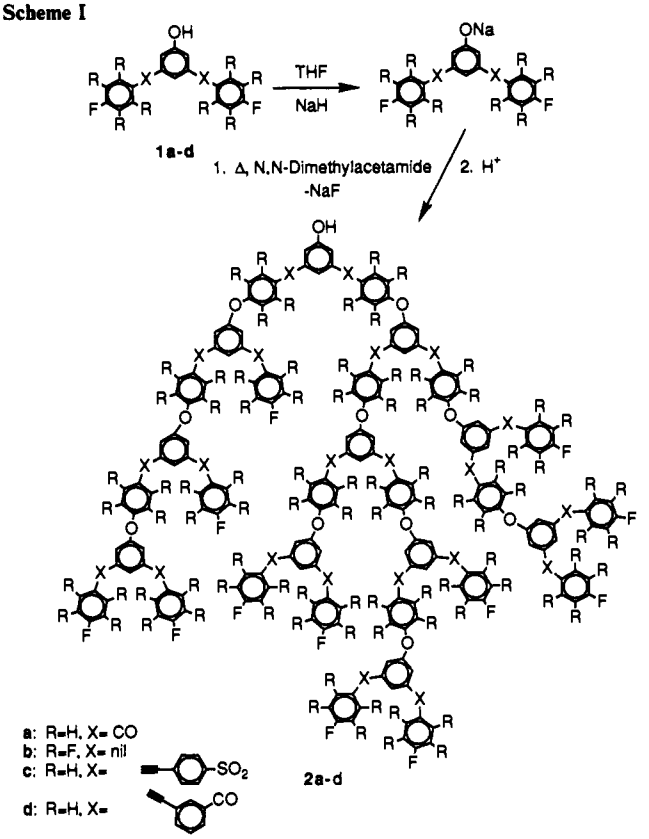
Scheme I



lecular weight polymers. Ideally every polymer molecule should have a single unreacted hydroxyl group and DP + 1 unreacted fluorophenyl groups. If cyclization is the dominant termination process, then the hydroxyl groups will be largely consumed and a polymer molecule will have DP unreacted fluorophenyl groups.

These dendritic macromolecules have high (0.35 g of **2a**/mL of THF at 25 °C) solubilities in typical organic solvents such as $CHCl_3$, THF, and toluene. In addition to size exclusion chromatography, we have characterized the new dendritic macromolecules by ^1H, ^{13}C, and ^{19}F NMR spectroscopies.[11] The spectra of all of the polymers showed resonances corresponding to either C_6H_4F or C_6F_5 terminal groups, which are only slightly perturbed from their positions in the monomers. All other resonances in the NMR spectra were consistent with transformation of phenol and fluorophenyl moieties into diaryl ethers. We have analyzed the ^1H and ^{13}C NMR spectra of the polymers in the hope of determining the degree of branching as described by Frechet et al. but have been unable to do so because of the distance separating the aryl fluorides.[8]

Thermal gravimetric analyses under nitrogen at 10 °C/min showed that all retain >95% of their mass up to 500 °C and have high thermal stability as do linear poly(ether ketone)s and poly(ether sulfone)s. We observe glass transition temperatures (Table I) ranging from 135 to 231 °C but no evidence for melting or crystallization. These T_g's are higher than one might expect for materials that have such large fractions of end groups. The T_g's appear to be independent of molecular weight in the case of polymers **2a** and **2b**, and the T_g for polymer **2c** derived from the most rigid monomer, **1c**, is, as might be expected, higher than the rest.

Table I. Polymerizations in Dimethylacetamide

monomer	conc (M)	yield[a] (%)	M_w[b]	M_n[b]	M_w/M_n[b]	T_g (°C)
1a	0.19	79	11 300	7 410	1.53	140
1a	0.75	85	19 100	9 040	2.11	144
1a	2.2	83	66 600	16 200	4.11	143
1b	0.04	73	29 200	17 300	1.69	152
1b	0.27	82	33 700	20 300	1.66	152
1b	1.0	50	134 000	35 500	3.78	151
1c	0.4	55	38 500	18 800	2.04	231
1d	0.5	66	38 700	8 880	4.36	135

[a] Yield of isolated polymer after one precipitation. [b] Size exclusion chromatography values versus polystyrene standards.

Reaction of AB_2 phenolate monomers containing two aryl fluorides activated by carbonyl, sulfonyl, or tetrafluorophenyl moieties permits the controlled syntheses of high molecular weight dendritic polymers. We are currently studying the physical properties and chemistries of these and related polymers.

Registry No. **1a** (homopolymer), 144812-31-7; **1b** (homopolymer), 144812-33-9; **1c** (homopolymer), 144812-35-1; **1d** (homopolymer), 144812-37-3.

Supplementary Material Available: Listings of analytical data for monomers **1a–d** and details of the general polymerization procedure, size exclusion chromatograms of various molecular weights of polymers **2a** and **2b**, and schemes outlining the syntheses of monomers **1a–d** (7 pages). Ordering information is given on any current masthead page.

(11) Polymer **2a**: ^1H NMR ($CDCl_3$) δ 7.85 (bs, 5 H), 7.68 (bs, 2 H), 7.12 (bs, 4 H); ^{13}C NMR δ 193.1, 165.8 (d, J = 256 Hz), 160.7, 155.9, 140.0, 139.8, 132.7, 131.9, 126.5, 118.0, 115.9 (d, J = 22 Hz); ^{19}F NMR δ −105.2. Anal. Calcd for $C_{20}H_{11}FO_3$: C, 75.47; H, 3.48; F, 5.97. Found: C, 75.41; H, 3.17; F, 5.83. Polymer **2b**: ^1H NMR (THF-d_8) δ 7.30–7.65 (m); ^{13}C NMR δ 159.5, 146.8 (d, J = 246 Hz), 146.6 (d, J = 230 Hz), 143.9 (d, J = 230 Hz), 143.0 (d, J = 264 Hz), 140.0 (d, J = 251 Hz), 134.8, 131.4, 131.0, 129.9, 120.5, 117.9 (t, J = 17 Hz), 116.5 (t, J = 17 Hz); ^{19}F NMR δ −141.6 (m, 4 F), −153.1 (bs, 2 F), −154.2 (bs, 1 F), −161.6 (bs, 2 F). Anal. Calcd for $C_{18}H_3F_{11}O$: C, 53.22; H, 0.74; F, 42.10. Found: C, 52.85; H, 0.79; F, 41.39. Polymer **2c**: ^1H NMR (THF-d_8) δ 7.96 (bs, 8 H), 7.65 (bs, 4 H), 7.57 (bs, 1 H), 7.28 (bs, 4 H), 7.15 (bs, 2 H); ^{13}C NMR δ 166.5 (d, J = 253 Hz), 162.0, 156.7, 143.5, 143.1, 139.0, 137.6, 133.2, 132.2, 131.7, 131.3, 128.7, 128.3, 128.2, 125.8, 124.5, 119.4, 117.5, 117.3, 91.3, 90.2; ^{19}F NMR δ −105.5. Anal. Calcd for $C_{34}H_{19}FO_5S_2$: C, 69.15; H, 3.22; F, 3.22; S, 10.84. Found: C, 68.82; H, 3.17; F, 3.27; S, 10.86. Polymer **2d**: ^1H NMR (THF-d_8) δ 7.95 (bs, 2 H), 7.83 (bs, 4 H), 7.65 (bs, 4 H), 7.58 (bs, 1 H), 7.50 (bs, 2 H), 7.25 (2 H), 7.22 (bs, 2 H), 7.16 (bs, 2 H); ^{13}C NMR δ 193.7, 159.2 (d, J = 254 Hz), 139.33, 133.46 (d, J = 26 Hz), 133.2, 131.5, 130.7, 129.6, 126.1, 123.7, 118.4, 116.2 (d, J = 21.6 Hz), 90.7, 90.6, 89.2; ^{19}F NMR δ −105.0. Anal. Calcd for $C_{36}H_{19}FO_3$: C, 83.39; H, 3.66; F, 3.66. Found: C, 82.27; H, 3.54; F, 3.58.

Catalytic Antibodies from Combinatorial Libraries

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It has been demonstrated that antibodies can be endowed with the catalytic abilities intrinsic to enzymes by hyperimmunization of mice with haptens that mimic stable representations of the transition states of selected reactions.[1] The successful generation of the catalytic antibodies depends on insight into the mechanism of the reaction to be catalyzed, synthesis of a hapten, and induction of a panel of hapten-binding antibodies. While the first two maneuvers are well within the purview of most chemists, the method by which monoclonal antibodies are currently produced is not a procedure which is easily adapted to most chemical laboratories. To overcome this problem, we have developed procedures for cloning the immunological repertoire into *Escherichia coli*.[2] In principle these methods can vastly increase

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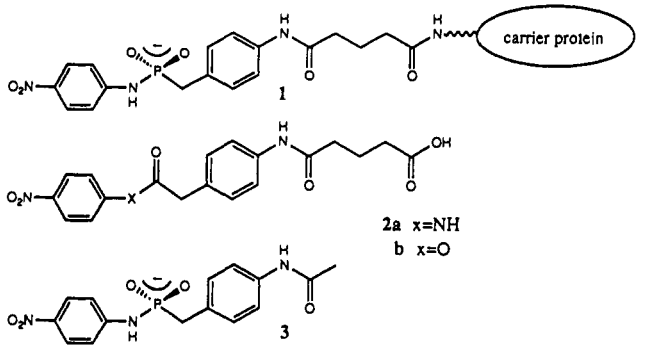

Figure 1. Transition-state analogue phosphonamidate **1** used to induce antibodies capable of hydrolyzing **2**. **3** is an inhibitor of the reaction.

the number of different antibodies which can be studied and in many cases can even bypass the need for immunization.[2,3] However, before these procedures could be generally adopted, it remained to be demonstrated that one could obtain catalytic antibodies from combinatorial libraries. We now report this accomplishment.

An Fab[4] combinatorial library in phage λ was generated[2b] from the spleen of a mouse immunized with phosphonamidate **1** (Figure 1) conjugated to keyhole limpet hemocyanin (KLH). The library was screened for binding to **1** conjugated to bovine serum albumin (BSA). Twenty-two phage clones were isolated that bound to **1**. Purified Fab's from six of these clones were assayed for catalytic activity, and three were found to be active for hydrolysis of the substrate **2b** (Figure 1).

In order to obtain enough antibody to carry out kinetic studies, we expressed one clone (1D) in the baculovirus expression system.[5] By transferring the antibody-encoding genes into insect cells, we increased the expression level approximately 10-fold from >0.5 to 5 mg/L. This increase in yield allowed us to obtain enough antibody for rigorous purification and kinetic characterization. The cell line producing the greatest amount of this Fab, as judged by the intensity of the ELISA signal, was selected, amplified, and used for large-scale expression. The purified Fab 1D was judged to be >95% pure as determined by silver staining of SDS-polyacrylamide gels and cross-reacted with anti-murine Fab and anti-κ antibodies on Western blots (data not shown). Control cells infected with wild-type virus and uninfected cells did not yield protein bound to the **1**-BSA conjugate.

Antibody activity was measured by monitoring the release of *p*-nitrophenol at 404 nm. Assays were performed in PBS (10 mM sodium phosphate, pH 7.2, 160 mM NaCl) containing 1-4 μM antibody, 31.25-500 μM substrate **2b** in 5% dioxane in a final volume of 800 μL. The initial rate of Fab 1D catalyzed hydrolysis measured as a function of substrate **2b** was observed to follow Michaelis-Menten kinetics (K_m = 115 μM, k_{cat} = 0.25 min^{-1}). The gene encoding this antibody was sequenced (data not shown) and found to differ from genes encoding catalysts isolated previously (**1**-KLH was again the immunogen) from our laboratory by conventional hybridoma procedures.[6] Furthermore, 1D did not hydrolyze amide **2a** (Figure 1), unlike some other antibodies we isolated previously.[6] Nevertheless, hapten **3** (Figure 1) was a potent inhibitor of the reaction.[7] Potent inhibition by the immunogen has been observed with other catalytic antibodies.[6]

We have isolated a catalytic antibody by cloning the immunological repertoire of a hyperimmunized mouse into phage λ.[2b] While early combinatorial antibody libraries, including the one studied here, utilized an immunization procedure, these methods are rapidly being replaced by semisynthetic libraries.[3c] Such libraries can provide a uniform and reproducible source of antibody molecules as starting materials. Thus, we envision that future catalytic antibody experiments will begin with screening of either immunized or semisynthetic combinatorial libraries for binding to selected haptens. Once catalysts are found, their rates and substrate specificities can be altered by mutagensis or genetic selection procedures.

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Supplementary Material Available: Listing of relevant molecular biological and kinetic assay procedures (5 pages). Ordering information is given on any current masthead page.

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Synthesis and Structure of a Transition-Metal-Substituted Silylene Complex, $(CO)_4OsSi(STol\text{-}p)[Ru(\eta^5\text{-}C_5Me_5)(PMe_3)_2]$

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Unsaturated silicon species are important reactive intermediates in silicon chemistry.[1] In addition, it is often assumed that metal complexes containing unsaturated silicon centers (as in silylene complexes L_nMSiX_2) are key intermediates in transition-metal-promoted transformations of silicon compounds, although little conclusive evidence exists to support such hypotheses.[2] Pannell,[3] Ogino,[4] and Turner[5] have reported mechanistic studies which

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