Poly(isoquinoline Reissert compound)s: Chemically Reactive Polyamides. 4

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ABSTRACT: Reissert compounds, 2-benzoyl-1,2-dihydroisoquinaldonitrile (**3**) and 2,2′-adipoylbis[1,2-dihydroisoquinaldonitrile] (**14**), have been prepared utilizing *N*,*N*-dimethylformamide as solvent in quantitative yields. Lithium cyanide as a cyanide source in Reissert compound **3** synthesis is reported for the first time. Synthesis and characterization of novel, reactive poly(isoquinoline Reissert compound)s **17a–d** are reported. Chemical modification of these polyamides via formation of the Reissert anion was demonstrated by methylation of the polyanion derived from **17b**.

Introduction

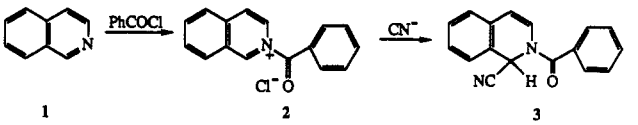
Since their discovery by Arnold Reissert,[1] Reissert compounds, α-(acylamino) nitriles, have proven useful as intermediates in the synthesis of various heterocyclic compounds, such as derivatives of isoquinoline, quinoline, quinazoline, etc., including alkaloids and other biologically active compounds.[2-4] These α-(acylamino) nitriles result from the initial formation of the acylium ion by the reaction of an acid chloride across the C=N bond of the heterocycles, followed by the addition of a cyanide nucleophile. For example, isoquinoline (**1**) reacts readily with benzoyl chloride and forms a σ-complex (**2**) which then reacts smoothly with a weak nucleophile, cyanide ion, to form the Reissert compound **3** (Scheme I).

The proton α to the cyano group of Reissert compounds is acidic, and the resultant carbanions react with a number of electrophiles.[2-4] For example, reaction of 2-benzoyl-1-cyano-1,2-dihydroisoquinoline (**3**) via its anion **4** with alkyl halides produces the alkylated derivative **5** which by alkaline hydrolysis is converted to the rearomatized alkylated isoquinoline **6**. Similarly, condensation with aldehdyes via the intermediate alkoxide **7** and cyclic alkoxide **8** produces the ester **9**. In the absence of an electrophile the Reissert anion rearomatizes by an intramolecular process with elimination of cyanide ion to produce the ketone **10** (Scheme II).

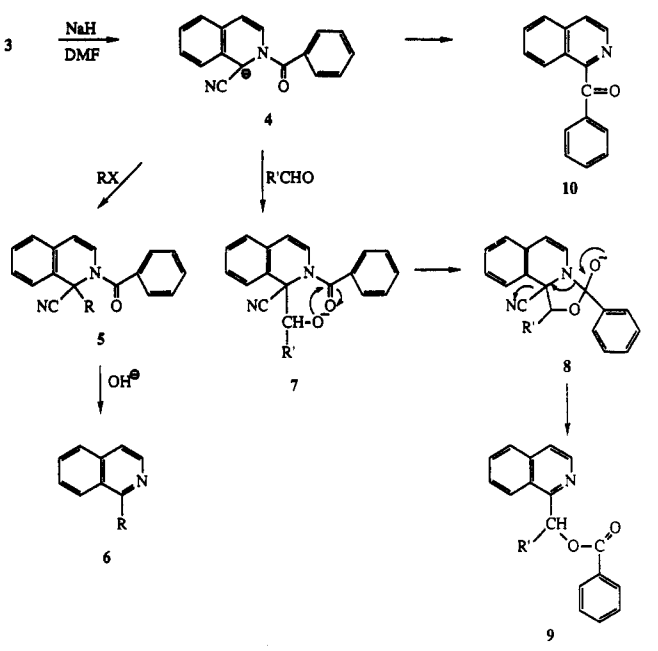
Functionalization and chemical modification of polymers are important areas in polymer chemistry.[5-7] The anion of the isoquinoline Reissert compound **4** has been shown to react with polymeric halides[8] and polymeric aldehydes[9] in essentially complete conversion. This allows ample opportunity to modify existing polymers.[8,9] We have also shown recently the utility of Reissert compounds in the synthesis of new monomers for specialty polymers.[10-13] Reissert anion **4** has also been successfully utilized in controlled anionic polymerization of acrylonitrile.[14] Elsewhere we have also described the utilization of acyclic Reissert compounds to produce novel polyamides.[13,15]

Currently, we are exploring Reissert reactions on generalized bis(heterocycle)s **11** with diacid chlorides in the presence of a cyanide source leading to the formation of poly(Reissert compound)s **13** as shown in Scheme III.[16]

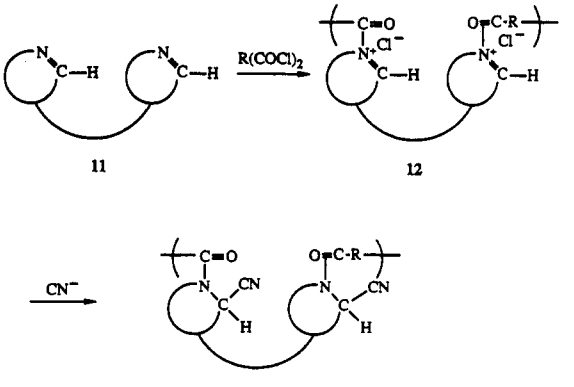
Scheme I



Scheme II



Scheme III



In this way we can incorporate the reactive nitrogen heterocycles into the polymer backbone. The reactivity associated with the Reissert moieties[2-4] of such poly-

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Scheme IV

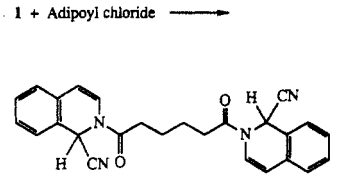

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Table I. Reissert Reactions on Isoquinoline

entry	reacn conditions	reacn time	yield (%)
1	adipoyl chloride, KCN, CH_2Cl_2–H_2O[17,18]	3–8 h	6–8
2	adipoyl chloride, TMSCN, CH_2Cl_2	24 h	71
3	adipoyl chloride, TMSCN, CH_2Cl_2, cat. $AlCl_3$	24 h	100
4	adipoyl chloride, TMSCN, NMP	24 h	71
5	adipoyl chloride, TMSCN, NMP, cat. $AlCl_3$	7 days	85
6	adipoyl chloride, TMSCN, CHP, cat. $AlCl_3$	7 days	85
7	PhCOCl, TMSCN, DMF, cat. $AlCl_3$	4 days	100
8	adipoyl chloride, TMSCN, DMF, cat. $AlCl_3$	2 days	100
9	PhCOCl, LiCN, DMF	36 h	71
10	adipoyl chloride, $[TMS(CN)_2]^-$, DMF, cat. $AlCl_3$	36 h	83

(Reissert compound)s **13** can be utilized to chemically modify the polymers. These chemical modifications can be judiciously applied to control the physical and chemical properties such as surface energy, dyeability, blendability, etc.

Results and Discussion

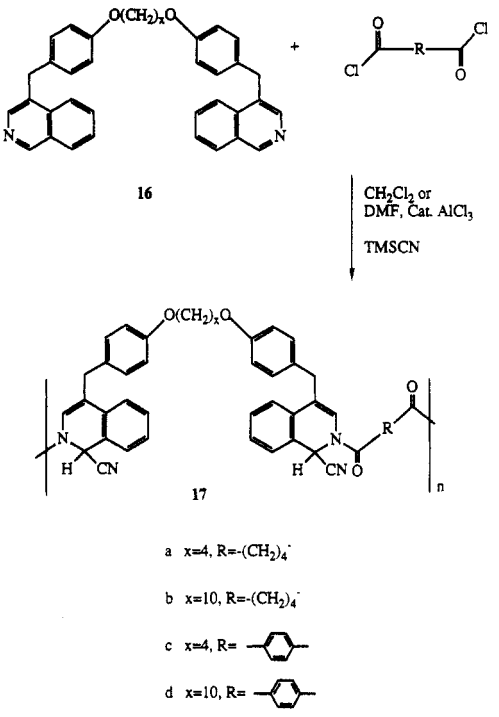
(a) Model Reactions. To get a high molecular weight polymer in any step growth polymerization, two requirements are the absence of side reactions and quantitative conversion to product. These factors necessitated exploration of the synthesis of model bis(Reissert compound) **14** by reacting isoquinoline with adipoyl chloride under various reaction conditions (Scheme IV). Popp et al. have reported the synthesis of bis(Reissert compound) **14** in 8–10% yield by a two-phase method.[17-20] We employed trimethylsilyl cyanide (TMSCN) as the cyanide ion source in a single-phase (dry methylene chloride) method[21,22] and obtained **14** in 71% yield (entry 2, Table I), but when a catalytic amount of aluminum chloride was present, we obtained a quantitative yield (entry 3, Table I).[23] However, dichloromethane was found to be a poor solvent for the polyamide-forming reaction because the oligomers precipitated from the reaction mixture even in the presence of LiCl. Solvents like *N*-methylpyrrolidinone (NMP) and cyclohexylpyrrolidinone (CHP) did not give satisfactory yields of **14** (entries 4–6, Table I).

However, when the Reissert reaction was carried out on isoquinoline with benzoyl chloride or adipoyl chloride in *N,N*-dimethylformamide (DMF)/TMSCN/catalytic amount of $AlCl_3$, a quantitative yield of Reissert compound (**3** or **14**) was obtained (entries 7 and 8, Table I).

Lithium cyanide is a useful, potent reagent for cyanation of various compounds and also soluble in many organic solvents. Indeed, the Reissert reaction on isoquinoline with PhCOCl, a catalytic amount of $AlCl_3$, and LiCN as a cyanide source in DMF yielded the corresponding Reissert product **3**, but only to an extent of 71% (entry 9, Table I). However, when isoquinoline was treated with LiCN and a catalytic amount of $AlCl_3$ in DMF under dry conditions, there was no reaction, indicating no side reactions. Our attempts toward use of diethylaluminum cyanide as a cyanide source were unsuccessful.

We are particularly interested in determining the factors which influence the sense and extent of stereoselection

Scheme V



a x=4, R=-$(CH_2)_4$-

b x=10, R=-$(CH_2)_4$-

c x=4, R=

d x=10, R=

Table II. Poly(isoquinoline Reissert compound)s

	polymer			mol wt (GPC in NMP, absolute)			TGA (10% loss in air)	DSC
entry	product	x	-R-	M_n/1000	M_w/1000	PD	(°C)	T_g (°C)
1	**17a**	4	-$(CH_2)_4$-	2.6	5	1.92	200	
2	**17b**	10	-$(CH_2)_4$-	1.4	13	9.29	280	
3	**17a**	4	-$(CH_2)_4$-	4.5	7.1	1.59	210	85
4	**17b**	10	-$(CH_2)_4$-	5.8	9.5	1.64	225	87
5	**17c**	4	*p*-C_6H_4-	4.5	6.0	1.33	313	119
6	**17d**	10	*p*-CH_6H_4-	16.1	22.6	1.4	388	78

associated with the addition of various nucleophiles to "Reissert iminium ion intermediates" (e.g., **2** and **12**) as it determines the properties of the molecule or polymer. In all the above experimental products utilizing adipoyl chloride as the acid chloride, we did not observe any diastereomers. We prepared the regiospecific cyanide reagent, $[TMS(CN)_2]^-$ (**15**), by following the methods of Evans et al.[24] When we carried out the Reissert reaction on isoquinoline with adipoyl chloride/catalytic $AlCl_3$ and **15** as a cyanide source, we obtained compound **14** with mp 144–5 °C. The earlier methods produced **14** with mp 184–5 °C (dec). Proton NMR spectra of the products were identical, indicating two differnet diastereomeric compounds. However, during purification (recrystallization) processes, the lower melting solid slowly converts to the higher melting solid.

(b) Polymerization Reactions. Poly(Reissert reaction)s on monomers **16a** [C_4-bis(isoquinoline)] and **16b** [C_{10}-bis(isoquinoline)] were carried out with adipoyl chloride (Scheme V).[25] When the poly(Reissert reaction) was carried out in dichloromethane, precipitation of the polyamide was observed (entries 1 and 2, Table II). Because monomer **16a** has the shorter aliphatic chain length, it is less soluble in dichloromethane than **16b**. This might be one of the reasons for the wide differences in the polydispersities (PD) of these two polymers. When we changed the solvent to DMF, we obtained slightly higher molecular weight oligomers and with narrow PD (entries 3 and 4, Table II).

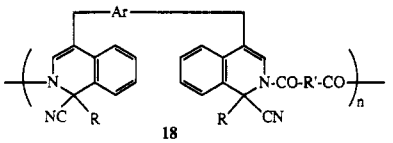
The NMR spectra of the bis(Reissert compound)s prepared by reaction of isoquinoline with adipoyl chloride[23]

and terephthaloyl chloride[23] and by reaction of the bis(isoquinoline)s with benzoyl chloride[12c] were compared to the polymeric Reissert compounds; these comparisons confirmed the formation of the Reissert units in polymers **17a-d**. Additionally, the presence of peaks assignable to the unreacted isoquinoline end groups could be detected; H_1 and H_3 appear well downfield in the proton NMR spectrum, at 9.17 and 8.39 ppm, respectively, well removed from the aromatic resonances of the Reissert units. Inasmuch as exactly equivalent amounts of bis(isoquinoline) and diacid chloride were used, one isoquinoline end group is expected per macromolecule; thus integration of isoquinoline end groups provides an estimate of molecular weight. These values were in accord with the more accurate GPC determinations.

TGA results showed thermal stability in air up to 210 °C (10% weight loss), and DSC results showed a glass transition at 85 °C and no melting for **17a**; for **17b**, TGA revealed 10% weight loss in air at 225 °C and T_g at 87 °C.

Reactions with terephthaloyl chloride as an acid chloride in DMF resulted in higher molecular weight polymers (entries 5 and 6, Table II). Correspondingly, the thermal stability of **17c** increased to 313 °C with a glass transition temperature of 119 °C; **17d** showed 10% weight loss in air at 388 °C and T_g at 78 °C.

(c) Polymer Modification Reactions. Poly(Reissert compound)s 17 prepared above can be subjected to chemical modification via the anion resulting from abstraction of the acidic proton α to the nitrile moiety as discussed earlier (Scheme II). Thus, poly(Reissert anion)s can be reacted with alkyl halides to form alkylated derivatives 18. This was demonstrated by methylation of

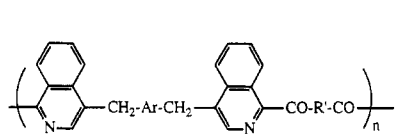


18

a. R=CH_3, R'=$(CH_2)_4$, Ar=p-$C_6H_4O(CH_2)_{10}OC_6H_4$-p

the anion of **17b**, yielding **18a** with ca. 60% conversion, as evidenced by partial loss of the acidic proton (H_1 of the isoquinoline nucleus) peak at 6.91 ppm and appearance of a methyl signal at 1.74 ppm in the ^1H NMR spectrum. **18a** exhibited significantly enhanced thermal stability, 368 °C for 10% weight loss, relative to **17b**, 225 °C for 10% weight loss. Moreover, the glass transition temperature was lowered significantly, from 87 °C for **17b** to 49 °C for **18a**.

Similarly, poly(aromatic ketone)s **19** can be produced by base-promoted rearrangement. Finally, polyesters of the type **20** can also be produced by condensation with an aldehyde (RCHO) (as shown for small Reissert molecules in Scheme II). We have not attempted these transformations.



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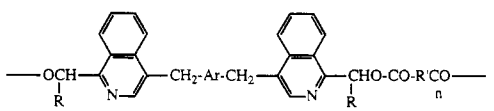

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Conclusions

A novel new class of reactive polyamides, poly(isoquinoline Reissert compound)s, has been prepared and characterized. The feasibility of chemically modifying these polymers via reactions of the anion of the Reissert moiety has been demonstrated. Reissert reactions in DMF proceed with excellent yield. The Reissert reaction on isoquinoline with benzoyl chloride in DMF using lithium cyanide has been reported for the first time.

Experimental Section

All melting points were determined on a Haake-Buchler melting point apparatus and are corrected. ^1H nuclear magnetic resonance (NMR) (DMSO-d_6) spectra were recorded on a Bruker 270-MHz instrument and a Hewlett-Packard 7550A graphics plotter; peaks relative to internal tetramethylsilane are represented as s (singlet), m (multiplet), bs (broad "singlet"), and bm (broad multiplet). Fourier transform infrared (FTIR) (KBr) spectra were recorded on a Nicolet MX-1. Thermogravimetric analyses (TGA) were carried out at 10 °C/min on a DuPont 951 TGA coupled to a DuPont 2100 thermal analyzer. Glass transition temperatures (T_g) were determined by a dual-cell DuPont 912 differential scanning calorimeter (DSC) coupled to the same data station as in the TGA at a heating rate of 10 °C/min. Absolute gel permeation chromatography (GPC) analyses were run on a Waters 150C equipped with a refractive index detector and a Viscotek Model 100 differential viscosity detector. Monomers, 1,4-bis(*p*-((4-isoquinolyl)methyl)phenoxy)butane (**16a**) [C_4-bis(isoquinoline)] and 1,10-bis(*p*-((4-isoquinolyl)methyl)phenoxy)decane (**16b**) [C_{10}-bis(isoquinoline)], were synthesized in large scale[11] and were recrystallized from ethyl acetate (4×) and then from ethanol (1×).

2-Benzoyl-1,2-dihydroisoquinaldonitrile (3). Method A. To a well-stirred solution of isoquinoline (0.0100 mol, 1.29 g) and a catalytic amount of $AlCl_3$ in DMF (10 mL) was added PhCOCl (0.0100 mol, 1.41 g) at 0 °C under a nitrogen atmosphere. This was followed by the addition of TMSCN (0.0130 mol, 1.74 mL). The reaction mixture was brought to room temperature, stirred for 4 days, and then quenched by pouring into water (250 mL). The pale brownish precipitate obtained was collected, taken up in ethyl acetate, washed with 8% HCl (1 × 75 mL), aqueous $NaHCO_3$ (3 × 75 mL), and brine (2 × 75 mL), and dried over Na_2SO_4. The solution was treated once with Norit, diluted with hexanes while hot, and kept for recrystallization. Crystals of Reissert compound **3** were filtered and dried: 2.54 g (100%), mp 122–3 °C (lit.[26] mp 122–3 °C).

Method B. To a well-stirred solution of isoquinoline (0.0100 mol, 1.29 g) and a catalytic amount of $AlCl_3$ in DMF (2 mL) was added PhCOCl (0.0100 mol, 1.41 g) at 0 °C under a nitrogen atmosphere. This was followed by the addition of LiCN (0.01 mol, 20 mL of a 0.5 M solution in DMF). The reaction mixture was brought to room temperature, stirred for 36 h, and then quenched by pouring into water (250 mL). It was extracted with ethyl acetate (3 × 75 mL). The organic layers were pooled, washed consecutively with saturated aqueous $NaHCO_3$, 8% HCl (1 × 75 mL), and water (3 × 75 mL), dried over Na_2SO_4, and concentrated to get crude product 3: 1.83 g (71%), mp 120–2 °C (lit.[26] mp 122–3 °C).

2,2′-Adipoylbis[1,2-dihydroisoquinaldonitrile] (14): DMF Method. To a well-stirred solution of isoquinoline (0.0200 mol, 2.58 g) and a catalytic amount of $AlCl_3$ in DMF (10 mL) was added adipoyl chloride (0.0100 mol, 1.83 g) under a nitrogen atmosphere. After 15 min TMSCN (0.0200 mol, 1.98 g) was added. Stirring was continued at room temperature for 48 h, and the reaction mixture was quenched by pouring into water (100 mL) and stirred for 3 h. The solid obtained was filtered and treated with aqueous saturated $NaHCO_3$, followed by aqueous 8% HCl. The pale yellow solid obtained was finally washed thoroughly with water, ethanol (10 mL), and ether (50 mL) and dried: 4.23 g (100%), mp 184–5 °C (dec) (lit.[23] mp 184–5 °C).

2,2′-Adipoylbis[1,2-dihydroisoquinaldonitrile] (14): $[TMSCN)_2]^-$ Method. To a well-stirred solution of isoquinoline (0.0200 mol, 2.58 g) and a catalytic amount of $AlCl_3$ in DMF (10 mL) was added adipoyl chloride (0.0100 mol, 1.83 g) under a nitrogen atmosphere. After 15 min $[TMS(CN)_2]^-$ (0.022 mol, prepared freshly and separately,[24] in DMF) was added. Stirring was continued at room temperature for 36 h, and the reaction mixture was quenched by pouring into water (1 L) and stirred

for 3 h. The solid obtained was filtered, washed with water, and dried: 3.5 g (83%), mp 144–7 °C. This product was twice treated with Norit and recrystallized from ethyl acetate. The melting point of the ethyl acetate soluble part remained 146–7 °C and the melting point of the ethyl acetate insoluble part was 180–2 °C (lit.[23] mp 184–5 °C). Proton NMR spectra of both products are in agreement with that obtained by the DMF method reported above.[23]

Typical Poly(Reissert reaction): Synthesis of 17b. To a well-stirred solution of C_{10}-bis(isoquinoline) (**16b**) (8.95 mmol, 5.4493 g) and a catalytic amount of $AlCl_3$ (<100 mg) in dry DMF (40 mL) was added adipoyl chloride (8.95 mmol, 1.6382 g in 10 mL of dry DMF) under a nitrogen atmosphere. After 20 min TMSCN (20 mmol, 3 mL) was added. Stirring was continued at room temperature for 3 days, and the reaction mixture was quenched by pouring into water (3 L) and stirred for 3 h. The solid obtained was consecutively treated with water (1 L) and aqueous HCl (1 L) and then dried (40 °C/1 mm) to obtain the desired polymer **17b**: 5.14 g. $[\eta]$ = 0.15 dL/g (THF, 25 °C). FTIR (KBr): 2927, 2855 (C–H), 1738, 1732, 1714, 1682, 1675, 1651, 1639, 1611, 1582, 1574, 1511, 1495 cm^{-1}. ^1H NMR: 1.24 (bs, 12H, $OCC(CH_2)_6$), 1.62 (bs, 8H, $OCCH_2$, $COCCH_2$), 2.2–2.9 (m, 4H, $COCH_2$), 3.8 (bm, 8H, Ar–CH_2–Ar′, OCH_2), 6.81 (bm, 4H, phenylene protons ortho to CH_2), 6.91 (s, 2H, H_1), 7.0–7.4 (bm, 12H, arom), 7.60 (bs, 2H, arom). Weak resonances due to isoquinoline end groups as in **16** were observed at 8.39 and 9.16 ppm, and a weak signal at 12.1 ppm is attributable to COOH end groups. GPC (absolute, NMP): M_n = 5800, M_w = 9500. TGA: thermally stable up to 225 °C (10% weight loss). DSC shows T_g at 87 °C.

Poly(alkylated Reissert compound) 18a. To a well-stirred solution of **17b** (100 mg) in dry DMF (10 mL) was added sodium hydride (200 mg, 60% dispersion oil) under a nitrogen atmosphere. After 15 min methyl iodide (2–3 mL) was added, and the reaction mixture was allowed to stir at room temperature overnight. The mixture was then poured into water (200 mL) and stirred for 3 h. The solid obtained was filtered and dried (40 °C/1 mm), 100 mg (100%). ^1H NMR: essentially the same as the ^1H NMR of **17b** except for the presence of a singlet at 1.74 ppm and the diminution of the H_1 singlet at 6.91 ppm; integration of the methyl singlet versus the CH_2 signals at 1.24 and 1.62 ppm as well as the H_1 singlet versus the aromatic protons indicated ca. 60% replacement of the acidic H_1 proton by the methyl group. TGA: thermally stable up to 368 °C (10% weight loss). DSC shows T_g at 49 °C.

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