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PREPARATION AND CHARACTERIZATION OF POLYMER-BOUND POLYDENTATE A--ETC(U)
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Synthetic procedures for attaching multidentate amines to organic polymers are described. These materials form the basis for the preparation of a wide variety of macrocyclic and chelating ligands that can be covalently attached to polymers. The reaction to produce Schiff base chelates is described and a series of covalently attached metal complexes prepared and identified. These systems have potential as catalysts for organic oxidations.

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# PREPARATION AND CHARACTERIZATION OF POLYMER-BOUND POLYDENTATE AMINES

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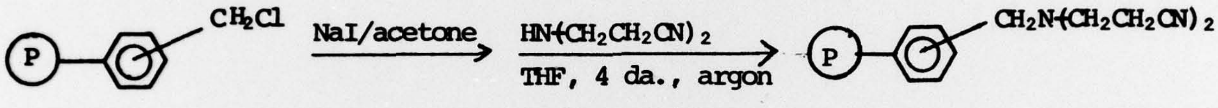
## Summary

Synthetic procedures for attaching multidentate amines to organic polymers are described. These materials form the basis for the preparation of a wide variety of macrocyclic and chelating ligands that can be covalently attached to polymers. The reaction to produce Schiff base chelates is described and a series of covalently attached metal complexes prepared and identified. These systems have potential as catalysts for organic oxidations.

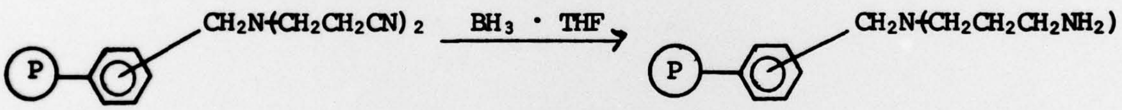
The practical advantages to be gained by immobilizing transition metal catalyst systems have been described.(1) This potential has spurred interest in heterogenizing homogeneous catalysts and in stabilizing coordinatively unsaturated species in the polymer matrix. Preparation of many materials consisting of a monodentate ligand covalently attached to an organic polymer have been described. Leaching of transition metal ions usually occurs from the polymer-bound monodentate ligand and this is the motivation for preparing polymer-bound chelating ligands, for example, a recently described polymer-bound bipyridine material.(2) General reviews(3-4) can be consulted for descriptions of other polymer-bound chelating agents that have been prepared. Our goal is to prepare chelating agents of first row transition metals in the hope that these materials may function as catalysts for catalytic oxidations. Homogeneous commercial processes based on these metals exist.

In view of the key role that the availability of polydentate amines have played in the development of chelate and macrocycle chemistry, we considered the polymer attachment of these amines to be a significant objective. Direct reaction of a chloromethylated polymer with a polydentate amine is not a feasible way to proceed because the different amine groups in the same molecule all have the potential of reacting with the chloromethyl groups of the polymer. The result would be a more highly crosslinked polymer with a variety of amine type functional groups. General preparations of polymeric substrates containing covalently attached polydentate amines as discrete units can be accomplished by the procedure reported here for bis-(3-aminopropyl)amine (DPT).

Macroreticular polystyrene(5) was chloromethylated with chloromethyl ethyl ether using $SnCl_4$ as catalyst.(6) Resin chlorine contents by this method were typically $\sim$5 wt %. Chloromethylated gel resins were prepared by standard aqueous suspension polymerization.(7) Thus styrene (0.76 moles), vinylbenzyl chloride(8) (0.09 moles) and divinylbenzene (0.15 moles) yielded a polymer nominally 15% crosslinked and 9% functionalized (theoretical % Cl = 2.80; found % Cl = 2.72). This polymer was then reacted with NaI in acetone(9) to yield a more reactive polymer and then with a 30-50 fold molar excess of bis-(2-cyanoethyl) amine.



This product was treated with a large excess of $\sim$1 M $BH_3 \cdot THF$ solution followed by 24 hours refluxing.



This functionalized resin, referred to as Ⓟ—DPT (dipropylenetriamine) is obtained after acid decomposition of the boron complexes followed by neutralization of the polymer. The nitrile absorbance in the infrared spectrum of the unreduced polymer was completely eliminated upon treatment with $BH_3 \cdot THF$. Unreacted halomethylated sites were removed by treatment with NaOMe/MeOH. (% N = 2.00, % Cl = 0.05, % I = 0.23). In order to demonstrate the feasibility of the polymer reactions proposed above, tne entire sequence of reactions was carried out in solution using benzyl chloride as the starting material.(10)

This scheme affords a polymer bound triamine capable of reacting with a host of aldehydes, ketones, etc., to generate multidentate Schiff Bases of unambiguous structure. As an example, the above polymer bound-DPT was reacted with salicylaldehyde (SAL) to produce a bright yellow polymer containing the pentadentate ligand SalDPT. The Cu(II) complex (dark green) was easily prepared by soaking the resin in a Cu(II) solution (% Cu = 2.16, ∿80% yield). The ESR spectrum of this polymer-bound Cu(II)SalDPT was similar to that obtained on a frozen glass (toluene-$CH_2Cl_2$) of the analogous copper complex. In addition to Cu(II) (dark green), polymer complexes were prepared just as easily using other metal salts. The colors of these polymer complexes (Mn(II) orange, Co(II) gold, Ni(II) light green, Zn(II) white-light yellow) were identical to the colors of the respective crystalline coordination compounds that were prepared and analyzed.(11) The polymer bound Co(II) SalDPT reversibly coordinated dioxygen. The ESR of the dioxygen adduct was identical to that obtained from a frozen glass (toluene-$CH_2Cl_2$) spectrum of the crystalline complex.(12) These results conclusively show that the desired reactions have been carried out on the chloromethylated polymer.

In a series of analogous experiments, both in solution and on the polymer it was shown that malononitrile can be used to provide covalently attached 1,3-diaminopropane. Also, bis-(2-cyanoethyl)phosphine can be employed in place of bis-(2-cyanoethyl)amine to covalently attach di-(3-aminopropyl) phosphine to polystyrene. Both of these substituted polymers could be reacted with aldehydes, and metal complexes prepared.

Currently under investigation in our laboratory is the use of Schiff base polymer bound Co(II) complexes as catalysts for the oxidation of substituted phenols.(13) The bound complexes are active catalysts and some display enhanced selectivity over the parent complex.

## ACKNOWLEDGEMENT

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