This is probably the first example of polyphosphazene preparation by an anionic mechanism (Scheme I). The NMR and GPC results support the formation of predominantly linear high molecular weight poly[bis(trifluoroethoxy)phosphazene] in nearly quantitative yield by a direct and relatively rapid synthesis with negligible amounts of byproducts.

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Synthesis of Porous Polystyrene with Chemically Active Surfaces

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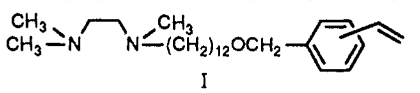
Two principle methods exist for placing chemically active functionalities onto polymer chains:[1] (a) attachment of the groups to a preformed polymer backbone and (b) polymerization of a monomer already bearing the desired group. The latter permits a less random polymer and is the method selected for our work. There is, however, a problem with the "tailored" monomer approach. If only a small percentage of the groups end up on the polymer surface (the remainder being effectively buried), then chemical reactivity would be seriously impaired. This can be especially troublesome for insoluble polymers lacking porosity. It is the purpose of the present communication to describe a strategy for synthesizing high surface area polystyrenes in which most of the chemically active appendages reside on the polymer surface where they can perform catalytically in the solid state.

Our synthesis was based on a recently reported polymerization of a "water pool" system consisting of styrene, divinylbenzene, water, and a surfactant.[2] The surfactant solubilizes water microdroplets ("pools") in the monomer. When the mixture is exposed to AIBN and light, a spongelike polymer is created with surface areas as large as 34 m^2/g. We reasoned that a monomer with the structure $XArCH{=}CH_2$, where X is a polar and chemically interesting moiety, would likely orient at the water-hydrocarbon interface with X immersed in or near the pools (Figure 1). If this occurs, and if the pools ultimately transform into surface irregularities during polymerization,[2] then the polar groups will become fixed to the polymer exterior. The concept is depicted in Figure 1.

Styrene derivative I was used in our experiments. The diamine unit served several purposes. (a) The polar group, especially when



I

protonated, should anchor the monomer to the water pools. (b) The total content of I in copolymers with styrene can be determined easily by elemental analysis of nitrogen. (c) The fraction of diamine on the polymer surface can be measured via the polymer's ability to complex and remove Cu^{2+} from solution. (d) The resulting polymer-Cu^{2+} complex would be a good candidate for phosphate ester catalysis, a subject of considerable practical importance.[3]

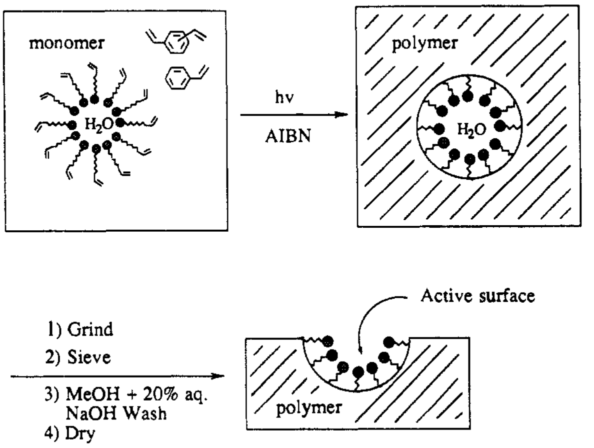


Figure 1. Scheme for producing porous polymers with chemically active surfaces. The shaded circles represent the diamino groups of I which adsorb into or onto the water pools that have been solubilized in the styrene/divinylbenzene solvent.

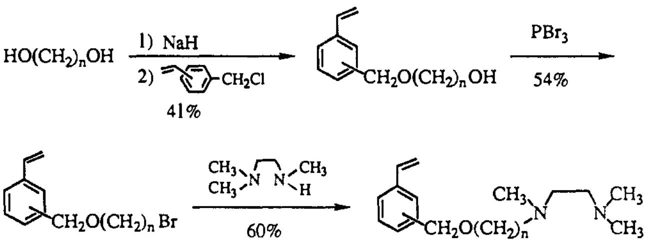


Figure 2. Synthesis of I where $n = 12$. Experiments (not reported) were also carried out on $n = 6$ with no substantial difference in results.

Table I. Water Pool Systems Used To Synthesize Porous Cross-Linked Polymers with High Surface Functionality[a]

polymer	[I], M	surfactant	[surfactant], M	$[H_2O]$, M (vol %)
1	0.10	AOT[b]	0.20	2.0 (3.6)
2	0.20	DDAB[c]	0.10	3.0[d] (5.4)
3	0.30	DDAB	0.15	4.5[d] (8.1)

[a] Prepared in styrene/divinylbenzene (6:4 w/w) with 2% AIBN initiator. [b] Aerosol O.T. 1,4-bis(2-ethylhexyl)sodium sulfosuccinate supplied by Fisher. [c] Dimethyldioctadecylammonium bromide supplied by Kodak. [d] Water contained HCl equimolar with I to generate the amine salt of I.

Monomer I, prepared as shown in Figure 2, was purified chromatographically on alumina (eluting with 7:3 ethyl acetate/methanol) to give a pale yellow oil that was identified (as were all the synthetic intermediates) by elemental analysis and spectroscopic examination. No attempt was made to optimize yields.

Polymerizations were carried out by irradiating for 6 h, in a Rayonet reactor, test tubes containing the three optically clear mixtures listed in Table I. Reacting systems became progressively more opaque with no apparent phase separation. Polymer plugs were removed, ground into powders with a Technilab micromill, sieved, washed with methanol to remove surfactant, and dried thoroughly.

According to BET adsorption analysis[4], polymers **1**-**3** had surface areas of 38, 19, and 8 m^2/g, respectively, compared with only 0.8 m^2/g for copolymer made without water pools being present.[5] Elemental analysis of the three polymers gave 0.128, 0.244, and 0.381 mmol of diamine/g of polymer, indicating total incorporation of I into the polymer matrix. All three polymers

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(4) We thank the Arakawa Chemical Co., Osaka, Japan, for carrying out the BET measurements. The method is based on the area occupied by adsorbed N_2.

(5) Polyethylene single crystals were also shown to have very high surface to volume ratios relative to polystyrene: Gordon, B., III; Butler, J. S.; Harrison, I. R. *J. Polym. Sci. Polym. Chem. Ed.* **1985**, *23*, 19.

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(150–250 mesh) were able to bind Cu^{2+} when stirred for 3 h with an excess of $CuCl_2$ in methanol at 25.0 °C. Quantitative assessment of the metal complexation by two different methods (elemental analysis of the polymer and spectrophotometric analysis of the methanol solution) agreed with each other and showed that 51%, 76%, and 89% of the diamine groups in **1**–**3** were exposed at the surface and at interstices where Cu^{2+} could reach the nitrogens. Since the amount of external diamine dropped to only 0.6% in copolymers formed without surfactant-stabilized water pools but of the same mesh size, the strategy for synthesizing porous polystyrene bearing chemically active surfaces obviously succeeded. The methodology might also be advantageously applied to open cell foams prepared from high internal-phase emulsions recently described in detail by Williams, Gray, and Wilkerson.[6] Potential applications include the development of high-capacity chiral stationary phases, an area we are beginning to explore.

Low levels of copper-coated porous polymer (150–250 mesh) displayed a modest heterogeneous catalysis in the hydrolysis of *p*-nitrophenyl diphenyl phosphate (pH = 8.00, 25.0 °C). For example, 8.0 mg of polymer **1** (representing 2.5×10^{-5} M Cu^{2+} had the polymer been water-soluble) hydrolyzed 2.5×10^{-4} M phosphate ester with a half-life of 2.5 h and a yield of 93%.[7,8] Under the same conditions but without catalyst, the half-life was about 60 h. Since a 10-fold excess of substrate was completely hydrolyzed by the solid catalyst, turnover must have taken place. When the substrate and the "virtual" polymer concentration were reversed from that given above, the substrate was totally and immediately adsorbed from the buffer onto the polymer surface. All attempts to recover adsorbed ester from the polymer, including sonication over dry tetrahydrofuran, furnished only a hydrolysis product, *p*-nitrophenol.

Acknowledgment. This work was supported by the Army Research Office. We thank Dow Chemical Co. for a gift of vinylbenzyl chloride.

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(6) Williams, J. M.; Gray, A. J.; Wilkerson, M. H. *Langmuir* **1990**, *6*, 437.

(7) This represents a 2.5-fold improvement in half-life over the best of the nonporous copper polymers previously described in ref 3.

(8) For lead references on polymer-based catalysts and polymer–copper complexes, see: ref 1.

The First Square-Planar Complex of Cd(II): $Cd(OAr)_2(THF)_2$ Where OAr = 2,6-Di-*tert*-butylphenoxide. A Structure Governed by Two Strong Covalent and Two Weak Dative Bonds

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As a part of our studies of the alkoxides of divalent metals,[1] we have solved the crystal structure of the title compound **1**, $Cd(OAr)_2(THF)_2$ (OAr = 2,6-*t*-$Bu_2C_6H_3O$). The structure of **1** is novel and prompts us to suggest consolidation of a few empirical arguments to rationalize the structures of main-group compounds having datively bound ligands. They are (1) dative bonds to heavier element acceptors are often significantly weaker than the corresponding bonds to lighter congeners, (2) such *weak* dative bonds may be considered "secondary bonds",[2] and (3) secondary bonds do not affect the geometrical arrangement of primary bonds and lone pairs about a central atom.[3] These arguments derive from Alcock's discussion of secondary bonds[2] and Haaland's recent discussion of dative bonds.[4]

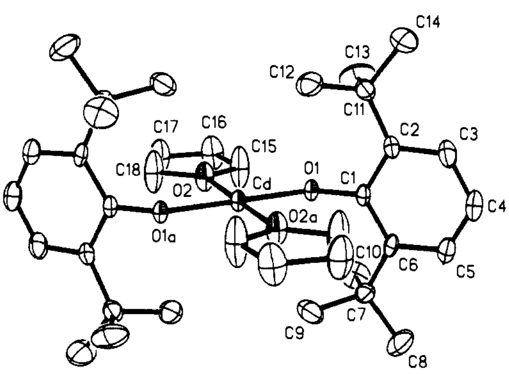

Figure 1. ORTEP of $Cd(OAr)_2(THF)_2$ (**1**, OAr = 2,6-*t*-$Bu_2C_6H_3O$). Hydrogen atoms were omitted for clarity. Cd resides on a crystallographic inversion center. Selected distances (Å): Cd–O(1), 2.058 (4); Cd–O(2), 2.498 (5); O(1)–C(1), 1.349 (7). Selected angles (deg): O(1)–Cd–O(2), 81.8 (2); O(1)–Cd–O(1A), 180.0 (1); O(2)–Cd–O(1A), 98.2 (2); O(2)–Cd–O(2A), 180.0 (1); Cd–O(1)–C(1), 127.6 (4).

Compound **1** was isolated as pale-yellow crystals from THF according to eq 1; a view of the molecular structure is shown in

$$Cd[N(SiMe_3)_2]_2 + 2ArOH \xrightarrow{THF} Cd(OAr)_2(THF)_2 + 2HN(SiMe_3)_2 \quad (1)$$

Figure 1.[5] Two distinctive features are evident: the crystallographically imposed square-planar geometry about Cd(II), which is unprecedented,[6] and the large difference (0.44 Å) between the Cd–O separations for the aryloxide ligand [$Cd–O_{aryloxide}$ = 2.058 (4) Å] and the THF ligand [$Cd–O_{THF}$ = 2.498 (5) Å]. The latter is consistent with a description of the $Cd–O_{aryloxide}$ vectors as normal covalent bonds, and the $Cd–O_{THF}$ vectors as dative bonds.[4] According to Haaland, dative bonds are generally less than half the strength of normal covalent bonds for a given atom pair and may be distinguished by significant differences in bond distances.[4]

The trans, square-planar geometry of **1** is not as readily justified. Square-planar geometries are typically enforced by $d^{8\pm1}$ configurations and strong ligand fields; on steric grounds, they are disfavored.[7] Ligand-field effects do not exist for main-group compounds, and a tetrahedral or distorted tetrahedral[4] arrangement for **1** is predicted by standard VSEPR arguments. Obviously, other influences must be responsible for the square-planar structure of **1**.

A useful comparison may be drawn to the structure of $Zn(OAr')_2(THF)_2$ (**2**, OAr′ = 2,4,6-*t*-$Bu_3C_6H_2O$), previously determined by Geerts, Huffman, and Caulton.[8] Compound **2** has the expected[4] distorted tetrahedral geometry, and the Zn–O distances involving the aryloxide [$Zr–O_{aryloxide}$ = 1.89 (1) Å] and THF [$Zn–O_{THF}$ = 2.08 (1) Å] ligands differ by only 0.19 Å.

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(2) Alcock, N. W. *Adv. Inorg. Chem. Radiochem.* **1972**, *15*, 1.

(3) Argument 3 is explicit in Alcock's discussion.[2]

(4) Haaland, A. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 992.

(5) Crystal data for **1**: $C_{36}H_{58}O_4Cd$, M_r = 667.2, monoclinic, $P2_1/n$, a = 9.621 (5) Å, b = 11.780 (4) Å, c = 16.032 (9) Å, β = 93.35 (5)°, V = 1813.9 (15) Å^3, T = 295 K, Z = 2, D_c = 1.222 g cm^{-3}, λ(Mo Kα) = 0.71073 Å. Of the 3208 unique intensities measured, 1848 with $F_o > 6.0\sigma(F_o)$ yielded $R(F)$ = 0.0393 and $R_w(F)$ = 0.0458.

(6) The coordination environment about cadmium is square pyramidal (CN 5) in (5,10,15,20-tetraphenylporphinato)cadmium(II) (Cd(TPP)),[6a] and z-out tetragonal (CN 6) in $Cd(TPP)(dioxane)_2$.[6b] A square-planar geometry was claimed in a Schiff-base chelate of Cd(II), but was not verified by a crystallographic determination.[6c] (a) Hazell, A. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1986**, *C42*, 296. (b) Rodesiler, P. F.; Griffeth, E. H.; Ellis, P. D.; Amma, E. L. *J. Chem. Soc., Chem. Commun.* **1980**, 492. (c) Blum, P. R.; Wei, R. M. C.; Cummings, S. C. *Inorg. Chem.* **1974**, *13*, 450.

(7) Huheey, J. L. *Inorg. Chemistry*, 3rd ed.; Harper and Row: New York, 1983; p 470.

(8) Geerts, R. L.; Huffman, J. C.; Caulton, K. G. *Inorg. Chem.* **1986**, *25*, 1803.

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