Table I. Product Analysis from Irradiation of BrU-Containing Deoxyhexanucleotides[a]

run	hexamer	free base, μM (%[b]) C	G	T	A	consumed hexamer, %	debrominated hexamer,[b] %	2-deoxyribonolactone-containing hexamer,[b] %
1	d(GCA^{Br}UGC)	0	0	0	39 (61)	38	10	47 (1)
2	d(GCG^{Br}UGC)	0	0	0	0	0	0	0
	d(CGCACG)					0		
3	d(GCC^{Br}UGC)	0	0	0	0	20	0	0
	d(CGGACG)					11		
4	d(GCA^{Br}UCG)	0	0	0	0.6 (1.3)	27[c]	5	4[d] (5)
5	d(GCA^{Br}UCG)	0	0	0	21 (41)	61	8	29 (5)
	d(CGTAGC)					0		
6	d(CG^{Br}UACG)	0	4 (24)	0	0	10	0	0

[a] Each of the reaction mixtures (30 μL) containing hexamer (1 mM base concentration) and NaCl (1 M) in 50 mM sodium cacodylate buffer (pH 7.0) in a capillary cell was irradiated for 30 min at 0 °C with a transilluminator (302 nm) under otherwise identical conditions. The reaction mixture was analyzed by HPLC under the conditions as described in Figure 1. [b] Yields based on consumed BrU-containing hexamer as determined by HPLC. [c] Considerable amounts of unknown photoproducts were detected. [d] Due to the overlapping of the peak of **5** with unknown products, the value was somewhat inaccurate.

with other unidentified products (run 4). By contrast, addition of complementary strand d(CGTAGC) to the reaction system resulted in more than 7-fold enhancement of the photoreactivity to cleanly produce **5** with efficient release of adenine (run 5). These results indicate that both the duplex structure and the 5'A^{Br}U sequence are essential for the efficient formation of the 2-deoxyribonolactone residue and free base release.[14,15]

The formation of **1** and adenine from d($G_1C_2A_3{}^{Br}U_4G_5C_6$) apparently indicates that the ribose C-1' hydrogen at A_3 is abstracted by an adjacent uracilyl-5-yl radical formed from BrU in the same strand of the duplex. The quantum yield (ϕ = 1.4 × 10^{-2} at 0 °C) for the formation of 2-deoxyribonolactone-containing oligomer **1** from duplex d(GCA^{Br}UGC)$_2$ is remarkably higher than that for the photoreduction of monomeric BrU in water containing 0.1 M 2-propanol (ϕ = 1.8 × 10^{-3})[16] or the photoreduction in the presence of a mixture of dG, dC, and dA in a 2:2:1 ratio under the same conditions (ϕ = 1.7 × 10^{-3}).[17,18] While the reason for the specific and highly efficient photoreaction of the 5'A^{Br}U sequence is unclear, an attractive mechanism appears to involve an intramolecular electron transfer from adenine at the 5'-side to an adjacent BrU in a specially oriented complex formed in the duplex (Scheme II).[1b,c,19,20] The resulting BrU anion radical would release Br anion to produce uracilyl-5-yl radical **6**, which can immediately abstract the adjacent C-1' hydrogen of the adenosine radical cation to give rise to cationic species **7**. Hydrolytic cleavage of the *N*-glycosidic bond of **7** would provide **1** with release of adenine.[21]

The present results strongly suggest that such C-1' hydrogen abstraction giving the 2-deoxyribonolactone residue may play an important role in the formation of the alkaline-labile lesion in UV-irradiated BrU-containing DNA.[1,2,5] Further studies on the mechanistic aspect of this novel photoreaction are in progress in our laboratory.

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(14) In fact, photoreaction of d(GCA^{Br}UGC)$_2$ is temperature dependent. Photoreaction of d(GCA^{Br}UGC)$_2$ proceeded much more slowly at 50 °C to give only 40% of the photoproducts obtained at 0 °C. Melting temperature (T_m) of d(GCA^{Br}UGC)$_2$ at 1.85 × 10^{-5} M was 33 °C.

(15) Neither 5'^{Br}UA (run 6) nor 5'T^{Br}U sequence in the middle of double stranded hexanucleotide induced free base release.

(16) Campbell, J. M.; Schulte-Frohlinde, D.; von Sonntag, C. *Photochem. Photobiol.* **1974**, *20*, 465.

(17) Quantum yield measurements were carried out at 0 °C in a merry-go-round apparatus by using 5-bromouracil as an actinometer.[15]

(18) For a similar enhanced photoreactivity of BrU in DNA, see; Wacker, A.; Dellweg, H.; Trager, L.; Kornhauser, A.; Lodemann, E.; Turck, G.; Selzer, R.; Chandra, P.; Ishimoto, M. *Photochem. Photobiol.* **1964**, *4*, 477.

(19) Examples for electron-transfer reactions of BrU by n,π^* excitation (308 nm) via the triplet manifold; see also: (a) Swanson, B. J.; Kutzer, J. C.; Koch, J. H. *J. Am. Chem. Soc.* **1981**, *103*, 1274. (b) Ito, S.; Saito, I.; Matsuura, T. *Ibid.* **1980**, *102*, 7535. (c) Dietz, T. M.; von Trebra, B. J.; Swanson, B. J.; Koch, T. H. *Ibid.* **1987**, *109*, 1793, and references therein.

(20) The reason why a 5'G^{Br}U sequence containing a more easily oxidizable guanine does not undergo this reaction (runs 2 and 6) is unclear. However, even if electron transfer from 5'G to BrU is faster, the back-electron-transfer rate and the subsequent reaction from G$^{\bullet+}$ would be quite different from those observed with 5'ABrU sequence. Electron transfer from photoexcited A to BrU in the complex would also be feasible.

(21) Since ribonolactone formation and adenine release occur under rigorously degassed conditions, oxygenation of ribose C1' radial is not involved.

Synthesis of Poly[bis(trifluoroethoxy)phosphazene] under Mild Conditions Using a Fluoride Initiator

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Polyphosphazenes are inorganic macromolecules with backbones consisting of alternating phosphorus and nitrogen atoms. A large range of polymer properties can be controlled by varying the structure of the substituents attached to the phosphorus atoms of the chain. It is possible to provide materials with such interesting properties as flame resistance, low-temperature flexibility, and biocompatibility.[1]

At the present time, there are two main synthetic routes to the polyphosphazenes: ring-opening polymerization of halogenated cyclotriphosphazenes followed by replacement of the halogens by hydrolytically stable groups,[2-4] and the condensation of substituted phosphoranimines.[5-7]

The latter method provides a route to a variety of poly(alkylphosphazenes) and poly(arylphosphazenes), thus expanding the field from the poly(alkoxyphosphazenes), poly(aryloxyphosphazenes), and poly(aminophosphazenes) of earlier efforts.[8,9] This approach, however, involves multistep synthesis of various substituted monomers and usually requires 2-12 days and high temperatures (160-220 °C) to produce polymer.[10]

One of the most important polyphosphazenes, poly[bis(2,2,2-trifluoroethoxy)phosphazene], can be prepared either by the ring-opening polymerization/halogen substitution method de-

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(8) Allcock, H. R. *ACS Symp. Ser.* **1988**, *360*, 250.
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(10) Neilson, R. H.; Wisian-Neilson, P. *Chem. Rev.* **1988**, *88*, 541.

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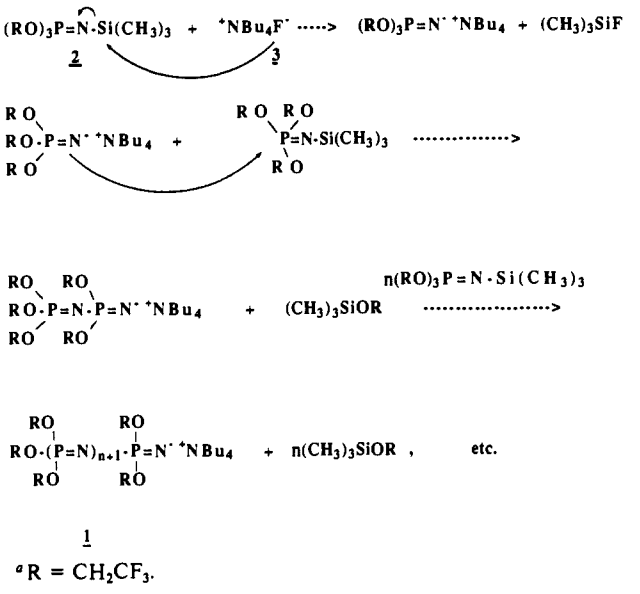
Scheme I[a]



[a] R = CH_2CF_3.

scribed above or, more directly, by the condensation of the appropriate phosphoranimine, obtained by the reaction of trimethylsilyl azide with tris(2,2,2-trifluoroethyl) phosphite.[11] The reaction employed is a variation of the Staudinger reaction of an azide with a phosphine.[12] The noncatalyzed polymerization step, however, also requires longer times and higher temperatures (48 h at 200 °C).[11]

It has been shown that it is possible to catalyze the ring-opening polymerization of the cyclohalophosphazenes by using Lewis acids such as BCl_3[13] and protonic acids such as toluenesulfonic, sulfobenzoic, or sulfamic.[14] On the other hand, we have found no reports of catalyzed polymerizations of the phosphoranimine monomers. It has been suggested that the substituted phosphoranimines are polymerized by a chain-growth mechanism rather than a step-growth process, since reactions terminated at low conversions have shown the presence of high polymer.[10]

We now report the synthesis of poly[bis(2,2,2-trifluoroethoxy)phosphazene] (**1**) from tris(2,2,2-trifluoroethoxy)-*N*-(trimethylsilyl)phosphoranimine (monomer) (**2**) using tetra-*n*-butylammonium fluoride (TBAF) (**3**) as an initiator. TBAF was used as the 1.0 mol/L THF solution (Aldrich Chemical Co.) as received. A plausible reaction sequence is proposed in Scheme I. Fluoride ion has a high affinity for the trimethylsilyl group, and its removal from the phosphoranimine creates an anionic center that attacks a partially positively charged phosphorus atom in the monomer molecule. Furthermore, the presence of the bulky ammonium counterion stabilizes the active anionic chain ends.

The synthesis of the monomer followed the literature procedure.[11] ^1H NMR spectra confirmed the monomer structure with a singlet at 0.1 ppm and a multiplet at 4.2 ppm, as reported previously.[15] The purity after a single vacuum distillation at 57 °C/0.5 Torr was 98%, as estimated from the NMR spectrum. The clear, colorless liquid monomer was treated in bulk with 1% (mol) of **3** in a flame-dried, septa-sealed glass flask equipped with a water-jacketed condenser under a dry nitrogen purge. After 1.5 h in an oil bath at 95 °C, the clear reaction liquid was allowed to cool, and a white solid formed. The solid easily dissolved in THF, and the solution was added to excess cold $CHCl_3$. A white precipitate formed immediately, and the mixture was stirred for a half-hour. Vacuum filtration afforded a fine, white powder in about 45% yield by weight. GPC data based on polystyrene standards indicated a molecular weight of about M_n = 10000. FT IR showed the expected broad absorption at 1271 cm^{-1}, which is evidence of the P=N backbone.[9] ^{31}P NMR showed a broad peak at −9.1 ppm, and the ^1H NMR spectra displayed a broad peak at 4.6 ppm, both in agreement with the literature.[11] An uncatalyzed sample of monomer required at least 48 h in a 190 °C oil bath to reach a comparable conversion, using similar apparatus. Since the solid polymer was found to be insoluble in the liquid monomer, ^{31}P NMR was used to follow the rate of polymer formation in diglyme with this initiator in a 125 °C oil bath and revealed 25% conversion to polymer at 0.5 h and nearly 100% conversion within 4 h. Figure 1 shows the ^{31}P NMR spectra obtained at 0, 0.5, and 4 h as the monomer signal at −12.1 ppm was gradually converted to the polymer signal (at −8.45 ppm). Small peaks in the spectra at −3 to −4 ppm may be ascribed to either end gropus, oligomers, or slight branching present in low ratio to the polymer peak (<4%). GPC measurement gave a molecular weight of about M_n = 20000 and a M_w/M_n ratio of 1.52 for the solution polymerization. In other experiments, polymers with molecular weights above 100000 were formed. Molecular weights and polydispersities of the polyphosphazenes prepared by the reported method are usually lower than those of the polymers prepared by the ring-opening/halogen substitution process.

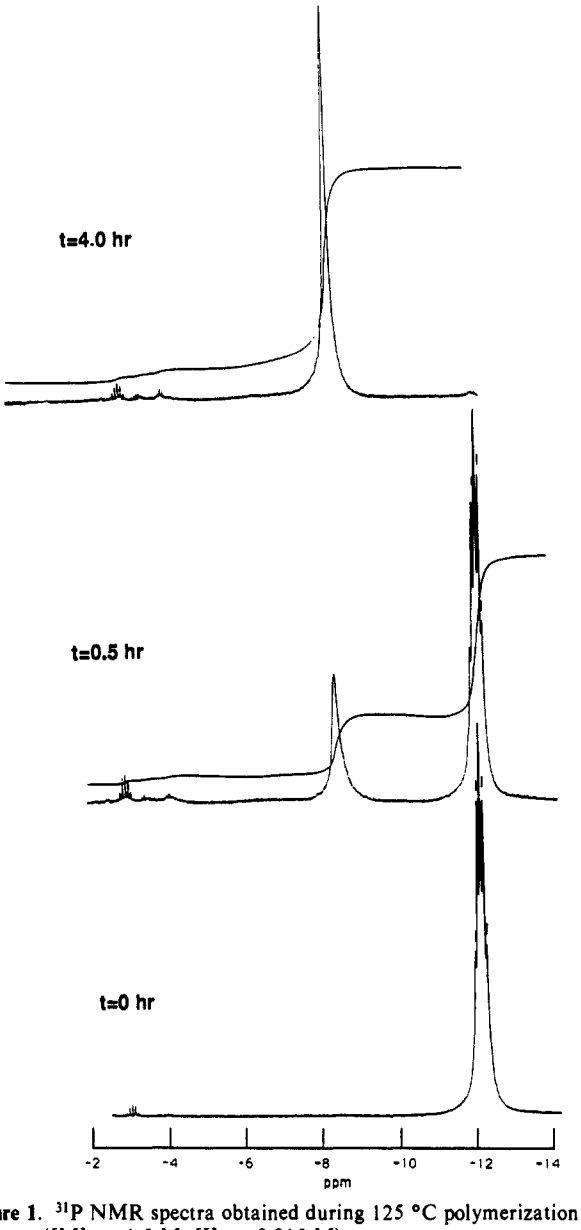


Figure 1. ^{31}P NMR spectra obtained during 125 °C polymerization in diglyme ($[M]_0$ = 1.5 M; $[I]_0$ = 0.015 M).

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(12) Staudinger, H.; Meyer, J. *Helv. Chim. Acta* **1919**, *2*, 635.
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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.

Acknowledgment. We thank Dr. Y. N. Gupta and Mr. Chihhwa Lin of our laboratory for assistance in acquiring ^{31}P NMR and ^{1}H NMR spectra. R.A.M. thanks PPG Industries, Inc., for financial support. K.M. acknowledges support from the National Science Foundation by the Presential Young Investigator Award.

Synthesis of Porous Polystyrene with Chemically Active Surfaces

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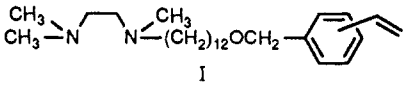
Two principle methods exist for placing chemically active functionalities onto polymer chains:[1] (a) attachment of the groups to a preformed polymer backbone and (b) polymerization of a monomer already bearing the desired group. The latter permits a less random polymer and is the method selected for 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]

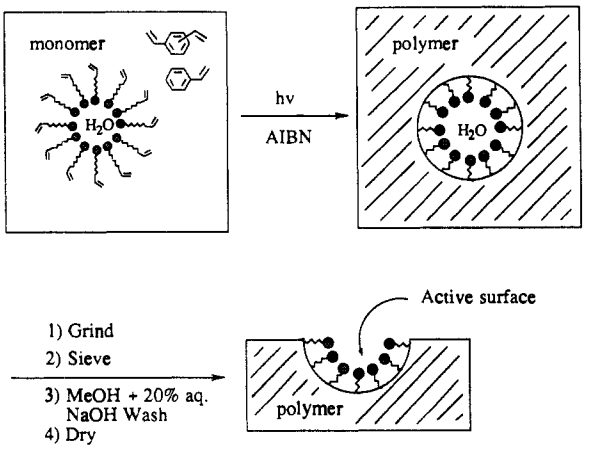


Figure 1. Scheme for producing porous polymers with chemically active surfaces. The shaded circles represent the diamino groups of I which adsorb into or onto the water pools that have been solubilized in the styrene/divinylbenzene solvent.

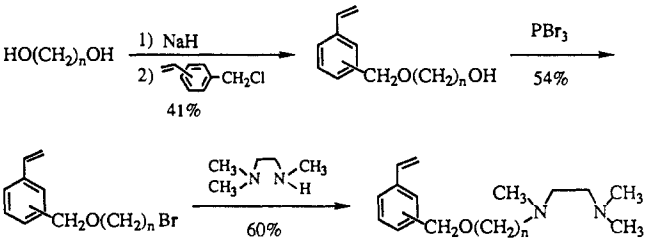


Figure 2. Synthesis of I where $n = 12$. Experiments (not reported) were also carried out on $n = 6$ with no substantial difference in results.

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.

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