28	Al-2	NCA-8	1:2:400	PO	80	20	79	73.1	77.3	1.64	94.6
29	Al-2	NCA-5	1:2:50	PO	80	2	90	8.5	19.3	1.21	44.0
30	Al-2	NCA-3	1:2:50	PO	80	2	94	7.8	25.6	1.12	30.5
31	Al-2	NCA-2	1:2:50	PO	80	2	90	6.6	22.6	1.12	29.2
32	Al-2	NCA-1	1:2:50	PO	80	2	89	-	- ⁱ	- ⁱ	-

^a All polymerizations were carried out using 4 μmol precatalyst and 0.6 mL solvent. ^b Polymer yields were determined gravimetrically. ^c M_{n,theo} = ([6-NCA-R]₀/[Cat]) × (MW of 6-NCA-R - MW of CO₂) × polymer yield. ^d M_n and Đ were determined by SEC-MALS measurements in THF. ^e Initiation efficiency = (M_{n,theo}/M_{n,SEC}) × 100. ^f Polymerization was carried out in THF with 100 equiv of PO. ^g Polymerization was carried out in THF with 10 equiv of PO. ^h Polymerization was carried out in THF with 0 equiv of PO. ⁱ Insoluble polymer products were obtained.

To investigate the effect of ligand design and metal center on the polymerization rate and the properties of the resulting polymers, we tested several other ferrocene-based metal compounds for NCA-8 polymerization. The structures were chosen based on our previous studies of other reactions⁴⁹ and known cobalt and chromium systems that displayed high activity in conjunction with [PPN]Cl in ring-opening polymerization/copolymerization,⁵⁰⁻⁵² and other reports on the coupling of CO₂ and epoxides.^{42, 53-55}

Two cobalt compounds, **Co-1** ((salfen^{COOMe})Co, salfen^{COOMe} = dimethyl 5,5'-((1*E*,1'*E*)-(ferrocene-1,2-diylbis(azaneylylidene))bis(methaneylylidene))bis(3-(*tert*-butyl)-4-hydroxybenzoate)) and **Co-2** ((salfen^{CCH})Co, salfen^{CCH} = 6,6'-((1*E*,1'*E*)-(ferrocene-1,2-diylbis(azaneylylidene))bis(methaneylylidene))bis(2-(*tert*-butyl)-4-ethynylphenol)), demonstrated high activity. The polymer obtained using **Co-1**, with an ester group at the para position of the aryloxide ring, displayed a molecular weight closer to the expected value and narrower molecular weight distribution than **Co-2**, with alkyne groups in the same position (Table 1, entry 3 vs. 5). In the case of chromium compounds, **Cr-1**, an analogue of **Co-1**, polymers with a higher molecular weight and narrower molecular weight distribution were obtained compared to **Cr-2**, an analogue of **Co-2** (Table 1, entry 4 vs. 6).

Our major goal with the metal compounds bearing a ferrocene backbone was to achieve the redox switchable copolymerization²²⁻³⁷ of NCA-8 and PO. Therefore, we started with an equivalent of (salfen)AlO^{*i*}Pr (**Al-1**), 2 equivalents of [PPN]Cl, 50 equivalents of NCA-8, and PO as a solvent. After heating at 80 °C for 0.5 hours to allow partial conversion (the reduced **Al-1** does not polymerize epoxides), ^{Ac}FcBAr^F (^{Ac}Fc = acetylferrocene, BAr^F = tetrakis(3,5-bis(trifluoromethyl)phenyl) borate) was added to oxidize **Al-1** and initiate the polymerization of PO (Figure S25). Unfortunately, only the poly(NCA-8) homopolymer was isolated at the end. We

also attempted to initiate the polymerization with the oxidized form of **Al-1**. However, upon the addition of the [PPN]Cl cocatalyst, the decomposition of the oxidized aluminum compound was observed, as evidenced by the color change from dark red to orange, and the formation of a black precipitate. The decomposition was attributed to the incompatibility between the ferrocenium backbone and the chloride anion.⁵⁶

Given the lack of redox switchable copolymerization, we then turned to metal compounds supported by a simple salph ligand (salph = *N,N'*-bis(3,5-di-*tert*-butylsalicylidene)-1,2-diaminobenzene) to study the role of the metal compound, [PPN]Cl, and PO in NCA-8 polymerization.

The aluminum compound (salph)AlCl (**Al-2**) demonstrated comparable activity to **Al-1**, and showed a higher yield of polymer and improved control of molecular weight compared to **Al-1** (Table 1, entry 7). We also prepared a series of analogous transition metal compounds, (salph)Co (**Co-3**),⁵⁷ (salph)CrCl (**Cr-3**),⁵⁷ and (salph)MnCl (**Mn-1**),⁵⁸ for comparison. Although these metal compounds exhibited a similar control of polymer molecular weight under the same reaction conditions, the yields of polymer were significantly curtailed in comparison with **Al-2** (Table 1, entries 8-10). Therefore, we chose to carry out further reactions with **Al-2**.

We first investigated the role of the [PPN]Cl cocatalyst. In a control experiment using only **Al-2** without [PPN]Cl, no polymerization was observed (Table 1, entry 11). However, when [PPN]Cl was used alone without the aluminum compound, the polymerization still occurred at a slower rate with a lower initiation efficiency, resulting in a higher polymer molecular weight and dispersity compared to when the aluminum compound was present (Table 1, entry 12). These findings suggest the importance of both the aluminum compound and the [PPN]Cl cocatalyst for the formation of the active species and controlling the polymerization. Then, we changed the

amount of [PPN]Cl from 2 to 1 to 5 equivalents (Table 1, entries 13-14). The reduced amount of cocatalyst led to a lower yield of polymer and initiation efficiency, while at higher cocatalyst loadings, a better control of polymer molecular weight but lower yield of polymer were observed. Therefore, 2 equivalents of [PPN]Cl was used for further polymerization of different NCA monomers, in agreement with other reports.^{42, 43}

To investigate the effect of the propylene oxide amount on initiation efficiency, we proceeded to conduct the polymerization using THF as a solvent and used PO as an additive to the reaction mixture to initiate the polymerization and trap the CO₂ released. Interestingly, when the polymerization was performed in THF with 100 equivalents of PO, the polymerization rate remained relatively unchanged, with a polymer yield of 89% after 2 hours (Table 1, entry 15). However, a significantly increased molecular weight of the resulting polymer was observed (105 kDa), while the polymer yield was similar to that obtained in neat PO (Table 1, entry 7), indicating a much lower initiation efficiency (9.8%). The polymerization in THF with 10 equivalents of PO exhibited a very low yield of polymer (18%) and initiation efficiency (7.1%, Table 1, entry 16). Eventually, no polymerization occurred at all in THF without PO, suggesting PO is essential to initiate the polymerization (Table 1, entry 17). All polymers, obtained from the polymerizations with 50 equivalents of monomer either using THF with PO or using neat PO, exhibited monomodal size exclusion chromatography (SEC) traces (Figure S51, S58-59). Specifically, the trace from the polymerization in neat PO displayed a shift toward a lower molecular weight as a result of high initiation efficiency (Figure 1B). Further investigation into the use of THF as a solvent revealed that the polymerizations with higher monomer feed ratios produced high molecular weight polymers (Table 1, entries 18-19). However, the yield of polymer decreased significantly as the monomer feed ratio increased, and the corresponding SEC traces displayed bimodal molecular

weight distributions (Figure S60-61). These results suggest that the polymerization needs to be performed in neat PO for optimal results.

We also attempted the polymerization in neat cyclohexene oxide (CHO) to investigate whether PO may be replaced with another epoxide (Table 1, entries 20-21). Eventually, the polymerization in neat CHO with an extended reaction time demonstrated a comparable molecular weight and dispersity of resulting polymer, and initiation efficiency to the one in neat PO (Table 1, entry 7). However, no polymer was obtained from the polymerization in neat CHO in 2 hours, indicating a slower polymerization rate.

All polymerizations were conducted in a sealed Schlenk tube at 80 °C. Since the reaction temperature is higher than the boiling point of PO, as commonly adopted for other polymerizations in neat PO,^{40, 59, 60} the effect of reaction temperature on the NCA polymerization was evaluated. In comparison with the polymerization at 80 °C (Table 1, entry 7), the polymerization at 50 °C (Table 1, entry 22) showed a similar initiation efficiency while the yield of polymer decreased even with a prolonged reaction time. However, the polymerization at room temperature (Table 1, entry 23) exhibited a significantly reduced yield of polymer (11%) and initiation efficiency (10.2%) after 24 hours, suggesting that a reaction temperature higher than 50 °C is necessary for efficient polymerizations.

To further optimize the catalytic system and achieve better control over the polymerization process, we employed a fluorinated salph aluminum compound, (salph-F)AlCl (**Al-3**). Coates and coworkers previously reported that **Al-3** can effectively suppress side reactions such as transesterification and epimerization in the copolymerization of propylene oxide and different cyclic anhydrides.⁶⁰ However, in our case, the NCA-8 polymerization with **Al-3** was significantly

slower than that with **Al-2**, and no major differences were observed in the polymer molecular weight and dispersity (Table 1, entry 13 vs. 24).

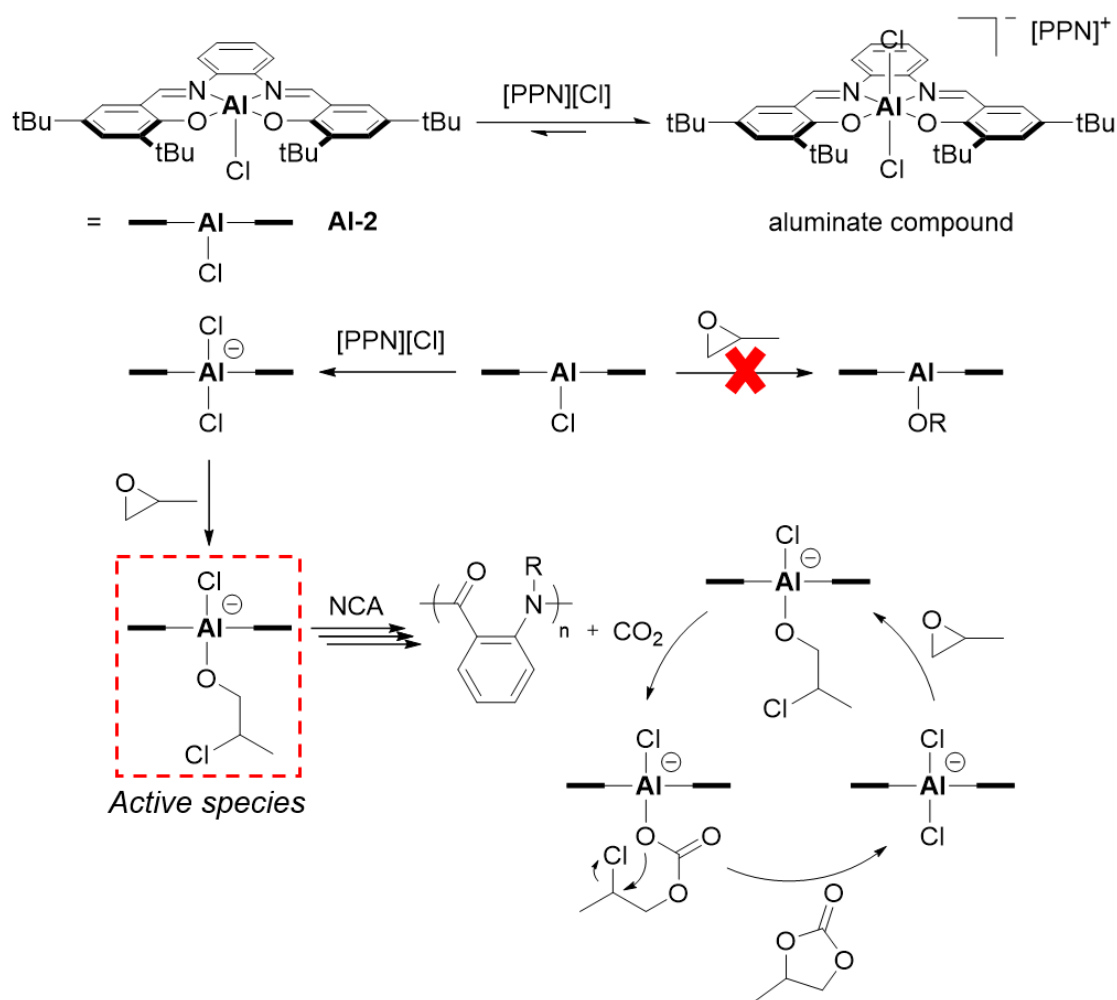
We also varied the monomer feed ratio to investigate the effect of monomer concentration on initiation efficiency (Table 1, entries 25-28). As the monomer feed ratio increased, the determined molecular weight of resulting polymers increased accordingly (Figure 1C). Importantly, the trend in the determined molecular weights showed that the polymer molecular weight became closer to the theoretical value at a higher monomer concentration. The good match between experimental and theoretical molecular weights suggests a greater initiation efficiency at higher monomer loadings, resulting in a well-controlled polymerization behavior.

In addition to the polymerization of NCA-8, this system was also able to achieve a high yield of polymers from the polymerization of different 6-NCA-R monomers in 2 hours regardless of the *N*-alkyl side chain length (Table 1, entries 29-32).

Control experiments were performed to verify that this system is inert toward propylene oxide (PO), cyclohexene oxide (CHO), and propylene carbonate (PC) (Table S3, entries 1-3). Importantly, none of these substrates was polymerized under the same reaction conditions employed for the NCA polymerization. In addition, the formation of polycarbonate by copolymerization of in situ generated CO₂ and epoxide was not observed over the NCA polymerization. The selective formation of polyamide is attributed to a low CO₂ pressure and high reaction temperature, suppressing the formation of polycarbonate, which is in agreement with other similar catalyst systems.^{42, 61-64}

Based on the results of our studies, we propose a mechanism for the ring-opening polymerization of 6-NCA-R (Scheme 2). Considering that **Al-2** is inactive toward NCAs in the absence of the cocatalyst [PPN]Cl, a neutral aluminum alkoxide cannot be formed by the insertion

of PO into an Al–Cl bond. Instead, the six-coordinated aluminate compound, (salph)AlCl₂[−], is generated from the reaction of **Al-2** and iminium salt, followed by a ring opening of PO by a chloride to form a monoalkoxide species, (salph)Al(OR)(Cl)[−]. Since all SEC traces of obtained polymers are monomodal, and the NCA polymerization cannot be initiated without PO, the active species initiating NCA polymerization is likely the monoalkoxide species; the bisalkoxide species, (salph)Al(OR)₂[−], is known to be produced in low quantities under similar conditions.^{65, 66} End group analysis by matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MS) confirmed the presence of an alkoxy end group generated from a ring opening of PO by a chloride (Figure S78). Importantly, CO₂ released in situ during propagation can be inserted into an Al–O bond of the monoalkoxide species. Then, the intramolecular backbiting of metal-bound carbonate occurs to produce cyclic carbonates and regenerate the monoalkoxide species for further CO₂ trapping.⁶⁷ The relatively low molecular weight distributions of obtained polymers and initiation efficiencies of the polymerizations at a low monomer concentration (*D* = 1.12–1.33; 29.2–44.0%; Table 1, entries 7, 29-31) suggest that CO₂ insertion into free Al monoalkoxide species is faster than additional initiation of NCA polymerization by the free Al monoalkoxide species once CO₂ starts to be generated by the decarboxylation process.



Scheme 2. Proposed mechanism showing the initiating species to form polyamide and cyclic carbonate ([PPN]⁺ moiety in the aluminate species is omitted for clarity).

In addition to homopolymerizations, the copolymerization of two different NCA monomers by sequential addition was attempted to confirm the presence of an active chain end (Table 2, entries 1-2). As the first monomer, NCA-8, was polymerized at 80 °C for the first 2 hours, the reaction mixture was cooled down to room temperature to add a second NCA monomer (NCA-5 or NCA-2), followed by heating again at 80 °C for another 2 hours. In both cases, the resulting polymers had molecular weights close to the corresponding theoretical molecular weights, and

their SEC traces were monomodal (Figure S73-74). The ^1H NMR spectra of the copolymers indicated that the ratio of the two NCA units in their structure is almost 1:1 (Figure S26 and 28).

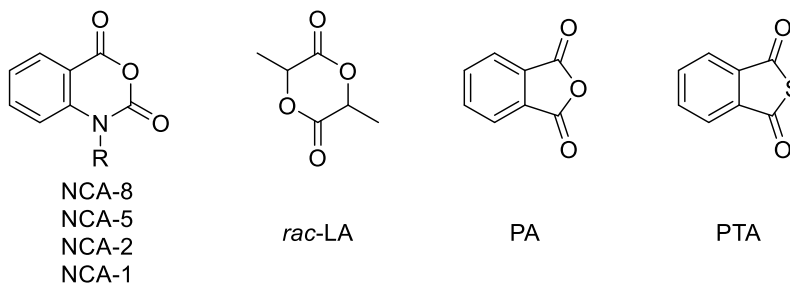
In addition, diffusion ordered NMR spectroscopy (DOSY) experiments showed that all components of the obtained polymers diffused at the same rate, suggesting the formation of copolymers (Figure S38-39). For example, the DOSY of the NCA-8 and NCA-2 copolymer displayed clearly distinguishable resonance peaks corresponding to the side chains of NCA-8 and NCA-2 at 4.82 and 3.82 ppm, respectively, and these peaks diffused together with other resonance peaks.

Similarly, the sequential copolymerization of NCA-8 and *rac*-lactide (*rac*-LA) was attempted (Table 2, entry 3). The conversion of lactide after 3 hours was 75%, however, the ^1H NMR spectrum of the purified copolymer showed that the degree of lactide incorporation was only 7.5% (Figure S30), likely due to the competing homopolymerization of *rac*-lactide initiated by residual aluminum alkoxide species. The resulting polymer had a monomodal molecular weight distribution (Figure S75), and its DOSY displayed a single peak on the y axis with resonances assigned to the poly(NCA-8) and polylactide at 5.19 ppm, indicating the formation of a copolymer (Figure S40).

Furthermore, a one-pot copolymerization of NCA and a cyclic anhydride requiring a similar initiating system was performed. The heterocyclic monomer mixture was heated at 80 °C in the presence of **AI-2**, [PPN]Cl, and PO. The resulting polymer from the copolymerization of NCA-8 and phthalic anhydride (PA) exhibited a molecular weight similar to that expected, but with a multimodal molecular weight distribution, likely due to the different reactivity of these monomers (Table 2, entry 4, Figure S76). The ^1H NMR spectrum of the polymer indicated a 1:1 composition

ratio between NCA and PA units (Figure S32), and DOSY confirmed the formation of a copolymer consisting of amide and ester units (Figure S41).

Table 2. Copolymerization of 6-NCA-R with various heterocyclic monomers.



	M1	M2	Yield (%) ^c	$M_{n,theo}$ (kDa) ^d	$M_{n,SEC}$ (kDa) ^e	\mathcal{D} ^e
1 ^a	NCA-8	NCA-5	48	10.1	9.3	1.31
2 ^a	NCA-8	NCA-2	54	10.2	12.0	1.34
3 ^a	NCA-8	<i>rac</i> -LA ^f	34	17.0	10.7	1.10
4 ^{b, g}	NCA-8	PA	80	35.0	26.0	1.37
5 ^b	NCA-1	PA	82	-	- ^h	- ^h
6 ^{b, g}	NCA-1	PTA	45	16.0	7.5	1.14

^a Sequential copolymerizations were carried out at 80 °C using 4 μmol **AI-2**, 0.6 mL PO. $[\mathbf{AI-2}]_0:[\text{PPNCl}]_0:[\text{M1}]_0:[\text{M2}]_0 = 1:2:50:50$. Reaction times: NCA (2 h) and lactide (3 h). ^b One-pot copolymerizations were carried out at 80 °C using 4 μmol **AI-2**, 1.2 mL PO. $[\mathbf{AI-2}]_0:[\text{PPNCl}]_0:[\text{M1}]_0:[\text{M2}]_0 = 1:2:100:100$. Reaction times: NCA and PA (2 h), NCA and PTA (6 h). ^c Polymer yields were determined gravimetrically. ^d $M_{n,theo} = ((\text{MW of 1}^{\text{st}} \text{ NCA} - \text{MW of CO}_2) \times [\text{1}^{\text{st}} \text{ NCA}]_0/[\text{Cat}] + (\text{MW of 2}^{\text{nd}} \text{ NCA} - \text{MW of CO}_2) \times [\text{2}^{\text{nd}} \text{ NCA}]_0/[\text{Cat}]) \times \text{polymer yield}$. For lactide copolymerization, $M_{n,theo} = (\text{MW of NCA} - \text{MW of CO}_2) \times [\text{NCA}]_0/[\text{Cat}] + (\text{MW of lactide}) \times [\text{lactide}]_0/[\text{Cat}] \times \text{conversion of lactide}$. For cyclic anhydride copolymerization, $M_{n,theo} = ((\text{MW of NCA} - \text{MW of CO}_2) \times [\text{NCA}]_0/[\text{Cat}] + (\text{MW of cyclic anhydride} + \text{MW of PO}) \times [\text{cyclic anhydride}]_0/[\text{Cat}]) \times \text{polymer yield}$. ^e M_n and \mathcal{D} were determined by SEC-MALS measurements in THF. ^f Conversion of lactide was determined by ¹H NMR spectroscopy. ^g SEC trace showed a multimodal molecular weight distribution. ^h Insoluble polymer products were obtained.

As the homopolymer of NCA-1 was readily soluble only in TFA, the substrate scope was expanded to NCA-1 with PA and phthalic thioanhydride (PTA) to evaluate the capability of this system to prepare a copolymer of polyamide and polyester/polythioester that would improve the solubility of poly(NCA-1) in common organic solvents (Table 2, entries 5-6). While the polymers obtained from the copolymerization of NCA-1 and PA were still insoluble in CHCl₃ and THF,

changing the comonomer from PA to PTA led to the resulting polymers being soluble in CHCl_3 , CH_2Cl_2 , and THF, allowing further characterization. Unlike the copolymerization of NCA-8 and PA, the polymers from both copolymerizations exhibited more cyclic anhydride units in their structure rather than maintaining the initial monomer ratio, likely due to the poor solubility of NCA-1 (Figure S34 and 36). The formation of the desired copolymers was confirmed by DOSY (Figure S42-43). Despite the low-molecular-weight copolymer of NCA-1 and PTA owing to the residual phthalic acid that was generated during the synthesis of PTA and acted as a chain transfer reagent,⁶⁸ these results suggest that this system can provide synthetic pathways to heteroatom (N, O, and S) containing polymers.

Returning to polyamide homopolymers, we varied the chain length to investigate the influence of the *N*-alkyl side chain length on solubility and thermal properties (Table 1, entries 29-32). Previous studies have shown that *N*-alkylated poly(*p*-benzamide)s are only soluble in THF when the alkyl chain length is no shorter than heptyl.⁶⁹ On the other hand, *N*-alkylated poly(*m*-benzamide)s generally exhibit better solubility, with even the *N*-methyl polymer being soluble in THF.⁷⁰ In our current study, we focused on poly(6-NCA-R), which is *de facto* poly(*o*-benzamide). Interestingly, the solubility of poly(6-NCA-R) falls between its para and meta counterparts. We found that poly(6-NCA-R) with alkyl chains as short as an ethyl group was soluble in THF (Table S1). Poly(NCA-1) is soluble in TFA and only slightly soluble in methylene chloride. Therefore, the ^1H NMR spectrum of poly(NCA-1) was obtained in a $\text{CF}_3\text{COOD}/\text{CDCl}_3$ mixture, which showed peak integrations matching the structure of an *N*-methyl aromatic polyamide (Figure 1D). The polymer structure was further confirmed by MALDI-TOF-MS, in which the spacing between adjacent peaks was consistent with the molar mass of the *N*-methyl aromatic amide repeating unit (Figure 1E).

The thermal properties of the poly(6-NCA-R) polymers were characterized by thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) (Table S2). The polymers all demonstrated high thermal stability. For example, poly(NCA-8) showed a $T_{d,5\%}$ (temperature at 5% weight loss) as high as 395 °C when heated at a scan rate of 5 °C/min under a nitrogen atmosphere (Figure 2A). This thermal stability is comparable to its para counterpart, which has a $T_{d,5\%}$ at 417 °C.⁶⁹ Given that the poly(6-NCA-R) polymers have similar $T_{d,5\%}$ values (Figure S79-82), the thermal stability seems to be determined by the nature of the backbone instead of the length of the side chain. The second heating DSC curve of poly(NCA-8) revealed a melting temperature T_m of 213 °C (Figure 2B). For previously reported *N*-alkylated poly(*p*-benzamides), the decrease in *N*-alkyl chain length caused an increase in the melting temperature of the polymer; however, poly(NCA-5), poly(NCA-3), poly(NCA-2), and poly(NCA-1) showed no melting transitions within the temperature window of -50 to 300 °C (Figure S90-93).⁶⁹ Although the *N*-alkylated poly(*p*-benzamide)s did not show every thermal transition from DSC analysis either, the 3rd heating DSC curves in the range of 30 to 400 °C were further collected for poly(NCA-5), poly(NCA-3), poly(NCA-2), and poly(NCA-1) in case additional thermal transitions can be observed in the high-temperature range. While a T_g of poly(NCA-1) was newly observed at 106 °C (Figure S94), we were not able to determine T_g values for the rest of the polymers due to weak thermal transitions, as also reported for *N*-alkylated poly(*p*-benzamide).⁶⁹ In addition, no T_m was observed in the high-temperature range, suggesting that the T_m of poly(6-NCA-R) with short side chains is close to its T_d or that thermal decomposition occurs before melting.

In comparison with homopolymers, the TGA and DTG curves of copolymers consisting of two different NCA monomer units showed a slightly lowered $T_{d,5\%}$ at 337 °C, and almost the same T_{max} (temperature of maximum peak) at 444 °C, respectively (Figure S83-84). This suggests that

the polyamide copolymers have similar thermal stability regardless of the identity of NCA comonomers due to the same backbone structure. However, copolymers of NCA and cyclic anhydrides displayed two-step degradations on TGA curves, which were reflected in two T_{\max} values on the DTG curves, implying that the copolymers have a gradient structure rather than a random distribution of each monomer unit (Figure S86-88). The thermal transition of the NCA-8 homopolymer was clearly observed from the DSC analysis, however, the DSC curves of copolymers with NCA-8 units exhibited weak T_m and T_c signals, owing to the formation of copolymers (Figure S95-97). The copolymers of NCA with PA and PTA had T_g at 46 and 63 °C, respectively (Figure S98-100). These values are attributable to segments of PA and PTA units given that the reported T_g values of poly(PA-*alt*-PO) and poly(PTA-*alt*-PO) are 46 and 63 °C, respectively.⁶⁸

The powder X-ray diffraction (PXRD) patterns were further collected to verify the crystallinity of the polymers (Figure S101-105). All poly(6-NCA-R), except poly(NCA-8), showed minor diffraction peaks at 26, 37, and 40 ° in 2θ , however, there were not many other peaks and the intensity of peaks was low, indicating the polymers are amorphous materials with some loosely packed crystalline domains. This is generally attributed to the rigid backbone of aromatic polyamides makes crystallization difficult. Considering the PXRD pattern of poly(NCA-8) with unclear broad peaks, the rest of the polymers with shorter side chains likely form minor lattices without disturbance of the steric hindrance from side chains. In addition, this observation suggests the octyl substituents in poly(NCA-8) are not long enough to crystallize by themselves.

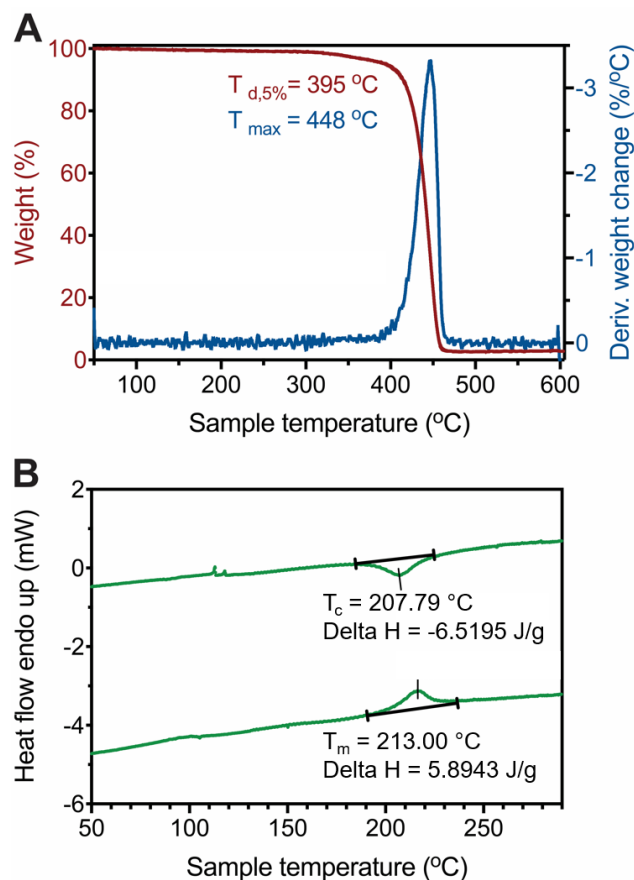


Figure 2. (A) Thermogravimetric analysis (TGA) and derivative thermogravimetry (DTG) curves of poly(NCA-8). (B) The second heating (bottom) and cooling (top) curves of differential scanning calorimetry (DSC) thermograms for poly(NCA-8) (Table 1, entry 7).

CONCLUSIONS

In conclusion, we successfully developed a catalytic system consisting of a Schiff base metal compound, [PPN]Cl, and propylene oxide for the polymerization of 6-NCA-R to *N*-alkylated ortho-aromatic polyamides. This is the first example of high molecular weight ortho-aromatic polyamide synthesis via ring-opening polymerization of β -NCA. Through the investigation of each component's role in the catalytic system, we were able to propose a mechanism for the polymerization of 6-NCA-R and achieve improved control over the polymerization process.

Additionally, we were able to tune the polymer solubility and thermal properties by varying the length of the *N*-alkyl chain as well as prepare heteroatom (N, O, and S) containing polymers by copolymerization of NCA and heterocyclic monomers. Overall, this study provides insight into the synthesis and characterization of *N*-alkylated ortho-aromatic polyamides, offering control over their solubility and thermal properties through rational design and optimization of the catalytic system and monomer structure. These findings open up new possibilities for the development of advanced polyamide materials with tailored properties for various applications.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge.

Experimental details, NMR spectra, UV-Vis spectra, SEC traces, MALDI-TOF spectrum, TGA traces, DSC traces, PXRD patterns.

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Notes

The authors declare no competing financial interest.

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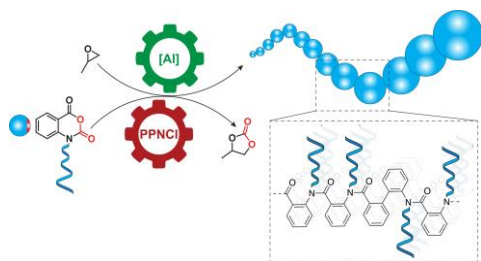
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The synthesis of ortho-aromatic polyamides with high molecular weights was accomplished via chain-growth polymerization for the first time by carrying out the ring-opening polymerization of aromatic *N*-carboxyanhydrides catalyzed by Schiff base transition metal complexes. Copolymerization of aromatic *N*-carboxyanhydrides with heterocyclic monomers was also possible and led to heteroatom (N, O, and S) containing copolymers.