## Heterocyclic Monomers via Reissert Chemistry

#### HARRY W. GIBSON, MELVIN L. RASCO,\* ZHENBIN NIU

Department of Chemistry, Virginia Tech, Blacksburg, Virginia 24061-0212

Received 22 April 2011; accepted 30 May 2011 DOI: 10.1002/pola.24821 Published online 28 June 2011 in Wiley Online Library (wileyonlinelibrary.com).

**ABSTRACT:** An AA bisphenolic monomer (**13**), an AB activated fluoro-phenolic monomer (**14**), and an  $AB_2$  alcohol-diester monomer precursor (**17**), all based on the isoquinoline nucleus, were prepared using Reissert compound chemistry. Additionally, model reactions established the efficiency of condensation of isoquinoline Reissert compounds with dihaloalkanes, providing evidence of the potential of this reaction to produce

#### INTRODUCTION

#### **Nitrogen-Containing Polymers**

Nitrogen-containing polymers are a special class of materials that exhibit useful features. Polyamides<sup>1(a)</sup> and polyimides<sup>1(b,c)</sup> are useful in a variety of applications. Quaternary salt polymers are used as anion exchange resins, coatings, adhesives, ion conductors and in water treatment and coagulation.<sup>2</sup> Aromatic nitrogen-containing polymers, such as polyimides,<sup>1(c)</sup> polyquinoxalines, polyquinolines, polybenzimidazoles, polybenzothiazoles, and polybenzoxazoles, exhibit excellent thermo-oxidative stability and retain useful mechanical properties at elevated temperatures for extended times.<sup>3</sup>

Of the engineering thermoplastics poly(arylene ether)s, both ketones<sup>4</sup> and sulfones,<sup>5</sup> are an outstanding family of materials that display excellent mechanical performance coupled with good thermal stability and heat resistance to loss of properties. Poly(arylene ether ketone)s are usually crystalline and thus are resistant to solvent attack; this makes them ideal for aerospace applications. They possess high moduli, are tough and wear resistant, and display low flammability.  $T_{\rm g}$ s for poly (ether ketone)s range from 100 to 200 °C and  $T_{\rm m}$ s from 300 to >400 °C. They can be processed at temperatures as high as 400 °C because of their excellent thermo-oxidative stability, and use temperatures can exceed 200 °C. However, in spite of the importance of heterocyclic polymers aforenoted, only a few examples of poly(arylene ether)s incorporating aromatic heterocyclic moieties have been reported.<sup>6</sup>

#### **Reissert Compounds**

Reissert compounds,  $\alpha$ -(acylamino)nitriles, were discovered in 1905 by Reissert.<sup>7</sup> Various nitrogen heterocycles, such

Correspondence to: H. W. Gibson (E-mail: hwgibson@vt.edu)

Journal of Polymer Science Part A: Polymer Chemistry, Vol. 49, 3842-3851 (2011) © 2011 Wiley Periodicals, Inc.

high molecular weight polymers, which was subsequently realized. @ 2011 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 49: 3842–3851, 2011

**KEYWORDS**: heteroatom-containing polymers; isoquinoline; polycondensation; poly(ether ketones); poly(ether sulfones); Reissert compounds

as pyridine, quinoline, benzimidazole, and phenanthridine, formally add an acyl cyanide across a carbon-nitrogen double bond to produce these derivatives.<sup>8</sup> Reissert compounds can be prepared by several protocols.<sup>7,9-11</sup> The isoquinoline Reissert compounds, **1** (Scheme 1), are the most studied cases.

The acidic proton alpha to the cyano group in Reissert compounds governs much of their chemistry.<sup>8</sup> Reissert anions react with aldehydes to form esters **2** via an intramolecular rearrangement driven by rearomatization (Scheme 1).<sup>8,12</sup> Hydrolysis of the esters affords the corresponding secondary alcohols **3**. This condensation process can be carried out with phenyllithium in ether-dioxane,<sup>8,12(a-c)</sup> with sodium hydride in dimethylformamide<sup>12(d,e)</sup> or under phase transfer conditions with 50% sodium hydroxide/acetonitrile; in the latter case, mixtures of the ester (**2**) and alcohol (**3**) or one of them exclusively result, depending on the reaction time and temperature.<sup>13,14</sup>

The anions react with alkyl halides, forming 1-alkyl derivatives **4**, whose basic hydrolysis affords 1-alkylisoquinolines (**5**) through rearomatization (Scheme 2).<sup>8,12(d),15,16</sup> An intramolecular rearrangement in the absence of an electrophile converts the Reissert anion into ketone **6**.<sup>8,12(d),15</sup> The tendency to undergo rearrangement versus alkylation depends on the nature of the acyl group (Scheme 3).<sup>16</sup>

#### **RESULTS AND DISCUSSION**

In view of the impressive properties of poly(arylene ether)s on the one hand and N-heterocyclic polymers on the other, the combination of these two classes of materials via Reissert compound chemistry was the objective of the work reported herein. This effort constituted a continuation of our

<sup>\*</sup>Present address: Dow Chemical Company, Freeport, Texas 77541.



SCHEME 1 Formation of the anion of an isoquinoline Reissert compound 1 and its reaction with an aldehyde to form the ester 2, which can undergo hydrolysis to the alcohol 3.

applications of Reissert compounds in polymer chemistry  $^{12(e,f),12(e),17-19}$  in addition to our interest in the stereochemistry of these compounds.<sup>20</sup>

## Difunctional Isoquinoline Monomers Activated Fluoroketone Phenol (AB) and Bisphenol (AA) Monomers

The initial target functionalities were activated fluoroketone phenol and diphenolic monomers for poly(ether ketone)s<sup>4</sup> and poly(ether sulfone)s.<sup>5</sup> The first step involved the synthesis of 4-substituted isoquinolines. This reaction followed the method reported<sup>21</sup> by Minter and Re as adapted by us earlier.<sup>22</sup> *p*-Benzyloxybenzaldehyde<sup>23</sup> on reaction with isoquinoline yielded the corresponding 4-substituted isoquinoline product **7** in quantitative yield (Scheme 4). Formation of the Reissert compound **8** from this 4-substituted isoquinoline via the methylene chloride/water two-phase method proceeded in a yield of 89%.

This next step in the arylene monomer synthesis was condensation of the Reissert compound with aldehydes to yield the secondary alcohols. Reactions of **8** with *p*-benzyloxybenzaldehyde and *p*-fluorobenzaldehyde yielded the expected alcohols **9** (100%) and **10** (91%), respectively, by condensation in 50% NaOH (Scheme 4).

Concomitant oxidation of the benzylic alcohols and the methylene units to carbonyls was carried out to make the resulting polymers more rigid along the backbone and remove the labile benzylic hydrogens, and in the fluoro compound activate it toward nucleophilic aromatic substitution. Sodium dichromate in refluxing glacial acetic acid (i.e., pyridinium chloro-



**SCHEME 2** Reaction of the anion of an isoquinoline Reissert compound with an alkyl halide to form **4**, which can be hydrolyzed under basic conditions to a 1-substituted isoquinoline **5**.

chromate) worked well for oxidation of the alcohol moiety, but the presence of the methylene signals at 5.2 ppm in the NMR spectrum of the product indicated that the benzylic methylene moiety was not oxidized. However, the use of manganese dioxide ( $MnO_2$ ) in refluxing benzene with a Dean-Stark trap<sup>22</sup> provided good yields of the diketones **11** (92%) and **12** (78%) from **9** and **10**, respectively (Scheme 4).

The last step in the heteroarylene ether monomer synthesis was deprotection of the benzyl ethers. Refluxing the dibenzyl ether **11** in HBr/acetic acid afforded the bisphenol **13** in quantitative yield. Similar treatment of the fluoro-benzyl ether **12** in HCl solution yielded AB monomer **14** in 96% yield (Scheme 4).

## AB<sub>2</sub> Monomer Containing Two Carboxylic Acid Moieties and an Alcohol Moiety

Methyl *p*-formylbenzoate on reaction with isoquinoline yielded the corresponding 4-substituted isoquinoline product **15** in an unoptimized yield of 40% (Scheme 5). Formation of the Reissert compound **16** from this 4-substituted isoquinoline via the methylene chloride/water two-phase method proceeded in an 85% yield. The 4-(*p*-carbomethoxy) Reissert compound **16** using the NaH/*N*,*N*-dimethylformamide (DMF) protocol in the condensation reaction with methyl *p*-formylbenzoate yielded ester **17** in 77% yield. Compound **17** can be hydrolyzed to give the dicarboxy alcohol compound **18**, an AB<sub>2</sub> type monomer for formation of hyperbranched heterocyclic polyesters.

### Other AA and AB Monomers

Here, it is appropriate to point out that the carboxy phenol (AB) monomer **21** could be readily prepared in high yield



**SCHEME 3** Rearrangement of an isoquinoline Reissert anion to a 1-acylisoquinoline **6**.



**SCHEME 4** Synthesis of AA monomer **13** and AB monomer **14**. Isoquinoline is converted to the 4-benzyl derivative **8**, which is converted to the Reissert compound **9**. Via its anion, compound **9** is converted to the alcohols **9** and **10** by condensations with *p*-benzyloxybenzaldehyde and *p*-fluorobenzaldehyde, respectively. Oxidations of **9** and **10** lead to the diketones **11** and **12**, whose deprotection affords **13** and **14**, respectively.

from Reissert compound **16** and *p*-benzyloxybenzyl chloride via intermediates **19** and **20** (Scheme 6), in the manner of conversion of **1** to **5**. Similarly, by the reaction of the anion of Reissert compound **16** with methyl *p*-bromomethylbenzoate, diacid (AA) monomer **23** can be readily accessed via intermediate **22**.

# Preliminary Studies of Efficiency of Reissert Reactions for Polymerization

### Model Studies: Monofunctional Reissert Compound with Monofunctional Alkyl Halides

To determine if the polymerization of bis(Reissert compound)s with dihaloalkanes via the anions was feasible, alkylation of the isoquinoline Reissert compound **1**,  $R = C_6 H_5$ with butyl halides was examined using the NaH/DMF method to form the 1-butylated Reissert compound (4, R = $C_6H_5$ ,  $R' = n-C_4H_9$ ; Scheme 2). This compound had been made previously, but by using a large excess of the butyl halide.<sup>12(d)</sup> Because step-growth polymerizations are carried out at exactly 1:1 stoichiometry, this study was essential to determine whether a quantitative yield could be obtained at this stoichiometry, thus insuring a high degree of polymerization (DP) according to the Carrothers equation: DP = 1/(1 - p), in which p is the fraction of conversion to the desired product. The first exercise was to determine the best halide to use. The bromide gave the highest yield (99.5%) in 2 h. Butyl chloride reacted slowly in this time frame (2 h) and the product was very crude, probably contaminated with the rearrangement product, 1-benzoylisoquinoline (6, R  $= C_6H_5$ ), as a result of the competitive rearrangement process; the yield was 59%. Butyl iodide reacted much faster (30 min) than the other two compounds, but there was a low yield (68%), probably due to elimination promoted by the basic conditions.

#### Model Studies: Monofunctional Reissert Compound with Difunctional Alkyl Halide

Next in the model study was the reaction of 2 equiv of the isoquinoline Reissert compound  $\mathbf{1}$ ,  $R = C_6H_5$  with an alkylene dibromide, in this case 1,10-dibromodecane. If the resulting dimer  $\mathbf{24}$  could be formed in 100% yield, it could be safely assumed that the condensation of dihaloalkanes with bis(Reissert compound)s is, in general, a feasible polymerization protocol. The reaction, in fact, did proceed to afford a quantitative yield of the dimer  $\mathbf{24}$  (Scheme 7).

### **Preliminary Polymerization Results**

The polymerization of bis(Reissert compound)  $25^{17(a)}$  with 1,10-dibromodecane was performed by the NaH/DMF method (Scheme 8). The rather rigid bis(Reissert compound) was not very soluble, requiring 15 mL of DMF per gram. It was postulated that maybe as the anion formed, it would become soluble, thereby enabling the bis(Reissert compound) to totally dissolve over a period of time. However, this was not the case: throughout the polymerization reaction, the bis(Reissert compound) could be seen floating in solution. After workup, low molecular weight polymer **26** was obtained (Table 1). The low molecular weight was



**SCHEME 5** Synthesis of AB<sub>2</sub> monomer **18**. Isoquinoline is converted to the 4-benzyl derivative **15**, which is converted to the Reissert compound **16**. Via its anion, compound **16** is converted to the ester **17** by condensation with *p*-carbomethoxybenzaldehyde. Hydrolysis of **17** will produce **18**.



**SCHEME 6** Proposed syntheses of AB monomer **21** and AA monomer **23**. Reissert compound **16** via its anion is reacted with *p*-benzyloxybenzyl chloride to form **19**, whose basic hydrolysis will produce **20**. The latter on deprotection will yield **21**. Reaction of **16** with *p*-carbomethoxybenzyl bromide will produce diester **22**, which on basic hydrolysis and acidification will afford **23**.

attributed to the insolubility of starting monomer in DMF and the resultant stoichiometric imbalance in solution.

Polymerization of the more flexible and hence more soluble  $(CH_2)_{10}$  bis(Reissert compound)  $27^{17(a)}$  with 1,10-dibromodecane and 1,5-dibromopentane also led to polymers **28** with low intrinsic viscosities (Scheme 9, Table 1). The n = 10 polymer **28a** did show promise with its intrinsic viscosity of 0.109 g/dL, but the low molecular weights of **28a** and **28b** were further evidenced by the brittle nature of their films cast onto Teflon from chloroform solution.

The most probable reason for the low molecular weights of **28a** and **28b** is rearrangement of the Reissert anion. Monomeric benzoyl Reissert compounds are known to rearrange (Scheme 3) and sometimes this rearrangement reaction is preferred over alkylation.<sup>16</sup> Thus, the rearrangement could be expected in the polymerization reactions of the bis(Reissert compound)s with dihaloalkanes, especially as the substrates are consumed and the rate of alkylation slows, and this would alter the stoichiometry and lead to low molecular weight.

We previously found that isoquinoline Reissert compound **1**,  $R = C_6H_5$  had a strong tendency to rearrange rather than alkylate, whereas the Reissert compound **29** from *ortho* toluyl chloride was alkylated in good yield.<sup>16</sup> In fact, even in the absence of an electrophile, the anion from the *o*-toluyl Reissert compound **29** did not rearrange. In this study, the reaction of the *o*-toluyl Reissert compound **29** with *n*-butyl bromide at exactly 1:1 stoichiometry afforded a quantitative yield of the expected product **30** (Scheme 10). Condensation of **29** with 1,5-dibromopentane at exactly 1:1 stoichiometry afforded a quantitative yield of the expected product **31**.

Subsequently, the use of 4,4'-coupled *o*-toluyl bis(Reissert compound) **32** (Scheme 11) in polymerization with dialde-

hydes produced polyester **33c** with high molecular weight (Table 1), substantiating the fact that the *o*-toluyl derivative is significantly less prone to rearrange than the benzoyl analog.<sup>19</sup> Indeed, the benzoyl analog **27** produced polymers **33a** and **33b** of lower molecular weight because of the competitive rearrangement process; in fact, the initially isolated sample of **33a** exhibited a very broad molecular weight distribution (MWD, Table 1), presumably because the rearrangement destroyed the reactive anionic end group and replaced it with the unreactive phenyl ketone moiety, as illustrated in structure **34** (Scheme 12), and upset the stoichiometric balance of the monomers. Fractionation did produce a sample with a reasonable MWD (Table 1).

#### CONCLUSIONS

Through the chemistry of Reissert compounds several new heterocyclic monomers and monomer precursors were prepared. These new monomers will be useful for the synthesis of heterocyclic poly(arylene ether ketone)s, poly(arylene ether sulfone)s, aromatic polyesters, and other polymers. These studies demonstrate that the versatile chemistry of Reissert compounds provides efficient syntheses of heterocyclic monomers for production of novel new polymers.

#### **EXPERIMENTAL**

#### General

Dichloromethane was obtained from Fisher Scientific and dried over molecular sieves before use. DMF was distilled from calcium hydride and tetrahydrofuran (THF) from sodium/benzophenone before use. Sodium hydride was used as 60 or 80% dispersion in mineral oil as obtained from Aldrich Chemicals. All other solvents were used as received from the vendor. Melting points were determined in a Meltemp II melting point apparatus and are corrected. NMR spectra were recorded on a Bruker 270 MHz instrument, a





SCHEME 8 Polymerization of bis(Reissert compound) 25 with 1,10-dibromodecane, leading to polymer 26.

400-MHz Varian Unity or a JEOL Eclipse 500 MHz machine using tetramethylsilane as an internal standard; the following abbreviations are used: b, broad; s, singlet; d, doublet; m, multiplet; t, triplet; ArH, aromatic hydrogen. FTIR spectra were recorded on a Nicolet MX-I with KBr pellets or films on salt plates. Thermogravimetric analysis (TGA) was done on a Perkin-Elmer 7700 Thermal Analysis System. Differential scanning calorimetry (DSC) was performed on a DuPont 2100 Dual-Sample machine at 10 °C/min. Gel permeation chromatography (GPC) was carried out in THF using either a Waters 150-C equipped with a Viscotek 100 viscometric detector to provide absolute molecular weights via the universal calibration or a Waters Model 590 using a refractive index detector and calibration with polystyrene standards. Mass spectra of compounds 13 and 14 were acquired on an in-house Agilent 6220 Accurate Mass TOF LC/MS Spectrometer. Elemental analyses were performed by Atlantic Microlab, Norcross, GA.

### 4-(p-Benzyloxybenzyl)isoquinoline (7)

A solution of 19.37 g (150 mmol) of isoquinoline, 152 mL (152 mmol) of 1.0 M NaBEt<sub>3</sub>H in THF was stirred for 30 min under N<sub>2</sub>. After *p*-benzyloxybenzaldehyde<sup>23</sup> (32.26 g, 152 mmol) was added, the mixture was stirred for 4 h, cooled to 0 °C and quenched with 320 mL of 0.5 N NaOH and 160 mL of 30% H<sub>2</sub>O<sub>2</sub>, both added dropwise in sequence. The resulting mixture was stirred for 3 h, poured into 2 L of water and stirred overnight. The product was extracted with

ether, which was dried over  $Na_2SO_4$  and evaporated to yield 47 g (100%) of crude product which was recrystallized from ethanol-water, mp 93.5–96.0 °C.

<sup>1</sup>H NMR (270 MHz, CDCl<sub>3</sub>):  $\delta$  4.33, s, 2H, ArCH<sub>2</sub>; 5.00, s, 2H, OCH<sub>2</sub>; 6.85, d (J = 8), 2H, ArH; 7.14, d (J = 8), 2H, ArH; 7.2–7.7, m, 7H, ArH; 7.92, d (J = 8), 1H, H<sub>5</sub>; 7.98, d (J = 8), 1H, H<sub>8</sub>; 8.40, s, 1H, H<sub>3</sub>; 9.18, s, 1H, H<sub>1</sub>. ELEM. ANAL, Calcd for C<sub>23</sub>H<sub>19</sub>NO: C, 84.89; H, 5.89; N, 4.30. Found: C, 84.91; H, 5.92.

### 2-Benzoyl-4-(*p*-benzyloxybenzyl)-1,2-dihydroisoquinaldonitrile (8)

To a three-necked round-bottomed flask fitted with a mechanical stirrer, dropping funnel, and N<sub>2</sub> inlet containing a mixture of 4-(*p*-benzyloxybenzyl)isoquinoline (**7**, 15.67 g, 50 mmol), 9.77 g (150 mmol) of KCN in 30 mL of water and 100 mL CH<sub>2</sub>Cl<sub>2</sub> was added benzoyl chloride (11.6 mL, 100 mmol) over 2 h; vigorous stirring was continued for 9 h, after which water (100 mL) was added and stirring continued for 2 h. The organic phase was washed  $3\times$  with water,  $2\times$ with 5% NaOH,  $1\times$  with satd. NaHCO<sub>3</sub>,  $3\times$  with water,  $3\times$ with 10% HCl, and  $3\times$  with water, dried over Na<sub>2</sub>SO<sub>4</sub> and evaporated. The crude product (20.3 g, 89%) was recrystallized from ethanol: mp 172.5–174.0 °C.

FTIR: amide C=O at 1668.9 cm<sup>-1</sup>. <sup>1</sup>H NMR (270 MHz, CDCl<sub>3</sub>):  $\delta$  3.75, AB q (J = 14), 2H, ArCH<sub>2</sub>; 5.0, s, 2H, OCH<sub>2</sub>; 6.4, bs, 1H, H<sub>3</sub>; 6.55, bs, 1H, H<sub>1</sub>; 6.85, d (J = 8), 2H, ArH;

Polymer	[η] (dL/g, CHCl <sub>3</sub> )	$M_{\rm n}^{\rm a}$ (kDa)	$M_{ m w}{}^{ m a}$ (kDa)	$T_{g}$ (°C)	TGA <sub>5% loss</sub> (°C, Air)
26	-	3.2	12	123	225
28a	0.109	-	-	72	198
28b	0.053	-	-	103	225
<b>33a</b> <sup>19</sup>	0.30	(1.2)	(40.0)	93	200
	0.36 <sup>b</sup>	(31.0) <sup>c</sup>	(69.0) <sup>c</sup>		
<b>33b</b> <sup>19</sup>	0.31	(4.1)	(35.4)	79	260
<b>33c</b> <sup>19</sup>	0.60	22.4	54.7	87	225

TABLE 1 Characterization of Polymers from Reissert Compounds

<sup>a</sup> Values without parentheses are based on GPC using polystyrene standards. Values in parentheses (xx) are absolute molecular weights determined by GPC with an in-line viscometer and the universal calibration.

**33d** derived therefrom possessed a tensile strength of 38 MPa and a maximum strain of 6%.

 $^{\rm c}$  After fractionation of the original sample by two reprecipitations from CHCl\_3 solution by the addition of CH\_3OH.

<sup>b</sup> A film of this sample of **33a** cast from chloroform displayed a tensile strength of 13 MPa and a maximum strain of 3%, whereas the polyol



**SCHEME 9** Polymerization of bis(Reissert compound) **27** with 1,10-dibromodecane and 1,5-dibromopentane, leading to polymers **28a** and **28b**, respectively.

7.15, d (J = 8), 2H, ArH; 7.2–7.7, m, 14H, ArH. ELEM. ANAL, Calcd for C<sub>31</sub>H<sub>24</sub>N<sub>2</sub>O<sub>2</sub>: C, 81.56; H, 5.30; N, 6.14. Found: C, 81.62; H, 5.34.

## 1-[4-(*p*-Benzyloxybenzyl)isoquinolyl] *p*-Benzyloxyphenyl Carbinol (9)

A mixture of 8.70 g (19 mmol) of Reissert compound **8**, *p*benzyloxybenzaldehyde<sup>23</sup> (4.4 g, 21 mmol) and a catalytic amount (0.12 g) of triethylbenzylammonium chloride in acetonitrile (100 mL) was stirred for 30 min at room temperature. A heat gun was used to keep the Reissert compound in solution. Then, 800 mL of 50% NaOH was added and stirring was continued for 45 min. The mixture was allowed to reflux for 30 min, during which time it became viscous and yellow. Water (500 mL) was added and the precipitate was filtered, dried and purified by recrystallization from ethanol: 10.2 g, 100%, mp 190.5–192.5 °C.

FTIR: OH at 3400 cm<sup>-1</sup>, no C=O. <sup>1</sup>H NMR (270 MHz, CDCl<sub>3</sub>):  $\delta$  4.35, s, 2H, ArCH<sub>2</sub>; 5.00, 2s, 4H, OCH<sub>2</sub>; 6.31, s, 1H, OH; 6.9, m, 4H, ArH; 7.0–7.7, m, 16H; 7.96, bd (J = 8), 2H, H<sub>8</sub>; 8.4, s, 1H, H<sub>3</sub>. ELEM. ANAL, Calcd for C<sub>37</sub>H<sub>31</sub>NO<sub>3</sub>: C, 82.66; H, 5.81; N, 2.61. Found: C, 82.57; H, 5.88; N, 2.56.

## 1-[4-(*p*-Benzyloxybenzyl)isoquinolyl] *p*-Fluorophenyl Carbinol (10)

This compound was analogously prepared from Reissert compound **8** and *p*-fluorobenzaldehyde: 91%, mp 157.0-159.0 °C (ethanol). FTIR: OH at 3400 cm<sup>-1</sup>, no C=0. <sup>1</sup>H NMR (270 MHz, CDCl<sub>3</sub>):  $\delta$  4.35, s, ArCH<sub>2</sub>; 5.02, s, 2H, OCH<sub>2</sub>; 6.2, s, 1H, OH; 6.35, s, 1H, CHO; 6.9–7.5, m, 13H, ArH; 7.61, t (J = 8), 1H, H<sub>6</sub>; 7.92 d, (J = 8), 1H, H<sub>5</sub>; 7.97, d (J = 8), 2H, H<sub>8</sub>; 8.40, s, 1H, H<sub>3</sub>. ELEM. ANAL, Calcd for C<sub>30</sub>H<sub>24</sub>FNO<sub>3</sub>: C, 80.16; H, 5.38; F, 4.23; N, 3.12. Found: C, 79.89; H, 5.38; N, 3.19.

### **Oxidation of Alcohols to Diketones: 11 and 12**

A mixture of the alcohol (9 or 10, 5 g), 150 mL of benzene, and 50 g of  $MnO_2$  was allowed to reflux for 2 days using a Dean–Stark trap. The mixture was filtered through Celite and the Celite was washed with chloroform. The  $MnO_2$ /Celite was Soxhlet extracted for 4 days with CHCl<sub>3</sub>. The combined extract was dried over  $Na_2SO_4$  and evaporated to yield the product, which was recrystallized from ethanol.

#### 1,4-Bis(p-benzyloxybenzoyl)isoquinoline (11)

Yield 92%, mp 152.5–155.0 °C. FTIR: C=O at 1655.6 cm<sup>-1</sup>. <sup>1</sup>H NMR (270 MHz, CDCl<sub>3</sub>):  $\delta$  5.15, s, 4H, OCH<sub>2</sub>; 7.0–7.1, m,



SCHEME 10 Reaction of *o*-toluyl Reissert compound 29 with *n*-butyl bromide and 1,5-dibromopentane, leading to 30 and 31, respectively.



**SCHEME 11** Polymers produced from bis(Reissert compound)s by condensation with dialdehydes. Bis(*o*-toluyl Reissert compound) **32** produced high molecular weight polymer **33c** (Table 1).

4H, ArH; 7.4–7.6, m, 4H, ArH; 7.65, t (J = 8), 1H, H<sub>7</sub>; 7.73, t (J = 8), 1H, H<sub>6</sub>; 7.85–8.00, m, 4H, ArH; 8.05, d (J = 8), 1H, H<sub>5</sub>; 8.18, d (J = 8), 1H, H<sub>8</sub>: 8.65, s, 1H, H<sub>3</sub>. ELEM. ANAL, Calcd for C<sub>37</sub>H<sub>27</sub>NO<sub>4</sub>: C, 80.86; H, 4.95; N, 2.55. Found: C, 80.81; H, 4.97; N, 2.51.

## 1-(p-Fluorobenzoyl)-4-(p-benzyloxybenzoyl)isoquinoline (12)

Yield 78%, mp 139.0–140.0 °C. IR: C=O at 1648.4 and 1668.9 cm<sup>-1</sup>. <sup>1</sup>H NMR (270 MHz, CDCl<sub>3</sub>):  $\delta$  5.2, s, 2H, OCH<sub>2</sub>; 7.05–7.95, m, 13H, ArH; 8.0–8.1, m, 3H, ArH; 8.25, d (J = 8), 1H, H<sub>8</sub>; 8.65, s, 1H, H<sub>3</sub>. ELEM. ANAL Calcd for C<sub>30</sub>H<sub>20</sub>FNO<sub>3</sub>: C, 78.08; H, 4.37; F, 4.12; N, 3.04. Found: C, 77.67; H, 4.35; N, 2.99.

#### 1,4-Bis(p-hydroxybenzoyl)isoquinoline (13)

HBr gas was bubbled through glacial acetic acid for 1 h. Then, 1.00 g (1.82 mmol) of the benzyl ether **11** was stirred into 15 mL of this reddish solution and a homogeneous solution resulted. After 15 min, solid (the salt) precipitated out of the solution. On refluxing, this solid went back into solution and after refluxing for 1 h another solid precipitated from solution. The reaction was stopped and the mixture was poured into water. The solution was made just basic (pH = 8) with NH<sub>4</sub>OH and CaCO<sub>3</sub> and filtered, yielding 0.67 g (100%) of crude product. The solid was boiled in deinonized (DI) water and collected by filtration (83%), mp: 155–157 °C.

FTIR: broad OH at 3300 cm<sup>-1</sup>, C=O at 1674 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  6.85–6.90, m, 4H, ArH; 7.64–7.67, m, 6H, ArH; 8.09, d (J = 8 Hz), 1H, H<sub>5</sub>; 8.12, d (J = 8 Hz), 1H, H<sub>8</sub>; 8.62, s, 1H, H<sub>3</sub>. <sup>13</sup>C NMR (DMSO- $d_6$ , 125 MHz):  $\delta$  116.0, 116.1, 125.2, 125.3, 126.5, 127.6, 128.9, 129.2, 131.7, 132.4, 133.4, 133.6, 133.9, 140.7, 159.4, 163.7, 163.8, 192.8, 193.7 (19 peaks as required). HR-ESIMS: Calcd for [M + H]<sup>+</sup>: 370.1079, found m/z, 370.1103 [M + H<sup>+</sup>], error: 6.4 ppm.

## 1-(*p*-Fluorobenzoyl)-4-(*p*-hydroxybenzoyl) isoquinoline (14)

A suspension of dibenzyl ether **12** (209 mg, 0.453 mmol) in 8 mL of HCl (30% aq.) was refluxed for 2 h. The solid did not dissolve. Acetic acid (5 ml) was added. The mixture was refluxed for another 4 h. After the bright yellow solution had cooled, NH<sub>4</sub>OH was added until pH = 8, causing fine powder to precipitate. The resulting suspension was extracted with CH<sub>2</sub>Cl<sub>2</sub> twice. The organic phase was washed with DI water ( $3\times$ ). A silica gel column was used to purify the crude product (CH<sub>2</sub>Cl<sub>2</sub>/MeOH = 98/2, v/v) and pale yellow solid was obtained (161 mg, 96%), mp: 98.1–100.0 °C.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  6.88, d (J = 7.6 Hz), 2H, ArH ortho to OH; 6.98, bs, 1H, OH; 7.17, t (J = 8.6 Hz), 2H, ArH ortho to F; 7.69, dd (J = 8.4, 1.2 Hz), 1H, H<sub>5</sub>; 7.85–7.76, m, 3H, ArH; 8.04, m, 2H, ArH; 8.12, d (J = 8.5 Hz), 1H, ArH; 8.20, d (J = 8.5 Hz), 1H, H<sub>8</sub>; 8.60, s, 1H, H<sub>3</sub>. <sup>13</sup>C NMR (DMSO- $d_6$ , 100 MHz):  $\delta$  115.8, 116.0, 116.2, 125.44, 126.2, 126.6, 129.1, 130.2, 132.3, 132.5, 132.5, 133.3, 133.6, 133.7, 134.8, 140.8, 158.2, 161.7, 165.6, 167.6, 192.8, 193.9 (theor. 19 C, found 23 C; four extra aromatic signals attributed to the presence of the phenolate anion in the polar solvent). HR-ESIMS: Calcd for [M + H]<sup>+</sup>: 372.1036, found m/z, 372.1062 [M + H<sup>+</sup>], error: 6.9 ppm.

### 4-(p-Carbomethoxybenzyl) isoquinoline (15)

This compound was synthesized from methyl *p*-formylbenzoate and isoquinoline by the procedure aforeoutlined for 7: 40%, mp 108.5–111.0 °C (hexane–ethyl acetate).

FTIR: C=0 at 1716.8 cm<sup>-1</sup>. <sup>1</sup>H NMR (270 MHz, CDCl<sub>3</sub>):  $\delta$  3.90, s, 3H, CH<sub>3</sub>; 4.45, s, 2H, CH<sub>2</sub>; 7.25, d (J = 8), 2H, ArH;



**SCHEME 12** The unreactive end-group moiety (in box) resulting from rearrangement of the anion derived from bis(Reissert compound) **27** in its reaction with dibromoalkanes.

7.55–7.70, m, 2H, ArH; 7.8, d (J = 8), 1H, ArH; 7.9–8.05, m, 3H, ArH; 8.45, s, 1H, H<sub>1</sub>; 9.20, s, 1H, H<sub>3</sub>. ELEM. ANAL, Calcd for C<sub>18</sub>H<sub>15</sub>NO<sub>2</sub>: C, 77.96; H, 5.45; N, 5.05. Found: C, 77.79; H, 5.48.

## 2-Benzoyl-4-(*p*-carbomethoxybenzyl)-1,2dihydroisoquinaldonitrile (16)

This Reissert compound was prepared from **15** in a manner analogous to that used to prepare **8**: 85%, mp 145.0–146.0 °C (hexane–ethyl acetate). FTIR: amide C=0 at 1668.9 cm<sup>-1</sup>; ester C=0 at 1716.8 cm<sup>-1</sup>. <sup>1</sup>H NMR (270 MHz, CDCl<sub>3</sub>):  $\delta$  3.85, s, 3H, CH<sub>3</sub>; 3.75–3.95, AB q (J = 14), 2H, ArCH<sub>2</sub>; 6.5, bs, 1H, H<sub>1</sub>; 6.6, bs, 1H, H<sub>3</sub>; 7.25–7.7, m, 11H, ArH; 7.9–8.0, m, 2H, ArH. ELEM. ANAL, Calcd for C<sub>26</sub>H<sub>20</sub>N<sub>2</sub>O<sub>3</sub>: C, 76.45; H, 4.94; N, 6.86. Found: C, 76.34; H, 4.99.

## 1-[4-(*p*-Carbomethoxybenzyl)isoquinolyl] *p*-(Carbomethoxy)phenyl Carbinyl Benzoate (17)

To a solution of 2.25 g (5.5 mmol) of Reissert compound **16** in 25 mL DMF at 0 °C, 0.175 g (5.8 mmol) of 80% dispersion of NaH was added. The solution immediately became red and after 10 min, 0.90 g (5.5 mmol) of *p*-carbomethoxy-benzaldehyde was added. The solution was stirred at 0 °C for 4 h and poured into water. The product was extracted with chloroform; the extract was dried over MgSO<sub>4</sub> and evaporated to yield yellow oil, 2.55 g (77%), which crystallized on standing and was recrystallized from ethanol as off-white solid, mp 177–180 °C.

FTIR: ester C=O at 1723.6 cm<sup>-1</sup>. <sup>1</sup>H NMR (270 MHz, CDCl<sub>3</sub>):  $\delta$  3.88, s, 3H, CH<sub>3</sub>; 3.89, s, 3H, CH<sub>3</sub>; 4.43, s, 2H, CH<sub>2</sub>; 7.4–8.95, m, 19H, ArH and Ar<sub>2</sub>CHO. ELEM. ANAL, Calcd for C<sub>34</sub>H<sub>27</sub>NO<sub>6</sub>: C, 74.85; H, 4.99; N, 2.57. Found: C, 74.42; H, 5.17; N, 2.52.

### 1-Butyl-2-benzoyl-1,2-dihydroisoquinaldonitrile (4: $R = C_6H_5$ , R' = n-Bu)

To a stirred solution of isoquinoline Reissert compound 1, R =  $C_6H_5$  (2.6030 g, 0.01 mol) in 40 mL of dry DMF at 0 °C, the butyl halide (0.01 mol) was added. After 10 min, NaH (0.4 g of 60% dispersion, 0.01 mol) was added and stirring was continued. When the mixture became clear yellow, it was poured onto cracked ice. The product was isolated as white solid and recrystallized from ethanol, mp 105–107 °C (lit. 106–107 °C<sup>12(d)</sup>).

### Dimer 24 from Isoquinoline Reissert Compound 1, $R = C_6H_5$ and 1,10-Dibromodecane

To a stirring solution of 1.301 g (5.00 mmol) of Reissert compound **1**,  $R = C_6H_5$  and 1,10-dibromodecane (0.7502 g, 2.5 mmol) in 15 mL of DMF at 0 °C, NaH (0.24 g of 60% dispersion, 6.0 mmol) was added. The solution immediately turned dark red. After stirring overnight at 25 °C, the solution was poured into 250 mL of water. Filtration yielded 1.657 g (100%) of white solid, a mixture of diastereomers, mp 75.0–85.0 °C. Purification was done using a silica gel column and 50/50 hexane/ethyl acetate.

IR: amide carbonyl at 1655 cm<sup>-1</sup>. NMR (270 MHz, CDCl<sub>3</sub>):  $\delta$  0.8–1.4, m, 16H, CH<sub>2</sub>; 2.25–2.50, m, 4H, diastereotopic CH<sub>2</sub>; 5.7, d (J = 8), 2H, H<sub>4</sub>; 6.5, d (J = 8), 2H, H<sub>3</sub>; 7.1–7.8, m, 18H,

ArH. ELEM. ANAL, Calcd for  $C_{44}H_{42}N_4O_2 \cdot 1/3(C_4H_8O_2)$ : C, 79.11%; H, 6.54%; N, 8.14%. Found: C, 78.90%; H, 6.57%; N, 8.26%.

## Polymer 26 from Bis(Reissert Compound) 25 with 1,10-Dibromodecane

To a 50 mL two-necked round bottom flask fitted with an N<sub>2</sub> inlet and outlet, 1.0000 g (1.606 mmol) of the bis(Reissert compound) 25<sup>17(a)</sup> and 15 mL of dry DMF (distilled from CaH<sub>2</sub> and stored over molecular sieves) were added. The Reissert compound was insoluble but the mixture was stirred at 0 °C for 15 min, at which time NaH (0.135 g, 60% dispersion, 35 mmol) was added. The solution immediately turned dark red. After stirring for 10 min, dibromodecane (0.495 g, 16 mmol) was added with the aid of 2 mL of DMF. After stirring under N<sub>2</sub> for 3 days, the mixture was precipitated into water; the solid was dissolved in DMF and precipitated into methanol: 1.233 g (100%) of white powder. <sup>1</sup>H NMR (270 MHz, CDCl<sub>3</sub>) demonstrated the disappearance of the acidic proton at 6.2 ppm and FTIR showed the amide carbonyl at 1662.1 cm<sup>-1</sup>. GPC:  $M_{\rm n} = 3.2$  kDa,  $M_{\rm w} = 12$  kDa. DSC:  $T_{\rm g} = 123$  °C. TGA: stable to 225 °C in air.

## Polymers 28a and 28b from Bis(Reissert Compound) 27 and Dihaloalkanes

The  $C_{10}$  bis(Reissert compound)  $27^{17(a)}$  (0.8711 g, 1.000 mmol) was dissolved in 8 mL DMF at 0 °C under N<sub>2</sub>. Then, the dibromoalkane (1.000 mmol) was added and the mixture was stirred for 30 min, at which time NaH (0.096 g of 60% dispersion, 2.4 mmol) was added. The solution immediately became viscous and dark red. Stirring was continued for 24-72 h, at which time the brownish mixture was precipitated into water. The solid was collected and precipitated twice into methanol from DMF using a blender. The polymer was dried in a drying pistol. Compound 28a: 73% yield (some spillage),  $[\eta] = 0.109$  dL/g (CHCl<sub>3</sub>, 25 °C). DSC:  $T_g = 72$  °C. TGA: 5% wt. loss @ 198 °C (in air). <sup>1</sup>H NMR confirmed total loss of the acidic proton of the Reissert compound at 6.5 ppm. IR: amide carbonyl at 1662.1 cm<sup>-1</sup>. **28b**: 80% yield,  $[\eta]$ = 0.053 dL/g (CHCl<sub>3</sub>, 25 °C). DSC:  $T_{\rm g}$  = 103 °C. TGA: 5% wt. loss @ 225 °C (in air).

#### 1-Butyl-2-(o-toluyl)-1,2-dihydroisoquinaldonitrile (30)

To a stirred solution of *o*-toluyl Reissert compound **29**<sup>16</sup> (1.000 g, 3.64 mmol) and *n*-bromobutane (0.4988 g, 3.64 mmol) in 20 mL DMF at 0 °C, NaH (0.1602 g, 60% dispersion, 4.00 mmol) was added. The solution immediately turned dark red; stirring was continued for 4 h. The solution was poured into 200 mL of water and the resulting white solid was filtered and dried, 1.22 g (100%). The product was purified by passage through a silica gel column with hexane–ethyl acetate, mp 85.0–87.0 °C.

IR: amide C=O at 1655 cm<sup>-1</sup>. <sup>1</sup>H NMR (270 MHz, CDCl<sub>3</sub>):  $\delta$  0.8, m, 3H, CH<sub>3</sub>; 1.1–1.4, m, 4H, inner CH<sub>2</sub>; 2.15 and 2.6, m, 2H, diastereotopic CH<sub>2</sub>; 2.35, s, 3H, CH<sub>3</sub>; 5.6, d (J = 8), 1H, H<sub>4</sub>; 6.3, d (J = 8), 1H, H<sub>3</sub>; 7.0, t (J = 8), 1H, H<sub>6</sub>; 7.65, t (J = 8), 1H, H<sub>7</sub>; 7.2–7.4, m, 6H, ArH. ELEM. ANAL, Calcd for C<sub>22</sub>H<sub>22</sub>N<sub>2</sub>O·1/4(C<sub>4</sub>H<sub>8</sub>O<sub>2</sub>): C, 78.38; H, 6.86; N, 7.95. Found: C, 78.56; H, 7.14; N, 7.67.

## Dimer 31 from *o*-Toluyl Reissert Compound 29 and 1,5-Dibromopentane

To a solution of *o*-toluyl Reissert compound **29**<sup>16</sup> (1.000 g, 3.64 mmol) and dibromopentane (0.4185 g, 1.82 mmol) in 20 mL DMF at 0 °C, NaH (0.1602 g, 60% dispersion, 4.0 mmol) was added. The initially dark red solution was stirred for 4 h and poured into 200 mL of water; the resulting white solid was filtered and dried: 1.289 g (100%). Purification was achieved using a silica gel column (60/40, hexane/ethyl acetate), mp 95.5–101.5 °C (mixture of diastereomers).

<sup>1</sup>H NMR (270 MHz, CDCl<sub>3</sub>):  $\delta$  1.1–1.4, m, 6H; 2.15 and 2.6, m, 4H, diastereotopic CH<sub>2</sub>; 2.35, s, 6H, CH<sub>3</sub>; 5.6, d (J = 8), 2H, H<sub>4</sub>; 6.2, d (J = 8), 2H, H<sub>3</sub>; 7.05, t (J = 8), 2H, H<sub>6</sub>; 7.6, m, 2H, H<sub>7</sub>; 7.2–7.4, m, 8H, ArH. ELEM. ANAL, Calcd for C<sub>41</sub>H<sub>36</sub>N<sub>4</sub>O<sub>2</sub>: C, 79.84; H, 5.88; N, 9.08. Found: C, 79.65; H, 6.27; N, 8.69.

The authors thank the Donors of the Petroleum Research Fund administered by the American Chemical Society for support of this research through grant 19625 AC7. They are grateful to the National Science Foundation for funds to purchase the Agilent 6220 Accurate Mass TOF LC/MS Spectrometer (CHE-0722638). They extend their gratitude to T. C. Ward and his students for gel permeation chromatography (GPC), DSC, and TGA determinations.

#### **REFERENCES AND NOTES**

**1** (a) Anton, A.; Baird, B. R. Kirk-Othmer Encyclopedia of Chemical Technology; John Wiley and Sons, Inc.: New York, 5th ed.; 2006; Vol. 19, pp 739–772; (b) Palmer, R. J. Kirk-Othmer Encyclopedia of Chemical Technology; John Wiley and Sons, Inc.: New York, 5th ed.; 2006; Vol. 19, pp 772–797; (c) Mathews, A. S.; Ha, C.-S. Curr Trends Polym Sci 2006, 10, 69–76; (d) Bryant, R. G. Kirk-Othmer Encyclopedia of Chemical Technology; John Wiley and Sons, Inc.: New York, 5th ed.; 2006; Vol. 20, pp 264–296.

2 (a) Hoover, M. F. J Macromol Sci Chem 1970, 4, 1327–1417; (b) Vorchheimer, N. Encyclopedia of Polymer Science And Engineering; John Wiley and Sons, Inc.: New York, 1987; Vol. 11, pp 489–507; (c) Guo, X.; Chang, R.-K.; Hussain, M. A. J Pharm Sci 2009, 98, 3886–3902; (d) Williams, S. R.; Long, T. E. Prog Polym Sci 2009, 34, 762–782.

**3** (a) de Abajo, J.; de la Campa, J. G. Adv Polym Sci 1999, 140, 23–59; (b) Critchley, J. P.; Wright, W. W. Heat-Resistant Polymers; Plenum Press: New York, 1983; (c) Hergenrother, P. M. Encyclopedia of Polymer Science and Engineering, 2nd ed.; John Wiley & Sons, Inc.: New York, 1988; Vol. 7, pp 639–665.

**4** Staniland, P. A. In Comprehensive Polymer Science; Allen, G.; Berington, J. C., Eds.; Pergamon Press: New York, 1989; Vol. 5, pp 484–497.

5 (a) Parodi, F. Comprehensive Polymer Science; Pergamon Press: New York, 1989; Vol. 5, pp 561–588; (b) Rao, V. L. Polym Rev 1999, 39, 655–711.

**6** (a) Hergenrother, P. M.; Connell, J. W.; Labadie, J. W.; Hedrick, J. L. Adv Polym Sci 1994, 117, 67–110; (b) Strukelj, M.; Hamier, J.; Elce, E.; Hay, A. S. J Polym Sci Part A: Polym Chem 1994, 32,

193–198; (c) Chan, K. P.; Wang, Y.-F.; Hay, A. S.; Hronowski, X. L.; Cotter, R. J. Macromolecules 1995, 28, 6705–6717; (d) Bottino, F. A.; Di Pasquale, G.; Leonardi, N.; Pollicino, A. J Macromol Sci Pure Appl Chem 1995, A32, 1947–1955; (e) Chan, K. P.; Yang, H.; Hay, A. S. J Polym Sci Part A: Polym Chem 1996, 34, 1923–1931; (f) Yang, H.; Hay, A. S. J Polym Sci Part A: Polym Chem 1996, 34, 2621–2632; (g) Kang, N.; Hill, A. R.; Hay, A. S. J Polym Sci Part A: Polym Chem 2004, 42, 5745–5753; (h) Zhang, Y.; Tian, Y.; Wang, L. J Polym Sci Part A: Polym Chem 2008, 109, 1524–1528; (i) Colquhoun, H. M.; Zhu, Z.; Williams, D. J.; Drew, M. G. B.; Cardin, C. J.; Gan, Y.; Crawford, A. G.; Marder, T. B. Chem Eur J 2010, 16, 907–918.

7 Reissert, A. Chem Ber 1905, 38, 1603-1614.

8 (a) McEwen, W. E.; Cobb, R. L. Chem Rev 1955, 55, 511–549; (b) Popp, F. D. Adv Heterocyclic Chem 1968, 9, 1–25; (c) Popp, F. D. Adv Heterocyclic Chem 1979, 24, 187–214; (d) Popp, F. D. In Quinolines, Part II; Jones, G., Ed.; John Wiley & Sons: New York, 1982, pp 353–375; (e) Cooney, J. V. Heterocyclic Chem 1983, 20, 823–837; (f) Duarte, F. F.; Popp, F. D. Heterocycles 1991, 32, 723–726.

**9** Grosheintz, J. M.; Fischer, H. O. L. J Am Chem Soc 1941, 63, 2021–2022.

**10** (a) Ruchirawat, S.; Phadungkul, N.; Chuankamnerdkarn, M.; Thebtaranonth, C. Heterocycles 1977, 6, 43–46; (b) Bhattacharjee, D.; Popp, F. D. J Heterocyclic Chem 1980, 17, 1211–1212; (c) Veeraraghavan, S.; Bhattarcharjee, D.; Popp, F. D. J Heterocyclic Chem 1981, 18, 443; (d) Kant, J.; Popp, F. D.; Joshi, B. L.; Uff, B. C. Chem Ind (Lond) 1984, 415–416; (e) Pandya, A.; Gibson, H. W. J Org Chem 1993, 58, 2851–2855.

**11** (a) Popp, F. D.; Blount, W. Chem Ind (Lond) 1961, 550; (b) Popp, F. D.; Blount, W.; Melvin, P. J. Org Chem 1961, 26, 4930–4932; (c) Popp, F. D.; Blount, W. J Org Chem 1962, 27, 297–298.

**12** (a) Walters, L. R.; Iyer, N. T.; McEwen, W. E. J Am Chem Soc 1958, 80, 1177–1181; (b) Popp, F. D.; Gibson, H. W. J Heterocyclic Chem 1964, 1, 51–52; (c) Gibson, H. W.; Popp, F. D. J Chem Soc 1966, 1860–1864; (d) Popp, F. D.; Wefer, J. M. J Heterocyclic Chem 1967, 4, 183–187; (e) Gibson, H. W. Macromolecules 1975, 8, 89–90; (f) Gibson, H. W.; Bailey, F. C. J Polym Sci Polym Chem Ed 1976, 14, 1661–1669.

13 Jonczyk, A. Bull Acad Polon Sci 1974, 22, 849-853.

14 Rozwadowska, M. D. Can J Chem 1977, 55, 164–170.

**15** Boekelheide, V.; Weinstock, J. J Am Chem Soc 1952, 74, 660–663.

16 Gibson, H. W. J Heterocyclic Chem 1970, 7, 1169-1172.

**17** (a) Gibson, H. W.; Guilani, B.; Rasco, M. L. Macromolecules 1991, 24, 3700–3703; (b) Gibson, H. W.; Pandya, A.; Rasco, M. L.; Guilani, B.; Hermann, C. K. F.; Leblanc, J.-P.; Jois, Y. H. R. Makromol Chem Macromol Symp 1992, 54/55, 413–421.

18 (a) Gibson, H. W. Macromolecules 1974, 7, 711–712; (b) Pandya,
A.; Gibson, H. W. Polym Bull 1991, 25, 17–24; (c) Pandya, A.; Gibson, H. W. Polym Commun 1991, 32, 134–136; (d) Jois, Y. H. R.; Gibson, H. W. Polym Commun 1991, 32, 168–170; (e) Gibson, H. W.; Guilani, B. Polym Commun 1991, 32, 324–328; (f) Leblanc, J.-P.; Jois, Y. H. R.; Gibson, H. W. Macromolecules 1992, 25, 6752–6755; (g) Leblanc, J.-P.; Gibson, H. W. Macromolecules 1993, 26, 4953–4955; (h) Jois, Y. H. R.; Gibson, H. W. Macromolecules 1993,

26, 6151–6154; (i) Pandya, A.; Yang, J.; Gibson, H. W. Macromolecules 1994, 27, 1367–1375; (j) Jois, Y.; Gibson, H. W. Macromolecules 1994, 27, 2912–2916; (k) Gibson, H. W.; Dotson, D. L. Polymer 1998, 39, 6483–6487; (l) Yang, J.; Gibson, H. W. Macromolecules 1999, 32, 8740–8746; (m) Yang, J.; Tyberg, C. S.; Gibson, H. W. Macromolecules 1999, 32, 8259–8268; (n) Gibson, H. W.; Brumfield, K. K.; Grisle, R.; Hermann, C. K. F. J Polym Sci Part A: Polym Chem 2010, 48, 3856–3867.

**19** Gibson, H. W.; Guilani, B. Macromolecules 1990, 23, 4339–4340.

**20** (a) Gibson, H. W. Tetrahedron Lett 1968, 9, 5549–5551; (b) Gibson, H. W. J Org Chem 1973, 38, 2851–2857; (c) Gibson, H. W.; Berg, M. A. G.; Dickson, J. C.; Lecavalier, P. R.; Wang, H.; Merola, J. S. J Org Chem 2007, 72, 5759–5770.

21 Minter, D. E.; Re, M. A. J Org Chem 1988, 53, 2653-2655.

22 Guilani, B.; Rasco, M. L.; Hermann, C. F. K.; Gibson, H. W. J Heterocyclic Chem 1990, 27, 1007–1009.

**23** Ruenitz, P. C.; Arrendale, R. F.; Schmidt, W. F.; Thompson, C. B.; Nanavati, N. T. J Med Chem 1989, 32, 192–197.