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Chemical Modification of Polymers. VIII. Reaction of Quinoline Reissert Compounds (1-Acyl-1,2-dihydroquinaldonitriles) with Polymeric Halides and Aldehydes

Harry W. Gibson* and F. C. Bailey

Webster Research Center, Xerox Corporation, Webster, New York 14580.

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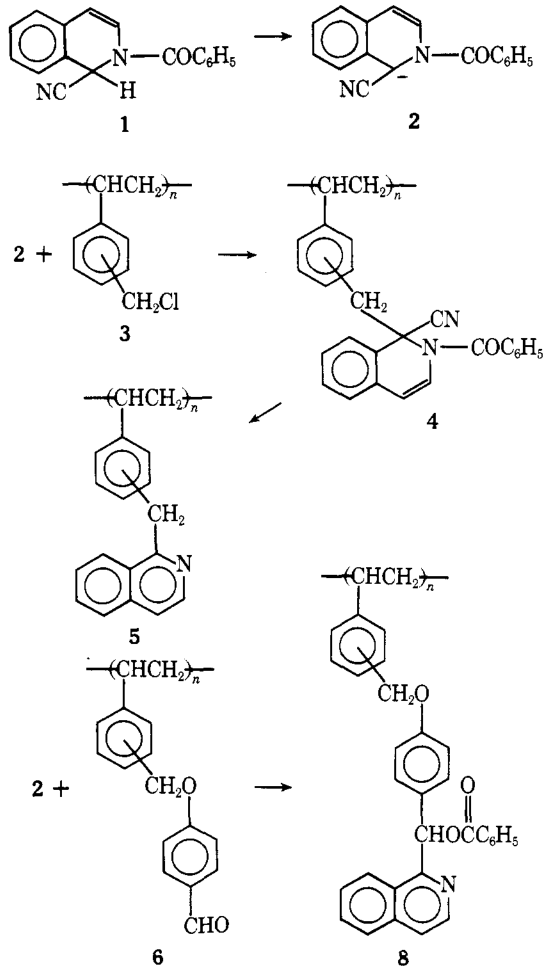
ABSTRACT: The quinoline Reissert compound reacts with poly(vinylbenzyl chloride) to about 70% conversion. Upon hydrolysis to the fully aromatic quinoline the resultant polymer is insoluble, presumably because of cross-linking. A soluble polymer results when the hydrolysis is carried out in the presence of phenol. Because the chloro groups are replaced by phenoxy moieties, the cross-linking is presumably circumvented. The quinoline Reissert compound also condenses with polymeric aldehydes in essentially quantitative conversion. Reactivity patterns of the quinoline Reissert compound vis-á-vis the isoquinoline Reissert compound are rationalized on the basis of the principle of hard and soft acids and bases.

Like other chemists, polymer chemists seek to alter the physical and chemical properties of molecules to optimize them for a particular end use. Traditionally this has been achieved by varying the structure of the monomers which are polymerized. An alternate approach is to modify chemically a pre-formed polymer. Until recently this tack was not followed to any great extent. In recent years, however, the chemical modification of polymers has received increasing attention.[1-4] Much of the work has dealt with insoluble polymers as reagents, growing from the protein synthesis matrix developed by Merrifield.[5]

We, too, have been interested in chemical modifications of polymers[6-12] as a means of controlably altering physicochemical characteristics. Our work has centered on soluble polymers because they are of greater utility for us and because they allow further insight into reaction processes.[10]

This approach to structure variation offers the following advantages: (1) it is possible to synthesize polymers that cannot be prepared by direct polymerization techniques[10] or only with difficulty; (2) a series of structurally related polymers of constant degree of polymerization, namely that of the starting polymer, can be prepared; (3) a series of structurally related polymers of constant tacticity, replicating that of the parent polymer, can be produced; (4) copolymers of desired composition can be prepared by stoichiometric control of sequential reactions.

We have reported the attachment of aza-aromatic moieties to polymers bearing haloalkyl[8,11] and formyl functions.[9,12] The two processes involved the use of an isoquinoline Reissert compound, namely 2-benzoyl-1,2-dihydroisoquinaldonitrile (**1**). This was reacted via the anion **2** with poly(vinylbenzyl chloride) (**3**) to give polymer **4**, which can be hydrolyzed to the aromatic system **5** in essentially quantitative conversion. **2** also reacts with polymeric aldehydes such as **6** to afford polymeric esters such as **8**. **8** was formed

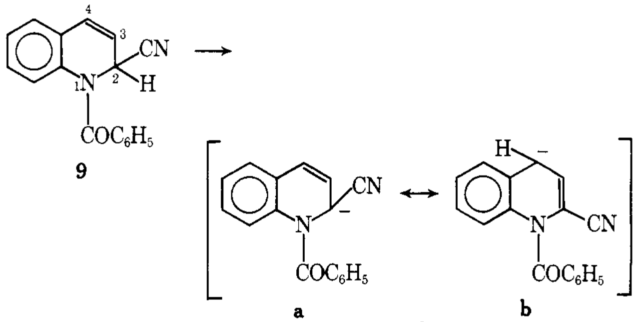


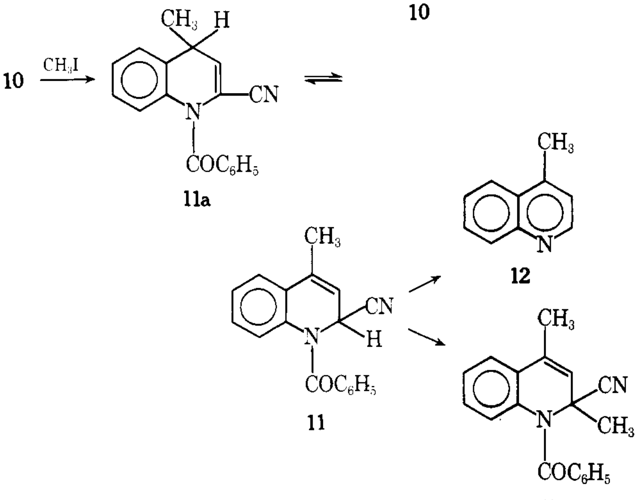
in quantitative conversion. Thus, these reactions afford efficient routes to polymers bearing polycyclic aromatic moieties through the intermediacy of Reissert compounds.

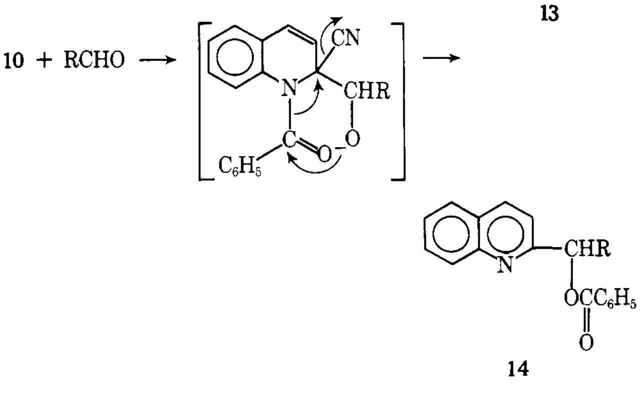
Inasmuch as quinoline derivatives are generally more available than their isoquinoline analogues, the applicability of these processes to quinoline Reissert compounds has been examined. This report is an account of that study.

Discussion

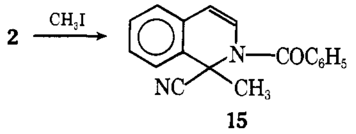
A. Reactivity Patterns of Quinoline vs. Isoquinoline Reissert Compounds. The anion **10** of the quinoline Reissert compound is readily formed by treatment of **9** with strong base. Because of its two resonance structures **10** has the properties of an ambident anion. Thus, for example, it undergoes reaction with methyl iodide to give the 4-alkyl derivative **11** (and/or its tautomer **11a**) which is hydrolyzable to the fully aromatic lepidine (**12**).[13] **11** is also subject to alkylation at the 2 position giving **13**.[13] However, reaction of anion **10** with aldehydes yields the product of attack at the 2 position, namely **14**.[14] As we have seen, like most ambident anions,[15] the reactive position is determined by its co-reactant and reaction conditions.

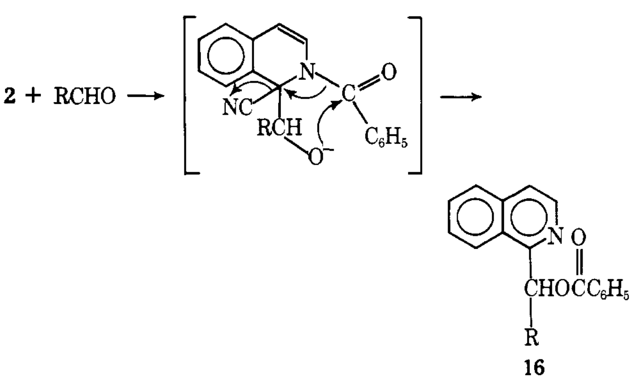




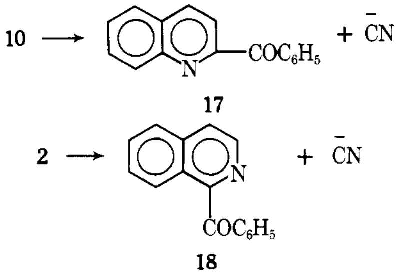


It is also instructive to compare the efficiencies of these processes for anions **2** and **10**. Alkylation of the isoquinoline anion **2** with methyl iodide at −10 °C in ether–dioxane using phenyllithium as the base leads to the isolation of 72% of the alkylated product **15**.[13] The methylation product **11** or its tautomer **11a** from reaction of the quinoline **10** under identical conditions was isolated in only 29% yield.[13] In dimethylformamide (DMF) at room temperature using sodium hydride as base **2** affords 98% of **15**, while **10** yielded a dark messy reaction mixture from which no **11** (and/or **11a**) was isolated.[16] In the case of aldehyde reactions in ether–dioxane at −10 °C using phenyllithium as the base, formation of ester **14** from **10** takes place in up to 28% higher yields than formation of **16** from **2**.[14] The only previously reported attempt to carry out such a transformation in DMF at room temperature using sodium hydride as base with **1** and benzaldehyde gave **16**, R = C_6H_5 in 65% yield[17] via **2**.





In spite of the stability one would expect from contributions of structures **10a** and **10b**, anion **10** rearranges in DMF at room temperature to ketone **17** more readily (92% yield) than **2** rearranges to **18** (56% yield).[17,18] In refluxing xylene, however, **18** is produced in higher yield than **17** (70% vs. 54%).[13]



B. Reaction of Quinoline Reissert Compounds and Poly(vinylbenzyl chloride). The anion **10** was allowed to react with poly(vinylbenzyl chloride) (**3**) in DMF at 0 °C under dry nitrogen under the conditions used to prepare isoquinoline analogue **4**. Elemental analysis of the purified polymer revealed that not all of the chloro groups of **3** had reacted. The extent of reaction is about 70%. The structure **19** (x = 0.3, y = 0.7) is based on the fact that methylation of **10** takes place at the 4 position; no direct structure proof for **19** is available. The ultraviolet spectrum of **19** is similar to that of monomeric analogue **11** (or **11a**).[13] The infrared spectrum (Figure 1) contains the expected carbonyl band at 1675 cm^{-1}. That no dialkylation took place is indicated by the fact that the molecular weight distribution (MWD) is relatively unchanged from **3**, i.e., no cross-linking occurred. Gel permeation chromatographic (GPC) analysis was used to ascertain relative molecular weights. $\bar{A}_n$ and

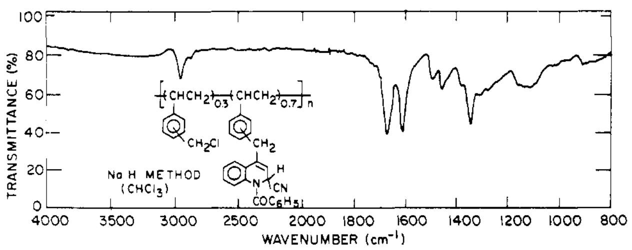
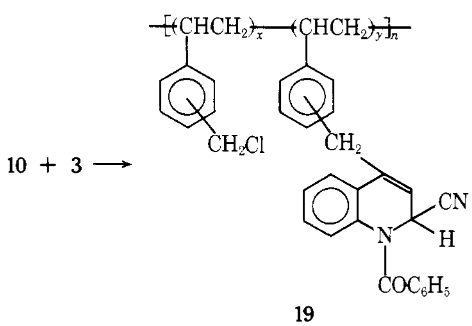


Figure 1. Infrared spectrum of poly{(vinylbenzyl chloride)-*co*-[4-(vinylbenzyl)-1-benzoyl-1,2-dihydroquinaldonitrile]} (**19**, $x = 0.3$, $y = 0.7$) in $CHCl_3$.

$\bar{A}_w$ are the number and weight average molecular sizes in terms of extended chain lengths in ångströms as determined on columns calibrated with polystyrene standards. These are proportional to $\bar{M}_n$ and $\bar{M}_w$, respectively. Thus, $\bar{A}_w/\bar{A}_n$ is taken as a measure of MWD.

Copolymer **19** is soluble in tetrahydrofuran, chloroform, benzene, etc. The next step in the synthetic sequence, however, is alkaline hydrolysis to convert the dihydroquinoline to the fully aromatic structure. When this is done with **19**, an insoluble polymer results. This insolubility could be due to one or both of two possible interactions. First hydrolysis of chloromethyl groups to hydroxymethyl groups could occur under these conditions; the hydroxymethyl groups could lead to insolubility through inter-chain ether formation. Most likely, quaternization by interaction of the now basic nitrogen of the quinoline with chloromethyl moieties in other polymer chains causes cross-linking.



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Two basic means of alleviating this problem are possible: (1) the best method would be to achieve complete conversion in the alkylation of **9** and **10**, i.e., formation of **19**, $x = 0$; (2) alternatively one could remove the problematic chlorines by reaction prior to the hydrolysis step, thus avoiding both cross-linking mechanisms.

To test the possibility that the Reissert compound **9** is less reactive than polycyclic analogues, the phenanthridine Reissert compound (**20**) and the benzo[*f*]quinoline Reissert compound (**21**) were synthesized. Reaction of **20** and **3** using sodium hydride–DMF took place in 90% conversion, yielding polymer **23**, whose ir spectrum (Figure 2) contains a strong carbonyl absorption at 1675 cm^{-1} and is very similar to that of **4**. It should be pointed out that alkylation of the anion **22** from **20** almost certainly takes place at the 2 position due to the presence of the benzo ring. Reaction of **21** and **3** by the same method led to copolymer **24**, i.e., about 50% conversion. Hydrolysis of this polymer led to an insoluble polymer. Thus, the result for **20** is in rather sharp contrast to those for **9** and **21**. The higher yield with **20** may be associated with localization of the negative charge of its anion at the 2 position, thus making it a better nucleophile. To delocalize the charge to the 4 position would disrupt the aromaticity of the 3,4-benzo ring, an energetically unfavorable possibility; the situation is then analogous to that of the isoquinoline Reissert anion **2** in which delocalization is similarly inhibited. In fact phenanthridines may also be considered substituted isoquinolines.

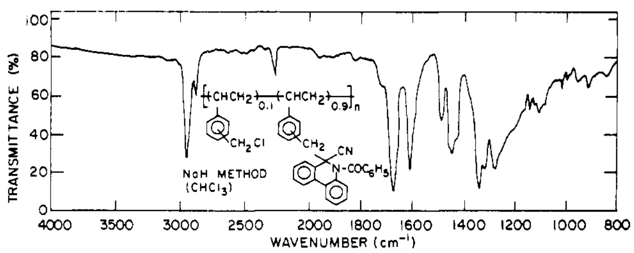
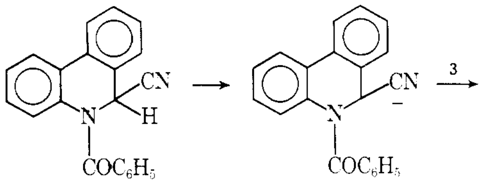
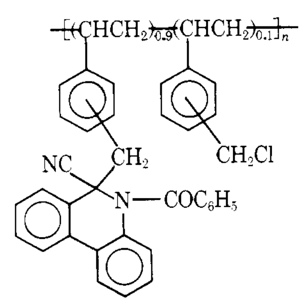


Figure 2. Infrared spectrum of poly{(vinylbenzyl chloride)-*co*-[6-(vinylbenzyl)-5-benzoyl-6-cyano-5,6-dihydrophenanthridine]} (**23**) in $CHCl_3$.



20 **22**



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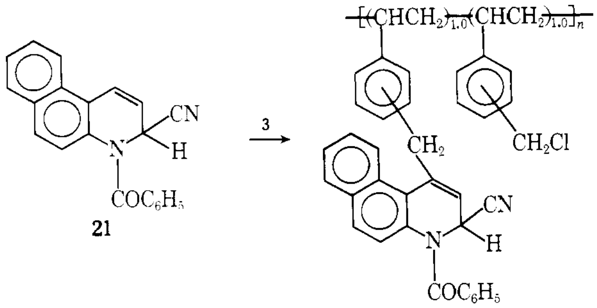

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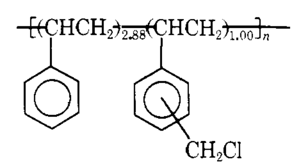
In an attempt to achieve higher conversion of chloromethyl groups, the alkylation reaction using **3** was carried out in tetrahydrofuran (THF) at −30 °C using phenyllithium as the base for formation of **10** from **9**. The reason for this was the reported superiority of this technique[13] for monomeric alkyl halides over the sodium hydride–DMF procedure.[16] However, the conversion was very low (~5%).

One possible explanation for the low conversions is that the pendant dihydroquinoline groups interfere with approaching anion **10** and thus sterically prevent displacement of chloride from the residual chloromethyl groups. To test this possibility a random copolymer (**25**) of styrene and vinylbenzyl chloride of 2.88 to 1.00 mol ratio was subjected to reaction with **9** via its anion **10** using sodium hydride–DMF. The dilution of reactive chloromethyl groups with styrene units would preclude or at least greatly reduce interaction of incoming **10** and pendant dihydroquinoline moieties. However, in spite of this only about 32% conversion occurred, giving a polymer of structure **26**, whose ir spectrum contains a medium intensity carbonyl band at



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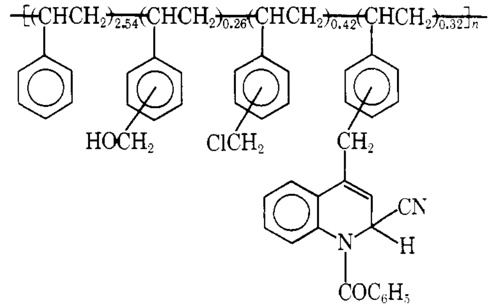

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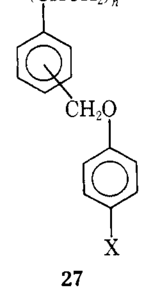
1675 cm^{-1}. Some styrene homopolymer must have been removed by fractionation since the ratio of styrene to other units dropped to 2.54:1.00. Some hydrolysis of chloromethyl to hydroxymethyl also seems to occur. The conversion in this case can probably be raised significantly inasmuch as the ratio of **10** to **25** was 0.91, less than stoichiometric, whereas the ratio of **10** to **3** used previously to achieve 70% conversion (to **19**) was 1.46. Hydrolysis of **26** with sodium hydroxide in water–THF–ethoxyethanol leads to a polymer which is insoluble as expected. The failure to achieve complete conversion in the alkylation of **10** with these polymers left us with the second alternative: to react the chloromethyl groups so that the cross-linking reactions could not occur. One technique which we conceived was to carry this out concurrent with hydrolysis. The reaction that was chosen was the coupling of the chloromethyl group with phenols, as exemplified by conversion of poly(vinylbenzyl chloride) (**3**) to the poly(para substituted phenoxymethylstyrene) (**27**). We previously studied this transformation and found it to be nearly quantitative under conditions similar to the hydrolysis reaction.[7]

The alkaline hydrolysis of copolymer **19**, $x = y = 0.5$, was carried out in the presence of phenol (about three equivalents based on available chloromethyl groups) and as expected successfully led to a soluble polymer. Elemental analysis (high O content) suggests the soluble polymer incorporates ethoxyethanol (cosolvent), but the exact nature of the product was not determined. Similarly hydrolysis–etherification of **26** successfully led to a soluble polymer containing little chlorine, in contrast to the hydrolysis in the absence of phenol mentioned above which left about 2% residual chlorine from the 3% found in starting polymer **26**. Again, high oxygen content suggests incorporation of ethoxyethanol by displacement of unreacted chloride, a reaction similar to the phenol reaction leading to benzyl ether **27**.



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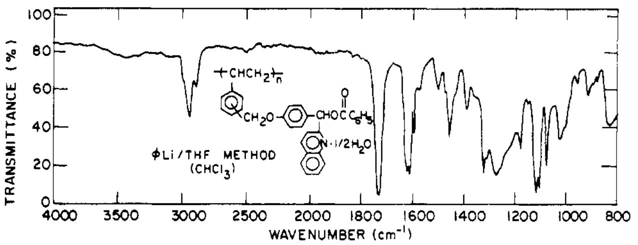


Figure 3. Infrared spectrum of CHCl$_3$ solution of poly[4-(vinylbenzyloxy)phenyl-2-quinolylcarbinyl benzoate hemihydrate] (**28**) prepared by the phenyllithium method.

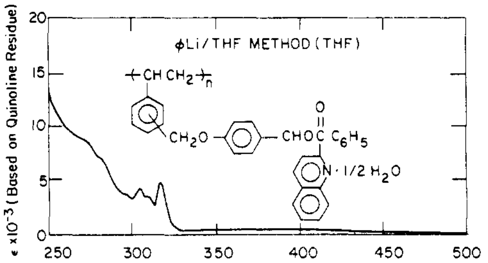
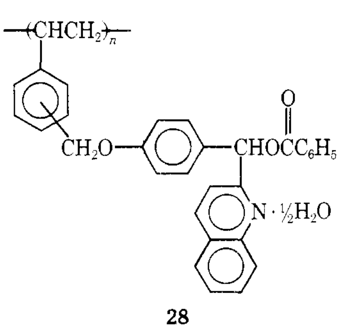


Figure 4. Ultraviolet-visible spectrum of THF solution of poly[4-(vinylbenzyloxy)phenyl-2-quinolylcarbinyl benzoate hemihydrate] (**28**) prepared by the phenyllithium method.

C. Reaction of Quinoline Reissert Compounds and Polymeric Aldehydes. In a previous report the reactions of the isoquinoline Reissert compound **1** (via its anion **2**) and polymeric aldehydes were shown to be essentially quantitative. In extending the reaction to the quinoline series using **9**, high conversion is desirable. However, unlike the reaction with poly(vinylbenzyl chloride) (**3**) incomplete conversion does not lead to ultimate cross-linking as in the hydrolysis of **19**.

The reaction of **6** and **9** was studied under two sets of conditions: NaH–DMF at room temperature and phenyllithium–THF at −30 to −40 °C. Under both conditions the conversion based on elemental analysis was essentially quantitative. By analogy to the product **14** from monomeric aldehydes, the product is poly[4-(vinylbenzyloxy)phenyl-2-quinolylcarbinyl benzoate] (**28**). The product appears to be the hemihydrate on the basis of its analysis and ir spectrum. The ir spectra of the two polymers (see Figure 3 for that of the phenyllithium product) are virtually identical and contain the expected ester carbonyl band at 1740 cm^{-1}, shifted from the 1690-cm^{-1} position in polymeric aldehyde **6**.[7,12] The ultraviolet spectra are identical with respect to λ_{max}. That of the product from the phenyllithium reaction is shown in Figure 4. The uv spectrum of the product from the sodium hydride reaction is less intense by a few percent, perhaps indicating slightly less than 100% conversion; also in the ir spectra the carbonyl band of the phenyllithium product is more intense (relative to the 1620-cm^{-1}



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band) than that of the NaH product. As expected both ir and uv spectra are very similar to those of the isoquinoline analogue **8**.[12]

Thus as expected on the basis of consideration of the reactivity patterns of quinoline Reissert compounds with monomeric aldehydes as opposed to those of their isoquinoline analogues, the reaction of **9** with polymeric aldehydes is just as efficient as those of **1**; both proceed essentially quantitatively. This behavior is in contrast to the reaction with polymeric alkyl halides discussed above.

D. Rationalization of Reactivity Patterns. The reactivity patterns of the Reissert compounds seem to be consistent with the hard and soft acid–base principles of Pearson.[19] Hardness and softness describe the availability and polarizability or delocalization of orbitals. For example a hard base is one with high electronegativity, low polarizability, and is difficult to oxidize, while a soft base has low electronegativity, high polarizability, and is easily oxidized. Solvents can be similarly classified; hydrogen bonding is a hard acid–base interaction as opposed to interactions in aprotic solvents which are soft. Soft nucleophiles react faster with soft electrophiles and vice versa. The rate of a soft–soft reaction is enhanced in a soft solvent. Thermodynamic stability parallels the kinetic effect.

Knowing that methyl iodide is a moderately soft electrophile, one can deduce that the 4 position of anion **10** is softer than the 2 position on the basis of formation of **11** (see above). The formation of **14** via the 2 position of anion **10** also argues for the hard character of this position, although the driving force of aromatization, which is more favorable via this route, may be a significant factor in production of **14**.

Furthermore the relative hardness of the isoquinoline Reissert anion **2** and the quinoline Reissert anion **10** can be assessed on the basis of their relative reactivities. In ether–dioxane the higher yield of **15** (72%) relative to **11** (29%) indicates that **2** is softer than **10**. This is substantiated by the fact that the yield of **15** increases in the softer solvent DMF, while that of **11** decreases. In line with this pattern the harder quinoline anion **10** is more reactive toward aldehydes in ether–dioxane than the soft isoquinoline anion. The rearrangement reactions in DMF which involve intramolecular attack of the anion on the hard amide carbonyl also support the harder nature of **10** vs. **2** on the basis of higher yield of **17** over **18**.

Turning now to the polymeric systems, the same principles seem to apply. The highly efficient reaction of the isoquinoline Reissert anion **2** with poly(vinylbenzyl chloride) is a consequence of the moderate softness of the anion and the chloromethyl group. A contributing factor is very likely the soft environment provided by the polymer backbone itself. In the present case the quinoline Reissert anion **10** is too hard and 70% conversion is achieved in DMF; in the harder solvent THF only ~5% conversion is achieved. The reaction of **10** with the styrene–vinylbenzyl chloride copolymer **25** showed that steric effects are not the key feature. However, the anion **22** of the phenanthridine Reissert compound **20** is much softer apparently, in keeping with its isoquinoline-type structure, and reacts with **3** to higher conversion (90%), giving **23**.

The reactions of both the isoquinoline and quinoline Reissert anions with polymeric aldehydes, which are hard electrophiles, occur in essentially complete conversion. Thus these results mirror those with monomeric aldehydes.

The facts that both Reissert compounds react well with aldehydes and that the isoquinoline is superior with halides mean that on the hardness scale the isoquinoline derivative lies between the halides and aldehydes while the quinoline compound lies closer to the aldehyde, either above or below. The high reactivity of the isoquinoline Reissert anion toward both halides and aldehydes is thus a consequence of its optimal hardness with respect to the two functionalities.

Conclusions

As demonstrated previously with isoquinoline Reissert compounds, the quinoline Reissert compounds also provide pathways to unique polymers. The reaction of the quinoline Reissert compounds with polymeric aldehydes is the more efficient of these processes. The reaction with polymers hearing displaceable halogens seems to be limited to phenanthridine (3,4-benzoquinoline) Reissert compounds, inasmuch as other quinolines give incomplete conversions. Incomplete conversion is undesirable because it leads to cross-linking and insolubility in the hydrolysis to the fully aromatic quinoline polymer; this can be overcome by hydrolysis in the presence of phenols, but the nature of the product is not fully known. The reactivity patterns of Reissert compounds with monomers and polymers can be rationalized in terms of Pearson's hard–soft acid–base principles.

Experimental Section

General. Elemental analyses were performed by Spang Microanalytical Laboratory, Ann Arbor, Mich. Melting points were taken in capillaries and are corrected. Gel permeation chromatography was carried out using 0.25% THF solutions on a Waters Instrument. Ir spectra were recorded on a Perkin-Elmer 237 instrument. Uv spectra were recorded on a Cary Model 15.

1-Benzoyl-1,2-dihydroquinaldonitrile (9). This compound was prepared in 75% yield from quinoline by the method of Popp and Blount:[20] mp 150–153 °C, reported mp 154–155 °C.[20]

Poly(vinylbenzyl chloride) (3). This polymer is the same sample previously reported.[8,11] It has $\bar{A}_n = 507$, $\bar{A}_w = 1068$, MDW = 2.11. It thus has $\bar{M}_n = 3.04 \times 10^4$.

Poly{(vinylbenzyl chloride)*co*-[4-(vinylbenzyl)-1-benzoyl-1,2-dihydroquinaldonitrile]} (19). A. To a stirred solution of 0.76 g (5.06 mequiv) of poly(vinylbenzyl chloride) and 1.90 g (7.31 mmol) of **9** in 30 ml of dry DMF under dry nitrogen at 0 to 5 °C was added 0.34 g (8 mmol) of 57% sodium hydride. After 1.5 h of stirring the mixture was poured into 200 ml of water and filtered. The solid was washed with 1 l. of water. Precipitation from THF solution (30 ml) by addition to 450 ml of hexane gave a tan solid, 1.65 g (100% yield of **19**). The polymer was subjected to three more such precipitations: ir 1660 cm^{-1} (C═O) (Figure 1). The uv spectrum is very similar to that of **13**.[13] Anal. Calcd for 70% conversion, i.e., for **19**, $x = 0.30$, $y = 0.70$: C, 81.16; H, 5.44; N, 6.34. Found: C, 80.50; H, 5.77; N, 6.65. GPC give $\bar{A}_n = 2147$, $\bar{A}_w = 3845$, MWD = 1.79.

B. To a stirred solution of 18.2 g (70.0 mmol) of **9** and 150 ml of dry THF under dry nitrogen at −30 to −40 °C was added an ethereal solution of phenyllithium prepared[21] from 0.97 g (0.140 g-atom) of lithium and 11.3 g (77.0 mmol) of bromobenzene. To the resultant deep red solution of the anion **10** was added a solution of 7.65 g (50.0 mequiv) of **3** in 50 ml of dry THF over 0.5 h. The solution was allowed to warm to −15 to −10 °C, maintained there for 1.5 h, then at 0 to 10 °C for 1 h, then at 20 °C for 2 h, and then poured into 1.8 l. of methanol –1.2 l. of water containing 40 g of sodium chloride. The solid was filtered, dried, and precipitated from THF solution by addition to hexane three times, followed by four times into ethanol and redried to a weight of 5.30 g (69% recovery based on **3**). Anal. Calcd for C_9H_9Cl: C, 70.82; H, 5.94; Cl, 23.23. Calcd for 10% conversion **19** ($x = 0.9$, $y = 0.1$): C, 72.29; H, 5.87; Cl, 20.63; N, 0.90. Found: C, 71.65; H, 5.69; Cl, 21.81; N, 0.69. GPC gave $\bar{A}_w = 591$, $\bar{A}_n = 1248$, MWD = 2.11.

Hydrolysis of 19. To a refluxing solution of 10.0 g (2.66 mequiv) of **19** ($x = 0.5$, $y = 0.5$), 6.0 g of water, 20 g of ethoxyethanol, and 46 g of THF was added 3.15 g (49 mmol) of 87% potassium hydroxide a pellet at a time. After 2 h of refluxing the solution was poured into 800 ml of ice–water and filtered. The solid after water washing and drying weighed 7.4 g and was insoluble in THF and other common solvents. It was washed with THF and ethoxyethanol. Anal. Found: C, 80.83; H, 6.18; N, 4.92; Cl, 0.70.

Phenanthridine Reissert Compound (5-Benzoyl-5,6-dihydro-6-cyanophenanthridine) (20). This compound was prepared in 6% yield by the usual method,[20] mp 140–145 °C (reported mp[22] 140–142 °C, yield 71%).

Benzo[*f*]quinoline Reissert Compound (1-Benzoyl-1,2-dihydrobenzo[*f*]quinaldonitrile) (21). This compound was prepared by the usual method[20] in 75% yield, mp 180–181.5 °C (reported[22] mp 182 °C, yield 94%).

Reaction of Phenanthridine Reissert Compound (20) with Poly(vinylbenzyl chloride) (3). The reaction of 1.18 g (7.75 mequiv) of **3** with 2.95 g (9.5 mmol) of **20** by the NaH method given above for the preparation of **19** followed by precipitation of the THF solution twice from methanol and twice from hexane led to the isolation of a colorless polymer. Anal. Calcd for 90% conversion, i.e., **23**: C, 83.71; H, 5.45; N, 6.33; Cl, 0.93. Found: C, 84.01; H, 5.68; N, 5.73; Cl, 0.93. The uv spectrum had: λ_{max} (ϵ) sh 342 nm (2.24×10^3), 316 nm (4.31×10^3), sh 268 (8.87×10^3), sh 256 nm (11.3×10^3); ir (C═O) 1675 cm^{-1} (Figure 2).

Also isolated from the methanol and hexane precipitant solutions was 6-benzoylphenanthridine (the rearrangement product of **20**), mp 150–154 °C (reported[23] mp 152 °C). Anal. Calcd for $C_{20}H_{13}NO$: C, 84.78; H, 4.63; N, 4.94. Found: C, 84.56; H, 4.18; N, 5.10.

Reaction of Benzo[*f*]quinoline Reissert Compound (21) and Poly(vinylbenzyl chloride) (3). This was carried out by the NaH procedure used for the preparation of **19** using 7.58 g (24.5 mmol) of **21** and 2.27 g (15.2 mequiv) of **3**. The product's (3.84 g, 88% based on 50% conversion, i.e., **24**) ir spectrum had a carbonyl absorption at 1670 cm^{-1}. Anal. Calcd for 50% conversion, i.e., **24**: C, 80.88; H, 5.40; N, 4.84. Found: C, 79.80; H, 5.84; N, 5.15. GPC gave $\bar{A}_n$ = 795, $\bar{A}_w$ = 1956, MWD = 2.46.

Hydrolysis of Copolymer 24. Copolymer **24** was hydrolyzed by the procedure given above for hydrolysis of **19**. The resultant polymer was insoluble and was therefore washed in a blendor four times with water and dried. Anal. Found: C, 75.52; H, 5.74; N, 3.94.

Poly[styrene-*co*-(vinylbenzyl chloride)] (25). This polymer was prepared by free-radical polymerization of styrene and vinylbenzyl chloride in a 3:1 molar feed ratio. The polymer was precipitated three times from benzene into hexane and once from THF into methanol. The resultant white powder had $\bar{A}_n$ = 1105, $\bar{A}_w$ = 2740, MWD = 2.48. Anal. Calcd for $2.88\ C_8H_8 \cdot 1.00 C_9H_9Cl$ C, 85.02; H, 7.14; Cl, 7.85. Found: C, 84.92; H, 6.98; Cl, 7.71.

Reaction of Quinoline Reissert Compound 9 and Poly[styrene-*co*-(vinylbenzyl chloride)] (25). This reaction was carried out in DMF by the procedure given for **19** using 5.20 g (20.0 mmol) of **9** and 9.12 g (22.0 mequiv) of **25**, and yielded 11.0 g of yellow powder. After three precipitations from THF into hexane and three into methanol, the pale yellow powder had $\bar{A}_n$ = 1398, $\bar{A}_w$ = 3313, MWD = 2.38. Anal. Calcd for a styrene to vinylbenzyl ratio of 2.54:1.00, 32% conversion and 26% hydrolysis of chloromethyl to hydroxymethyl (i.e., **26**): C, 86.25; H, 6.89; N, 1.84; Cl, 3.10. Found: C, 86.29; H, 6.87; N, 1.85; Cl, 3.09. Ir (C═O) 1675 cm^{-1}.

Hydrolysis of 26. This reaction was carried out by the procedure given above for hydrolysis of **19** and gave a polymer insoluble in THF and DMF. It was washed in a blendor with water six times and with methanol once. Anal. Found: C, 85.50; H, 6.99; N, 1.51; Cl, 2.28.

Hydrolysis of 19 in the Presence of Phenol. A solution of 1.0 g (2.67 mequiv) of **19**, $x = y = 0.5$, 0.47 g (5 mmol) of phenol, 0.41 g (8 mmol) of 87% potassium hydroxide, 1 ml of water, 3 ml of ethoxyethanol, and 16 ml of dioxane was refluxed for 22 h, poured into 250 ml of ice–water, and filtered. THF solutions of the polymer were precipitated three times from 1% NaOH, twice from water, and once from methanol, leaving 1.02 g of pale yellow polymer $\bar{A}_n$ = 1477, $\bar{A}_w$ = 2742, MWD = 1.86. Anal. Found: C, 82.47; H, 5.79; N, 3.63; Cl, 0.37.

Hydrolysis of 26 in the Presence of Phenol. A solution of 1.50 g (1 mequiv quinoline residue, 1.31 mequiv chloride residue) of **26**, 0.4 g (4 mmol) of 87% potassium hydroxide, 0.24 g (2.5 mmol) of phenol, 1 ml of water, 3 ml of ethoxyethanol, and 20 ml of dioxane was refluxed for 12 h, poured into ice–water, and filtered. The solid was precipitated from THF solutions twice with 1% NaOH and twice with methanol to give 1.32 g of yellow powder, $\bar{A}_n$ = 985, $\bar{A}_w$ = 1793, MWD = 1.82. Anal. Found: C, 87.70; H, 6.69; N, 1.43; Cl, 0.67.

Poly[4-(vinylbenzyloxy)benzaldehyde] (6). This was prepared as previously described[7] from **3**. It had $\bar{A}_n$ = 1193, $\bar{A}_w$ = 2568, MWD = 2.15. Anal. Calcd for $C_{16}H_{14}O_2$: C, 80.65; H, 5.92. Found: C, 80.86; H, 6.38. The uv spectrum (THF) had: λ_{max} (ϵ) sh 328 nm (496), sh 282 nm (18.0×10^3), 273 nm (20.4×10^3); ir (C═O) 1690 cm^{-1}.

Reaction of Quinoline Reissert Compound (9) and (6). A. The reaction of 2.38 g (10 mequiv) of **6** and 3.90 g (15 mmol) of **9** in DMF (42 ml) using NaH was carried out as the synthesis of **19** from **9** and **3** (see above). The crude solid, obtained in quantitative yield (4.72 g), was precipitated three times from THF into 80% ethanol and once into water and dried in vacuo at 36 °C for 18 h (2.46 g). Anal. Calcd for $C_{32}H_{25}NO_3$: C, 81.51; H, 5.35; N, 2.97. Calcd for $C_{32}H_{25}NO \cdot \frac{1}{2}H_2O$: C, 79.98; H, 5.45; N, 2.92. Found: C, 79.90; H, 5.25; N, 2.80. The ir spectrum had a strong 1740-cm^{-1} band (C═O). The uv spectrum (THF) had: λ_{max} (ϵ) 317 nm (5.5×10^3), sh 308 nm (4.8×10^3), 304 nm (5.4×10^3), sh 296, 282, 272 nm. GPC gave $\bar{A}_n$ = 604, $\bar{A}_w$ = 2562, MWD = 4.24.

B. Reaction of 7.80 g (30 mmol) of **9** and 4.76 g (20 mequiv) of **6** in THF using phenyllithium (prepared[21] from 0.088 g-atom of lithium and 32 mmol of bromobenzene) by the procedure for reaction of **3** and **9** (see above) led to the isolation of 8.7 g (87% yield) of nearly white solid after one precipitation from THF solution with 85% aqueous ethanol. After one more precipitation into 85% ethanol and one into water the polymer was dried in vacuo at 36 °C (6.46 g). Anal. Calcd for $C_{32}N_{25}NO_3$: C, 81.51; H, 5.34; N, 2.97. Calcd for $C_{32}H_{25}NO_3 \cdot \frac{1}{2}H_2O$: C, 79.98; H, 5.45; N, 2.92. Found: C, 80.09; H, 5.16; N, 2.90. The ir and uv spectra are shown in Figures 3 and 4, respectively. GPC gave $\bar{A}_n$ = 1226, $\bar{A}_w$ = 2913, MWD = 2.37.

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