Preparation and Characterization of Polymer-bound Polydentate Amines

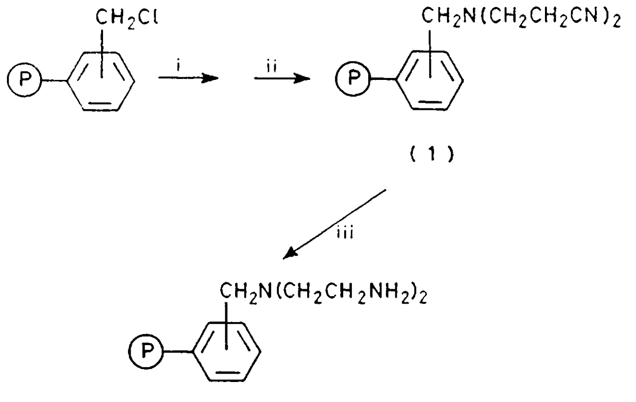
By Russell S. Drago and John H. Gaul
(*Department of Chemistry, University of Illinois, Urbana, Illinois* 61801)

Summary Synthetic procedures for attaching multidentate amines to organic polymers are described, to produce materials which may be used 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 have been prepared and identified.

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 co-ordinatively unsaturated species in the polymer matrix. Preparations of many materials consisting of a monodentate ligand covalently attached to an organic polymer have been described. Since leaching of transition metal ions usually occurs from the polymer-bound monodentate ligand polymer-bound chelating ligands have been prepared: *e.g.*, a polymer-bound bipyridine,[2] and other polymer-bound chelating agents that have been prepared have been reviewed.[3,4] 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.

Polydentate amines have played a key role in the development of chelate and macrocycle chemistry, and so the polymer attachment of these amines would be important. Direct reaction of a chloromethylated polymer with a polydentate amine is not feasible because all the different amine groups in the same molecule may react with the chloromethyl groups of the polymer, resulting in a more highly crosslinked polymer with a variety of amine type functional groups. Polymeric substrates containing covalently attached polydentate amines as discrete units may be prepared by the general procedure reported here for bis-(3-aminopropyl)amine (dpt).

Macroreticular polystyrene (kindly provided by Dr. Carl Brubaker) was chloromethylated with chloromethyl ethyl ether using $SnCl_4$ as catalyst,[5] to give resin chlorine contents typically of *ca.* 5 wt %. Chloromethylated gel resins were prepared by standard aqueous suspension polymerization.[6] Thus styrene (0·76 mol), vinylbenzyl chloride (60% *meta*, 40% *para*; kindly provided by Dow Chemical Co., Michigan) (0·09 mol), and divinylbenzene (0·15 mol) yielded a polymer nominally 15% crosslinked and 9% functionalized (% Cl: calc., 2·80; found, 2·72). This polymer was then treated with NaI in acetone[7] to yield a more reactive polymer and then with a 30—50 fold molar excess of bis-(2-cyanoethyl)amine (Scheme). The product (**1**) was treated with a large excess of *ca.* 1 M BH_3·tetrahydrofuran (THF) solution followed by refluxing for 24 h. The functionalized resin (**2**) was obtained after acid decomposition of the boron complexes followed by neutralization of the polymer. The nitrile i.r. absorption of the unreduced polymer was eliminated upon treatment with



(1)

(2)

SCHEME. i; NaI, Me_2CO. ii; $HN(CH_2CH_2CN)_2$, THF, 4 days, argon. iii; $BH_3{\cdot}THF$.

$BH_3{\cdot}THF$. Unchanged halogenomethylated sites were removed by treatment with NaOMe–MeOH (N, 2·00; Cl, 0·05; I, 0·23%). In order to demonstrate the feasibility of these polymer reactions, the entire sequence was carried out in solution using benzyl chloride as the starting material.†

The polymer-bound triamine (**2**) is capable of reacting with many aldehydes, ketones, *etc.*, to generate multidentate Schiff bases of unambiguous structure. *E.g.* reaction of (**2**) with salicylaldehyde (sal) produced a bright yellow polymer containing the pentadentate ligand saldpt, the Cu^{II} complex of which (dark green) was easily prepared by soaking the resin in a solution containing Cu^{II} (% Cu 2·16; *ca.* 80% yield). The e.s.r. spectrum of this polymer-bound Cu^{II}(saldpt) was similar to that obtained for a frozen glass (toluene–CH_2Cl_2) of the analogous non-polymer complex. Polymer complexes were prepared similarly using other metal salts, and their colours (Mn^{II} orange, Co^{II} gold, Ni^{II} light green, and Zn^{II} white-cream) were identical to those of the respective crystalline non-polymer co-ordination compounds that were prepared independently.[8] The polymer bound Co^{II}(saldpt) reversibly co-ordinated dioxygen. The e.s.r. spectrum of the dioxygen adduct was identical to that for a frozen glass (toluene–CH_2Cl_2) of the crystalline non-polymeric complex.[9] These results show that the desired reactions have been carried out on the chloromethylated polymer.

Analogous experiments, both in solution and on the polymer, showed 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 attach bis-(3-aminopropyl)phosphine covalently to polystyrene. Both these substituted polymers reacted with aldehydes, and metal complexes could be prepared.

We are now investigating the use of Schiff-base polymer-bound Co^{II} complexes as catalysts for the oxidation of substituted phenols.[10] The bound complexes are active catalysts and some display enhanced selectivity over the parent complex.

The authors acknowledge the Office of Naval Research for financial support of this research.

(*Received, 2nd April* 1979; *Com.* 349.)

---

† The identity of the benzyldipropyltriamine (benzyl-dpt) was verified by its i.r. and mass spectra, and C, H, and N analyses.

[1] See, *e.g.*, J. C. Bailar, Jr., *Cat. Rev. Sci. Eng.*, 1974, **10**, 17; C. C. Leznoff, *Chem. Soc. Rev.*, 1974, **3**, 65; C. U. Pittman, Jr. and G. O. Evans, *Chem. Tech.*, 1973, 560; J. I. Crowley and H. Rapoport, *Accounts Chem. Res.*, 1976, **9**, 135; *Progr. Polymer Sci.*, 1977, **5**, 95.

[2] R. J. Card and D. C. Neckers, *J. Amer. Chem. Soc.*, 1977, **99**, 7733.

[3] E. Blasius and B. Brozio, *Chelates in Analyt. Chem.*, 1967, **1**, 49.

[4] E. Tsuchida and H. Nishida, *Adv. Polymer Sci.*, 1977, **24**, 1.

[5] K. W. Pepper, H. M. Paisley, and M. A. Young, *J. Chem. Soc.*, 1953, 4097.

[6] W. P. Hohenstein and H. Mark, *J. Polymer Sci.*, 1946, **1**, 127, 5.

[7] V. V. Korshak, F. V. Rogozhim, and V. A. Davankov, *Izvest. Akad. Nauk S.S.S.R., Ser. khim.*, 1965, **10**, 1912.

[8] Prepared by the procedure reported by L. Sacconi and I. Bertini, *J. Amer. Chem. Soc.*, 1966, **88**, 5180.

[9] B. S. Tovrog, D. J. Kitko, and R. S. Drago, *J. Amer. Chem. Soc.*, 1976, **98**, 5144 and references therein.

[10] See *e.g.*, A. Nashinaga, K. Wathnaba, and T. Matsuura *Tetrahedron Letters*, 1974, **14**, 1291.