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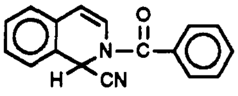
Polymers from Reissert Compounds. 3.[1] Polyesters from Reactions of Dialdehydes with Reissert Compounds Derived from Bis(isoquinolines)

Reissert compounds such as 2-benzoyl-1,2-dihydroisoquinaldonitrile (1) have been known since their discovery in 1905.[2] They are formed from imines of the aromatic type such as isoquinoline[3] or acyclic imines[4] by the formal addition of an acyl cyanide. In practice they are made by reaction of the imine with an acid chloride in the presence of a cyanide source, either in a two-phase system (CH_2Cl_2/H_2O, KCN) or an anhydrous organic medium [CH_2Cl_2, $(CH_3)_3SiCN$].[3]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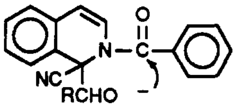
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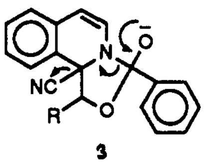
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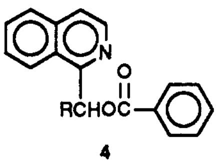
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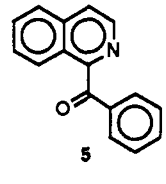
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Reissert compounds owe their well-demonstrated synthetic utility[3,4] to the acidity of the proton α to the cyano moiety. The corresponding conjugate bases can be alkylated or condensed with aldehydes; for example, reaction of the anion of 1 with benzaldehyde produces the ester 4 via cyclization of the initially formed alkoxide 2 and subsequent elimination of cyanide ion from 3, driven by rearomatization.[5] In the absence of an electrophile, Reissert anions may undergo an N to C acyl rearrangement to produce ketones;[6] the anion of 1 yields 1-benzoylisoquinoline (5), for example.

In spite of the utilization of these compounds in organic synthesis, the only incursion of Reissert compounds in polymer chemistry appears to be some polymer modification work in which heterocyclic groups were attached to polymers reported by us some years ago.[7]

In this paper, we describe the utilization of Reissert chemistry, specifically the aldehyde condensation, to produce novel N-heterocyclic polymers.

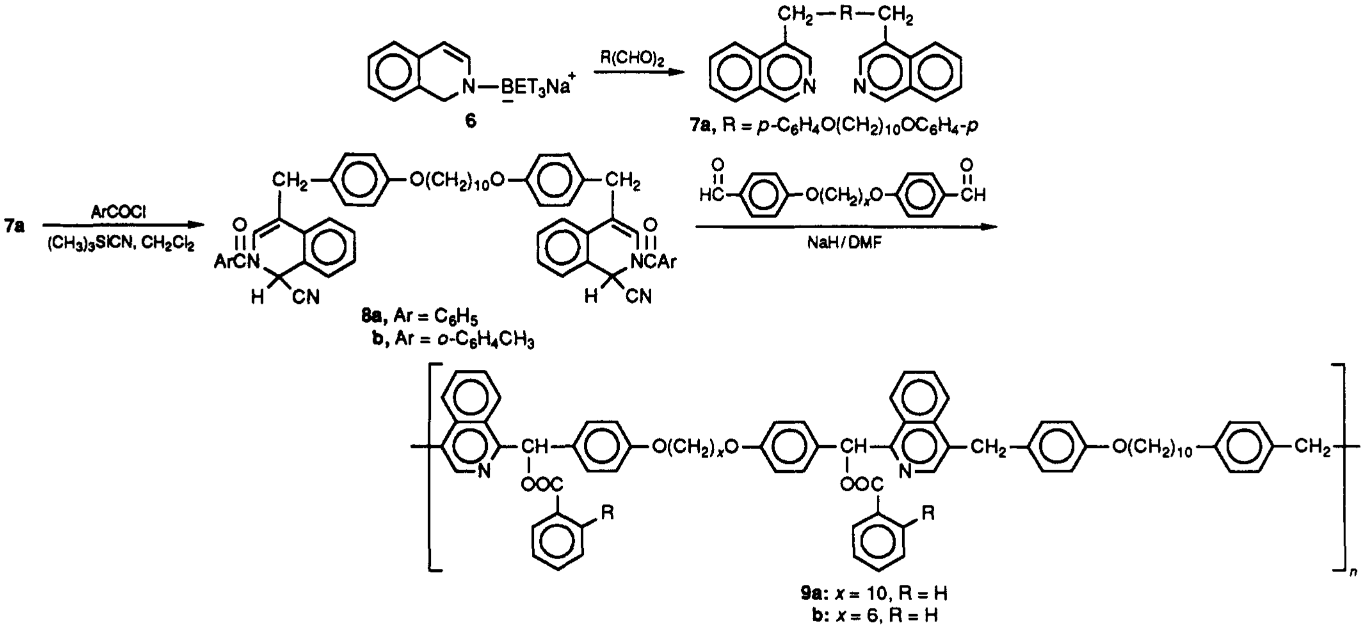
Discussion. While the reactive species are carbanions, the polymerizations are of the step-growth type. Hence, a number of requirements must be met in order to produce high molecular weight products. First, difunctional Reissert compound monomers must be used. Second, the reaction must proceed without side reactions to high conversion. Of course, highly pure monomers and proper stoichiometry are critical as well.

Though there are a number of other potential ways to develop difunctional Reissert monomers, which will be described in due course, for this work we chose to adapt a reaction reported by Minter and Re[8] for 4-alkylation of the enamine 6 (Scheme I; derived in situ from isoquinoline and sodium triethylborohydride) by reaction with aldehydes. By using difunctional aldehydes in this process, we produced a family of novel 4,4-coupled bis(isoquinolines) 7 in good yields from isoquinoline via 6; this work is reported in detail elsewhere.[9] In this work 7a was prepared in 98% yield.

Bis(isoquinoline) 7a was converted to the bis(isoquinoline) Reissert compound 8a in 89% yield by treatment with slight excesses of benzoyl chloride and trimethylsilyl cyanide in CH_2Cl_2 at room temperature for 2–4 days. Although the diastereomers of 8a could not easily be separated, an analytically pure mixture of isomers was produced by column chromatography followed by recrystallization.

The anion of 8a was formed at −15 °C by treatment of a dimethylformamide (DMF) solution with a 55% dispersion of NaH in mineral oil under dry nitrogen. Fifteen minutes later an exactly stoichiometric weight of pure 1,10-bis(*p*-formylphenoxy)decane[9] was added. The solution was warmed to 0 °C and kept there for 12 h followed by 12 h at 25 °C. After isolation, purification by reprecipitation, and drying, polyester 9a exhibited T_g = 79 °C, an ester carbonyl absorption at 1720 cm^{-1} in the infrared (IR) spectrum, and complete loss of the amide carbonyl peak of 7a at 1668 cm^{-1}. The polymer had [η] = 0.31 dL/g in DMF at 25 °C. However, gel permeation

Scheme I



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chromatography (GPC, viscosity detector, THF) provided absolute M_n = 4.1K, M_w = 35K, and MWD = 8.54.

Reaction (−15 °C/addition, 0 °C/12 h, 25 °C/60.5 h) of **8a** with the analogous dialdehyde containing a C_6 spacer rather than a C_{10} spacer, i.e., 1,6-bis(*p*-formylphenoxy)hexane,[9] produced polymer **9b**, which displayed T_g = 93 °C, ester carbonyl at 1721 cm^{-1}, and $[\eta]$ = 0.30 dL/g ($CHCl_3$, 30 °C). GPC (viscosity detector, THF) gave the following absolute values: M_n = 1200, M_w = 40K, and MWD = 33.8! Polyester **8b** was fractionated twice by addition of methanol to a $CHCl_3$ solution to cause phase separation. The fractionated sample of **9b** thus produced had $[\eta]$ = 0.36 dL/g ($CHCl_3$, 30 °C), M_n = 31K, M_w = 69K, and MWD = 2.21.

Polymer **9b** was also synthesized by using *n*-BuLi as base in tetrahydrofuran (THF) at −78 °C (26.5 h). The polymer's IR spectrum was identical with that of the sample prepared with NaH/DMF, but its $[\eta]$ = 0.16 dL/g ($CHCl_3$, 25 °C), the lower molecular weight perhaps due to limited solubility of **8a** in THF (3% at −78 °C) and/or nucleophilic attack of BuLi on the amide carbonyl moiety.

Step-growth polymerizations should ideally, in the absence of side reactions, produce polymers with MWD ≤ 2; i.e., MWD = $1 + P$, where P is conversion. The MWD's above (8.54 and 33.8) therefore suggested to us that a side reaction, namely rearrangement of Reissert anions at chain ends in a fashion analogous to conversion of **1** to **5**, was competing with the polymerization process. Such a unimolecular process will become statistically more significant as the reaction proceeds because of diminution of functional group concentrations, lowering the bimolecular chain extension rate more strongly than that of the rearrangement. In model compounds the rearrangement product **5** displays its carbonyl absorption in the infrared spectrum at ca. 1660–1670 cm^{-1}. Thus, it coincides with the amide carbonyl absorption of the Reissert compound **1**. Moreover, Reissert compounds do not display cyano absorptions in the IR spectra. It is, therefore, not possible to detect this process by infrared spectroscopy on the polymers.

On the basis of this rearrangement hypothesis and the fact we established some time ago that inclusion of an ortho substituent on the *N*-aroyl group essentially prevents the rearrangement,[10] we made the bis(*o*-toluoyl Reissert compound) **8b** in 96% yield. Again, purification by chromatography and recrystallization produced an analytically pure sample, though it was a mixture of diastereomers. Bis(Reissert compound) **8b** was then reacted with 1,10-bis(*p*-formylphenoxy)decane[9] by using the NaH/DMF method to form polymer **9c**, which had T_g = 87 °C and $[\eta]$ = 0.60 dL/g ($CHCl_3$, 25 °C). Polyester **9c** possessed the following absolute values: M_n = 17K, M_w = 52K, MWD = 3.0, determined by GPC in THF. Thus, while some rearrangement apparently still takes place, it is substantially diminished by incorporation of the *o*-methyl substituent.

In this work we have clearly demonstrated the potential of suitably designed Reissert compound monomers in polymerization. We also point out some of the unique features of polymers **9**. First, note that in these polyesters the isoquinoline moieties are part of the polymer's backbone. Second, the pendant esters are precursors of carbinol functionalities. Also noteworthy is the presence of the basic nitrogen, allowing for quaternization. Through manipulation of these molecular components and the spacers (Ar in **8** and R in **7**) a wide range of physical and chemical properties can be achieved by this novel chemistry. We are presently exploring these possibilities.

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References and Notes

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