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Experimental Section

Materials. All of the volatile materials were checked for purity before use by GLPC (50-m SE-30 or 25-m FFAP glass capillary column) and were found to be of the purity quoted.

The standard, *p*-di-*tert*-butylbenzene (Aldrich Chemical Co.), was recrystallized from dichloromethane (>99.9%).

p-Dinitrobenzene (mp 122–124 °C), 2,6-di-*tert*-butyl-1,4-benzoquinone (>98% pure), mp 65.6–66.5 °C, and tetrabutylammonium fluoride (1 M in THF) were used as received (Aldrich Chemical Co.).

Phenyldimethylsilane (Petrarch Systems Inc.) (>99.8%) was used as supplied.

Dimethyl sulfoxide, Me$_2$SO (British Drug Houses), was purified by being passed through a column (80 cm) of neutral alumina (Camag 507-C). The Me$_2$SO was treated with potassium hydroxide for 3 h at 90 °C and distilled at reduced pressure.

α,α,α-Trifluoroacetophenone was prepared by treating trifluoroacetic acid with an ether solution of phenylmagnesium bromide.[17] Fractional distillation (69–70 °C (30 mm)) (lit.[18] bp 75 °C (37 mm)) gave the product in 58% yield: IR (neat) 5.78 (CO) μm; MS, m/e 174, 105 (>99.6%).

α-Fluoroacetophenone was prepared by treating fluoroacetyl chloride with benzene in the presence of aluminum trichloride.[19] Fractional distillation, bp 70–72 °C (1.5 mm) (lit.[19] bp 65–70 °C (1 mm)) gave the product in 81% yield: mp 26–27 °C (lit.[19] mp 27–28 °C); NMR (CDCl$_3$) δ 5.57 (d, 2 H, J = 47.5 Hz), 7.36–8.10 (m, 5 H); IR (neat) 5.86 (CO) μm; MS, m/e 183, 105.

Cyclopropyl phenyl ketone (Aldrich Chemical Co.) was redistilled, bp 90 °C (2.8 mm) (lit.[20] bp 121–123 °C (15 mm)) (>99.6%).

Instrumental Methods. GLPC Analysis. All quantitative values were determined by using standard calibration curves constructed using known mixtures of the authentic materials. The areas were determined by using a HP5840A GLPC terminal interfaced to a HP 5840A gas chromatograph fitted with a FID and a capillary injector. A 50-m SE-30 or a 25-m FFAP glass capillary column was used for the analytical separations.

GLPC/IR data were obtained on a Nicolet 7199 FT/IR spectrometer interfaced to a Varian 3700 gas chromatograph.

GLPC/MS data were obtained on a VG 7070E mass spectrometer fitted with a Visa 6000 gas chromatograph using a 30-m OV-351 glass capillary column. The spectrometer was interfaced to a VG11-250 data system.

EPR spectra were obtained on a BRUKER CR 400 spectrometer with a 100-KHz modulation and a VARIAN 12 in. magnet system with a fieldial regulator. The magnetic field and microwave frequency were monitored by a ALPHA 3009 NMR gaussmeter and a HPX532B microwave frequency meter.

Reduction of Ketones with Phenyldimethylsilane. In one branch of an H-tube was placed a Me$_2$SO solution of the ketone (0.17 M, 0.5 mmol) and phenyldimethylsilane (0.17 M, 10.5 mmol) and in the other branch was placed 0.5 mL of a 0.5 M THF solution of tetra-*n*-butylammonium fluoride, if the fluoride was to be added. The reaction vessel was degassed, by the freeze–thaw method, sealed, and thermostated at either 40 °C or 62 °C. After equilibration the solutions were mixed and allowed to react for the times indicated. The reaction mixture was treated with 10 mL of 1 N hydrochloric acid, and the organic material was extracted with dichloromethane. The organic solution was washed 3 times with water, dried over anhydrous sodium sulfate, and analyzed by GLPC, GLPC/MS, and GLPC/IR.

Control experiments showed that the organic material was not lost during the isolation procedure.

In the case of the reduction reactions of cyclopropyl phenyl ketone, the first-formed alkoxydimethylphenylsilane, upon hydrolysis, forms α-cyclopropylbenzyl alcohol. When this alcohol was treated with 1 N hydrochloric acid under the conditions of hydrolysis it could be converted to 1-phenyl-4-chloro-1-butene.

EPR of Reaction Mixtures with the Phenyldimethylsilane–TBAF Reagent. An H-tube constructed such that one branch of the tube was a quartz EPR tube was used as a reaction vessel. In one branch of the tube was placed a Me$_2$SO solution of *p*-dinitrobenzene (0.03 M, 0.05 mmol) and phenyldimethylsilane (0.13 M, 0.2 mmol), and in the other branch was placed a Me$_2$SO solution of TBAF in THF (0.03 M, 0.05 mmol). The reaction mixtures were degassed, sealed, and mixed at 23 °C. The ESR were carried out as quickly as possible. The procedure was used not only for DNB but for the spectrum obtained from silane and DTBQ. The spectrum obtained from the reaction of cyclopropyl phenyl ketone was obtained in the same manner, except that when no signal was observed the tube was opened to the atmosphere and subsequently the spectrum appeared almost immediately.

Registry No. I, 434-45-7; II, 450-95-3; III, 3481-02-5; IV, 340-04-5; VIII, 450-94-2; IX, 1007-03-0; X, 1794-47-4; trifluoroacetic acid, 76-05-1; phenyl bromide, 108-86-1; fluoroacetyl chloride, 359-06-8; benzene, 71-43-2; phenyldimethylsilane, 766-77-8; acetophenone, 98-86-2.

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Chemical Modification of Polystyrene Resins. Approaches to the Binding of Reactive Functionalities to Polystyrene Resins through a Dimethylene Spacer

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By an appropriate sequence of simple and often quantitative chemical steps, reticulated bromopolystyrene or (chloromethyl)polystyrene can be modified to support any of hydroxy, halo, acyloxy, sulfonoxy, amino, sulfonamido, thio, phosphino, or other chemical groups on a two-carbon spacer extending from the insoluble matrix. This structural feature can enhance stability, reactivity, and/or selectivity in many applications of functionalized polystyrenes as reagents or catalysts. For example, *p*-lithiated polystyrene reacts with ethylene oxide to afford *p*-(2-hydroxyethyl)polystyrene free from grafted oligoethylene glycol. (2-Hydroxyethyl)polystyrene is tosylated rapidly and quantitatively by treatment with diisopropylamine and tosyl chloride in refluxing carbon tetrachloride while a similar reaction of the supported alcohol with tosyl chloride in a tertiary amine leads directly and quantitatively to the quaternary ammonium salt resin. Other simple procedures have been devised to transform the tosylated polymer into primary, secondary, or tertiary amines without overalkylation.

For three decades now,[1,2] cross-linked polystyrene resins carrying chemically reactive groups have proliferated in form and application, variously as photochemical, acylation, phase-transfer or other catalysts,[3] chemical reagents,[3]

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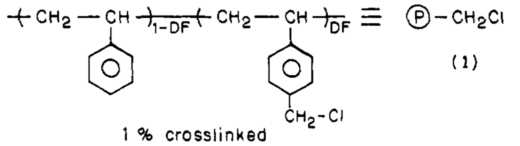
reaction cosolvents,[4] separation media,[5] protecting groups and supports in solid-phase syntheses,[2,3,6] or chiral auxiliaries in asymmetric processes.[7] Generally, these solid materials, together with attached products or byproducts, are easily removed from the mixture at the end of a reaction by filtration, often considerably simplifying product purification and increasing isolated yield; they can frequently be regenerated for future reuse.[3]

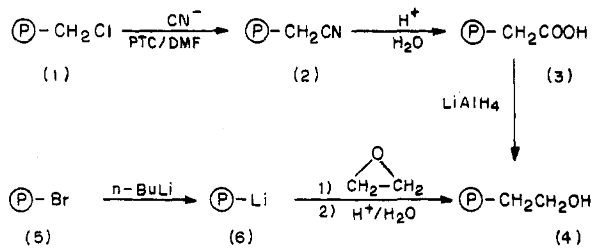
Currently, most such functional or reactive polymers are prepared from (chloromethyl)polystyrene,[8] Ⓟ–CH_2Cl (structure 1), itself easy to make or buy, through displacement of the polymer's benzylic chloride by appropriate nucleophiles, generally substituted heteroatoms, frequently under phase-transfer conditions.[9] However, benzyl–heteroatom bonds are relatively fragile, since resonance stabilizes the partial charges developed during their rupture: hence, benzylic quaternary phosphonium and ammonium salts are dealkylated[10] by mild heating or under the action of nucleophiles. Similarly, it is well-known[11] that benzylic amines, sulfides, esters, and ethers may be cleaved in the presence of protonic or Lewis acids; as well, benzyl–nitrogen, –sulfur, or –oxygen bonds are rather susceptible to hydrogenolysis.[12] Oxidation or alkylation may also take place at benzylic methylene groups[11] which have been made particularly acidic by being bound at once to both an aryl carbon and an electronegative heteroatom.



(1)

The very lability of substituents bound through benzylic linkages to polystyrene makes (chloromethyl)polystyrene the support of choice in solid-phase peptide synthesis,[2] as controlled separation of the finished peptide can be achieved readily.[2,13a] However, numerous instances of undesirable side reactions[3,7c,d,10a,13b] affecting the reactivity or regenerability of other reactive polymers containing benzylic bonds have suggested that the development of new, more stable anchoring linkages might lead to further significant advances in polymer-supported chemistry.

Scheme I



Direct connection of a pendant heteroatom to a polystyrene aryl is a synthetically more difficult but often a still feasible[14] alternative; however, though bonds from phenyl to the common heteroatoms are very stable, resonance stabilization of the partial charge developed on an arylated atom activates it to leave other substituents. For example, alkylanilium salts and -anilines, as well as phenolic esters, are relatively easy to cleave;[11] many aryl-substituted elements are also relatively easy to oxidize, since the products are conjugated.

An attractive alternative to structures derived from Ⓟ–CH_2Cl would result from the incorporation of a second methylene group between the polymer and its pendant functionality, as in Ⓟ–CH_2CH_2X.[8] Such structures incorporating a two-carbon spacer do not suffer from benzylic deactivation and may possess increased reactivity and other desirable properties.[7a,15]

A possible drawback to the use of a dimethylene spacer between the aromatic rings of polystyrene and the functional groups is its susceptibility to elimination to form a conjugated styrenic structure; however, this should not be a hindrance if the polymer-bound functionalities are poor leaving groups under basic conditions.

Results and Discussion

Some (2-X-ethyl)polystyrenes, Ⓟ–CH_2CH_2X, have been prepared from the corresponding (2-X-ethyl)styrene monomers, which are made and purified by classical chemical methods before being copolymerized with styrene by appropriate initiators.[16] Others come from the chemical modification of existing polymers: this strategy is generally the more versatile, since a single functionalized polymer, once available, can act as precursor to any of several others, according to applied reagent and reaction conditions. However, each conversion step must be quantitative since any unreacted precursor functionalities or polymer-bound side products will remain in the final material and possibly interfere in its function. Reactions of polymer-bound species are often slower than for the soluble analogues, being rate-limited by the speed of diffusion of a soluble reagent into the matrix: though reactions accelerate in more swollen polymers (either less cross-linked, or immersed in better solvents), relatively forceful conditions may still be necessary to achieve acceptable rates.[1,10a] Moreover, even with a moderate degree of functionalization[8] (DF), local concentrations of reactive sites within the matrix can be extremely high, so the consequences of their

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(8) The designations (chloromethyl)polystyrene, Ⓟ–CH_2Cl, (2-X-ethyl)polystyrene, Ⓟ–CH_2CH_2X, etc. refer to polystyrene resins substituted on their aromatic rings with the functionalities shown in parentheses. The polymers are characterized by their degree of functionalization DF which indicates the mole fraction of styrene repeating units carrying the desired functionalities.

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mutual interactions (disproportionation, cross-linking, etc.) should not be ignored.[17]

Preparation of Spacer-Containing Polystyrene

Two procedures are available for the introduction of a two-carbon spacer group onto preformed polystyrene resins (Scheme I). The first involves a stepwise extension with the well-known (chloromethyl)polystyrene (1) as an intermediate, while the second proceeds via activation of the aromatic rings of polystyrene followed by direct addition of a two-carbon moiety.

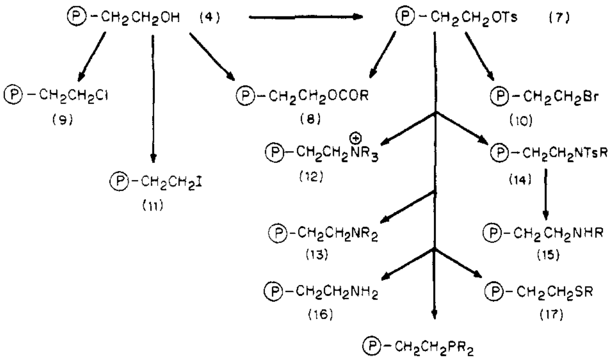
(a) Chain Extension of (Chloromethyl)polystyrene. This procedure has already received some attention due to the ready commercial availability of the reactive starting material. Most notable among the 2C-substituted polymers prepared by this method are the cyanomethyl,[9,18,19] carboxymethyl,[15a] methylsulfinyl,[18,19] and *p*-vinyl and *p*-oxirane[20] derivatives of polystyrene. However, as is the case with numerous other reactive polymers prepared by chemical modification, the polymers may be of uneven quality having been poorly characterized or prepared in low functional yields.

For example, (cyanomethyl)polystyrene prepared by nucleophilic displacement on 1 in dimethyl sulfoxide is clearly contaminated with oxidation products.[19] The same displacement reaction carried out under phase-transfer conditions in 1,2-dichloroethane or in wet dimethylformamide (DMF)[9a] affords a slightly colored polymer. In contrast, we have found that the reaction of choice appears to involve the use of solid–liquid–solid phase-transfer conditions in dry DMF under inert atmosphere; this reaction affords Ⓟ-CH_2CN (2) in quantitative yield and free from colored impurities.

Hydrolysis of 2 to the corresponding carboxylated polymer 3 is best carried out by swelling 2 in glacial acetic acid followed by treatment with 6 N aqueous sulfuric acid. Polymer 3 contains no remaining nitrogen, while titration of the carboxylic acid groups confirms that the reaction is quantitative. Reduction of 3 to (2-hydroxyethyl)polystyrene 4 can be done by using either borane or lithium aluminum hydride in THF. Here again, care should be taken to swell the polymer fully to ensure penetration of the reducing agent and reach quantitative conversion. This is confirmed by the various analyses of derivatives prepared in subsequent steps using 4 as a starting material, as will be described below.

(b) Direct Addition of a Two-Carbon Unit to Polystyrene Rings. Attempts to directly introduce a functionalized two-carbon spacer onto polystyrene by Friedel–Crafts alkylation with dihalide[21] lead to excessive cross-linking of the polymer matrix, reducing later swelling and reactivity. Cross-linking is also observed upon alkylating dihalides or cyclic halonium ions with metalated polymer.[14] However, high yields of 2-hydroxyethyl adducts, without dimerization or rearrangement, result from the reactions of various aryl lithium compounds with ethylene oxide;[22] moreover, lithium alkoxides and hydroxides are completely inert toward excess epoxide, no ethers being recovered from such mixtures even after heating under pressure.[23] Hence, lithiopolystyrene (6) prepared from bromopolystyrene (5),[14] upon treatment with an excess of condensed ethylene oxide and then acidified produces 4 directly (Scheme I), without trace of grafted oligoethylene glycol. IR analysis of 4 prepared by both modification methods described above display peak-to-peak correspondence with each other, and indeed, with 4 prepared from the pure monomers.[16a] Polymers prepared via 1 and 5 are both functionalized almost exclusively at the para position.

Scheme II



Chemical Modification of Ⓟ-CH_2CH_2OH

A number of reactions were carried out with functionalized polymer 4 as starting material (Scheme II). Analyses of the products of these experiments confirmed our ability to carry out simple but quantitative functional group conversions in the solid phase of polymers of the type Ⓟ-CH_2CH_2X; moreover, certain of these products were themselves good intermediates toward others, even to stable and active polymeric reagents or catalysts useful in other fields of chemistry.

(a) Tosylates and Carboxylic Esters. Classical tosylation of 4 using *p*-toluenesulfonyl chloride in cold pyridine can be carried out satisfactorily but requires that the reaction mixture be kept stirring at low temperature for 5 days. Increasing the reaction temperature results in unacceptable side reactions involving the solvent. To accelerate the overall process and avoid the occurrence of this side reaction we have developed a new tosylation procedure whereby a stoichiometric amount of diisopropylamine is used as acid acceptor. The reaction, which can be carried out in refluxing carbon tetrachloride or similar solvents, affords [2-((tolylsulfonyl)oxy)ethyl]polystyrene (7) within hours without side-product formation or decomposition. The active intermediate is probably the tertiary dialkyl sulfonamide initially formed in an exothermic reaction upon mixing of the reagents; isolation of the product tosylate is possible as it is inert to further displacement by the hindered diisopropylamine which is liberated (see below). This new and very efficient tosylation procedure may find applications elsewhere.

The tosyloxy derivative 7 can be transformed directly into primary acyl esters 8 by nucleophilic displacements with carboxylate anions. The tosylate is particularly suited for this displacement reaction as it is a leaving group less prone to elimination than the chloride, bromide, or iodide. The substitution reaction is best done in a polar aprotic solvent such as DMF, rather than under phase-transfer

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Table I. Polymer Modification Reactions

$P\text{-}CH_2CH_2X^1 \rightarrow P\text{-}CH_2CH_2X^2$

starting polymer				final polymer			functional yield, %
	X^1	DF	reagents		X^2	DF	
4	OH	0.29	TsCl, (*i*-Pr)$_2$NH	**7**	OTs	0.29	100
4	OH	0.31	3,5-(NO$_2$)$_2$PhCOCl	**8a**	OCOPh-3,5-(NO$_2$)$_2$	0.31	100
7	OTs	0.31	3-NOPhCOOK	**8b**	OCOPh-3-NO	0.29	94
4	OH	0.24	SOCl$_2$, pyridine	**9**	Cl	0.24	100
7	OTs	0.29	MgBr$_2$	**10**	Br	0.29	100
4	OH	0.29	Me$_3$SiCl, NaI	**11**	I	0.29	100
4	OH	0.24	TsCl, pyridine	**12**	$^+$NC$_5$H$_5$	0.24	100
7	OTs	0.24	pyrrolidine	**13a**	pyrrolidyl	0.24	100
7	OTs	0.29	sodium imidazolide	**13b**	imidazolyl	0.28	97
7	OTs	0.20	Na$_2$CO$_3$, *N*-methyl-*p*-toluenesulfonamide	**14**	NTsCH$_3$	0.20	100
14	NTsCH$_3$	0.26	Na–naphthalene	**15**	NHCH$_3$	0.21	81
7	OTs	0.29	potassium phthalimide, NH$_2$NH$_2$	**16**	NH$_2$	0.28	97
7	OTs	0.31	butanethiol	**17**	SBu	0.25	81
7	OTs	0.31	LiPPh$_2$	**18**	PPh$_2$	0.29	94

conditions, since the liberated tosylate would compete with carboxylate nucleophiles for transport by phase-transfer catalyst. Thus, the reaction with *m*-nitrobenzoic acid in dry DMF and anhydrous potassium carbonate or cesium fluoride proceeds in essentially quantitative yield as evidenced by both elemental and spectroscopic analyses.

Alternatively, [2-(acyloxy)ethyl]polystyrenes can be obtained more directly from **4** without scission of C–O. For example, acylation with 3,5-dinitrobenzoyl chloride proved particularly useful for the evaluation of the degree of functionalization of polymer **4**, through quantitative elemental as well as qualitative spectroscopic analyses of the nitrogen-containing product **8**, thereby confirming that our procedures for the preparation of **4** can be optimized to afford quantitative conversion from **1** or **5**.

(b) Chloride, Bromide, and Iodide. (2-Chloroethyl)-polystyrene (**9**) had not been reported previously; it can be prepared easily and quantitatively from **4** swollen in carbon tetrachloride by using excess thionyl chloride in the presence of a catalytic amount of pyridine.

The preparation of (2-bromoethyl)polystyrene (**10**) is much less easily accomplished, as many of the common procedures that are used in the bromination of alcohols are not sufficiently clean to be used in the preparation of a highly pure polymer. Thus, reactions involving phosphorous tribromide[15a] lead to resins which retain some phosphorus, likely due to a small amount of phosphite cross-linking. The use of hydrobromic acid under phase-transfer conditions leads to a product which has no remaining alcohol groups but has suffered a small loss of functionality and of mechanical properties, probably through a Friedel–Crafts cross-linking side reaction. The reaction of **4** with lithium bromide and chlorotrimethylsilane in acetonitrile[24] only proceeds to 90% completion at best, as halosilanes, placed in an aromatic environment such as must exist within the polymer beads, tend to transform some of the alcohol moieties to the silyl ethers, which the brominating agent cannot cleave; these are hydrolyzed back to starting material upon workup, with the appearance of a residual C–O peak at 1046 cm^{-1} on the FTIR spectrum. The bromine-substituted resin **10** is finally best prepared from tosylated polymer **7** and magnesium bromide, in a displacement reaction which takes advantage of the affinity of magnesium cations for tosyl anions.

The more powerful NaI–chlorotrimethylsilane–acetonitrile reagent,[25] which is capable of cleaving even dialkyl ethers, converts **4** quantitatively into hydriodinated resin **11**, possibly more cleanly and certainly more cheaply than the CH$_3$I–triphenyl phosphite–DMF combination previously employed.[26]

(c) Amines and Sulfonamides. The preparation of quaternary ammonium salts **12** is easily carried out through the intermediacy of tosylated resin **7** using a one-pot procedure whereby the hydroxyethyl polymer **4** is treated simultaneously with toluene sulfonyl chloride and an unhindered tertiary amine such as pyridine. The resulting resin which contains tosylate as a counterion can be transformed into the corresponding quaternary ammonium chloride or bromide by a simple ion-exchange process.

A similar reaction attempted on the isolated tosylate resin **7** with a nonhindered secondary amine such as pyrrolidine in Me$_2$SO or DMF results in significant amounts of quaternization as well as elimination. Substituting pyridine as a less polar and only weakly nucleophilic solvent in this reaction results in the exclusive formation of the desired product **13**. Though *N*-alkylimidazoles are even more susceptible to overalkylation during their preparation in neutral media,[27] stirring polymeric tosylate **7** in DMF with preformed sodium imidazolide, a relatively much stronger nucleophile (though still a weak base), affords **13b** without side products. Steric crowding in diisopropylamine is so severe that it does not react with **7** even after an overnight reflux in the pure amine.

The synthesis of secondary amine resins such as **15** is shown in Scheme II. The key compound in this reaction sequence is the tertiary sulfonamide **14** which is formed by alkylation of the anion of *N*-alkyl-*p*-toluenesulfonamide with polymer **7**; the sulfonamide **14** is then cleaved to the secondary amine **15** in an overall process which is not prone to overalkylation.

The polymer-bound primary amine **16** is readily prepared from the corresponding tosylate by using a classical Gabriel synthesis[11] via the corresponding phthalimido derivative.

Polymer-bound sulfides such as **17** are prepared by reaction of polymeric tosylate **7** with thiols under phase-transfer conditions. For example, butanethiol reacts in the

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quantitative displacement of tosylate from **7** when the reaction is performed in hot toluene in the presence of hexadecyltributylphosphonium bromide and anhydrous powdered potassium carbonate.

Finally, a polymer-bound tertiary phosphine **18** is obtained upon treatment of **7** with lithium diphenylphosphide[28] in THF–Me_2SO.

Conclusion

As can be seen in Table I, it is often possible to achieve quantitative conversion in the preparation of stable and reactive resins containing dimethylene spacers between functional groups and the aromatic rings of polystyrene. Such polymers with two-carbon spacers have enhanced properties that can be exploited in a number of practical applications. We are currently investigating several reactive polymers based on this work for applications as reagents, supports, or protecting groups in organic synthesis.

Experimental Section

Materials. Bromopolystyrene[14] and (chloromethyl)polystyrene[1] were prepared from commercial 1% cross-linked polystyrene resin[29] (SX-1 Bio-Beads, 200–400 mesh, from Bio-Rad Laboratories); hexadecyltributylphosphonium bromide was also synthesized from available chemicals. Thionyl chloride was freshly distilled from limonene,[30] and concentrated hydrobromic acid from stannous chloride; sodium iodide was dried at 120 °C overnight. Where specified, organic reaction solvents and liquid reagents were dried by distillation from sodium/benzophenone ketyl (ethers) or calcium hydride or carbide (amines, hydrocarbons, acetonitrile, dimethylformamide) or by distilling onto or standing over molecular sieves (dimethyl sulfoxide, others). Otherwise, technical grade wash solvents and reagent grade solid reagents were used as received.

Infrared spectra of KBr pellets were measured on a Nicolet 10-DX FTIR. Polymer halogen content was measured on-site by Volhard titration using a Parr peroxide bomb with 200–300-mg samples; other quantitative elemental analyses were performed by MHW Laboratories (Phoenix, AZ).[29b] Acid titration of polymer-bound carboxylate was performed by back-titration of the basified suspension. The degrees of functionalization of the polymers (DF) given below represents the fraction of aromatic rings that possess the desired functionalities.

(Cyanomethyl)polystyrene (2). Partly chloromethylated polystyrene (1) with DF = 0.31 $[(C_{10}H_{10})_{0.01}\cdot(C_8H_8)_{0.68}\cdot(C_9H_9Cl)_{0.31}]$ (59.1 g, 151 mequiv of Cl), powdered sodium cyanide (12.0 g, 245 mequiv), and tetrabutylammonium chloride crystals (1.0 g, 3.6 mequiv) were stirred together in 600 mL of dry DMF at 80 °C under a nitrogen atmosphere for 16 h. The pale orange suspension was filtered and the residue washed with H_2O (3×), methyl ethyl ketone (MEK, 1×), CH_2Cl_2 (1×), CH_3OH (2×) and dried under vacuum overnight, yielding 56.3 g of a very pale beige powder: IR (KBr) peak absent at 1265 cm^{-1} for chloride precursor, peak present at 2250 cm^{-1} (w, CN). Anal. Calcd for $(C_{10}H_{10})_{0.01}\cdot(C_8H_8)_{0.68}\cdot(C_{10}H_9N)_{0.31}$: N, 3.73; Cl, 0. Found: N, 3.85; Cl, 0.

(Carboxymethyl)polystyrene (3). The (cyanomethyl)polystyrene (2) prepared above, $[(C_{10}H_{10})_{0.01}\cdot(C_8H_8)_{0.68}\cdot(C_{10}H_9N)_{0.31}]$ (55.2 g, 152 mequiv), 30 mL of water (1700 mequiv), 300 mL of glacial acetic acid, and 30 mL of concentrated sulfuric acid were mixed and refluxed with stirring under nitrogen for 19 h. The pale suspension was filtered and the residue washed with H_2O (3×), MEK (1×), CH_2Cl_2 (1×), CH_3OH (2×) and dried under vacuum overnight, yielding 58.5 g of a pale beige-yellow powder: IR (KBr) peak absent at 2250 cm^{-1} for nitrile precursor, peaks present at 3000 (br, COOH), 1710 (s, C=O, dimer), and 1294 cm^{-1} (m, CO–O, dimer). Acid–base analysis indicates a capacity of 2.55 mequiv/g for DF = 0.31. Anal. Calcd for $(C_{10}H_{10})_{0.01}\cdot(C_8H_8)_{0.68}\cdot(C_{10}H_{10}O_2)_{0.31}$: N, 0. Found: N, <0.2.

(2-Hydroxyethyl)polystyrene (4) and [2-(3,5-Dinitrobenzoxy)ethyl]polystyrene (8a). Method A. A suspension of 50.0 g (127 mequiv of COOH) of (carboxymethyl)polystyrene (3) $[(C_{10}H_{10})_{0.01}\cdot(C_8H_8)_{0.68}\cdot(C_{10}H_{10}O_2)_{0.31}]$ in 500 mL of dry THF under nitrogen was treated with portions of $LiAlH_4$ powder (7.1 g, 748 mequiv of hydride) with some observable fizzing; then the mixture was refluxed for 12 h. Upon cooling, the gray suspension was treated dropwise with 7 mL of H_2O, 7 mL of 15% NaOH/H_2O, and then 21 mL of H_2O, giving a yellow suspension which was easily filtered, the residue being then washed with 3 N HCl/H_2O (2×), concentrated HCl/H_2O (1×), H_2O (3×), THF (1×), CH_2Cl_2 (1×), and CH_3OH (2×) and dried under vacuum overnight, yielding 48.8 g of a very pale beige powder: IR (KBr) peaks absent at 3000, 1710, and 1294 cm^{-1} for carboxy precursor, peaks present at 3400 (br, CH_2O–H) and 1046 cm^{-1} (s, CH_2–O). Anal. Calcd for $(C_{10}H_{10})_{0.01}\cdot(C_8H_8)_{0.68}\cdot(C_{10}H_{12}O)_{0.31}$: C, 87.90; H, 7.90; N, 0. Found: C, 87.03; H, 7.61; N, 0.

A sample of the product (0.53 g, 1.4 mequiv) was heated with 3,5-dinitrobenzoyl chloride (0.73 g, 3.2 mequiv) in 6 mL of dry pyridine at 100 °C under nitrogen for 2 h and then the yellow-green suspension was filtered and the residue washed with H_2O (3×), MEK (1×), CH_2Cl_2 (1×), and CH_3OH (2×) and dried under vacuum overnight, yeilding 0.76 g as a pale yellow-beige powder **8a**: IR (KBr) peaks absent at 3400 and 1046 cm^{-1} for alcohol precursor, peaks present at 3098 (w, Ar H), 1733 (s, C=O), 1547 (s, Ar NO_2), 1344 (s, Ar NO_2), 1277 (s, CO–O), 1164 (m, CO–O), 721 cm^{-1} (m, Ar NO_2). Anal. Calcd for $(C_{10}H_{10})_{0.01}\cdot(C_8H_8)_{0.68}\cdot(C_{17}H_{14}N_2O_6)_{0.31}$: C, 72.84; H, 5.59; N, 4.87. Found: C, 73.04; H, 5.59; N, 4.87.

Method B. Partly brominated polystyrene **5** with DF = 0.42 $[(C_{10}H_{10})_{0.01}\cdot(C_8H_8)_{0.57}\cdot(C_8H_7Br)_{0.42}]$ (20.00 g, 60 mequiv) was suspended in 50 mL of dry benzene under nitrogen. *n*-BuLi/hexane (2.2 M, 60 mL, 132 mequiv) was injected into this pale orange suspension, and the whole was stirred at 60 °C for 3 h. The liquid phase was removed by filtration, and the beige residue, still under nitrogen, was resuspended in 200 mL of dry THF and cooled to −50 °C, before receiving condensed ethylene oxide by injection (9.5 mL, 190 mequiv) then being further stirred under a CO_2-cooled condenser for 18 h while gradually being warmed to room temperature. The pale orange-yellow suspension was then filtered and the residue washed with THF–H_2O (3:1, 1×), THF–H_2O–concentrated HCl/H_2O (8:2:1, 1×), H_2O (3×), THF (1×), CH_3OH (2×), and Et_2O (1×) and then dried under vacuum overnight: IR (KBr) peaks absent at 1487, 1408, 1073, 1010, and 718 cm^{-1} for aryl bromide precursor and at 1150–1060 cm^{-1} for ether side products (CH_2–O–CH_2), peaks present are same as in **4** made by method A. Anal. Calcd for $(C_{10}H_{10})_{0.01}\cdot(C_8H_8)_{0.57}\cdot(C_{10}H_{12}O)_{0.42}$: C, 86.58; H, 7.96; O, 5.47; Br, 0. Found: C, 86.51; H, 8.05; O, 5.51; Br, 0.

A sample of the above product (0.13 g, 0.44 mequiv) treated with 3,5-dinitrobenzoyl chloride (0.13 g, 0.55 mequiv) as in method A yielded 0.20 g of pale powder: IR (KBr) identical with **8a** prepared as in method A. Anal. Calcd for $(C_{10}H_{10})_{0.01}\cdot(C_8H_8)_{0.57}(C_{17}H_{14}N_2O_6)_{0.42}$: N, 5.76. Found: N, 5.66.

[((*p*-Tolylsulfonyl)oxy)ethyl]polystyrene (7). (2-Hydroxyethyl)polystyrene with DF = 0.29 $[(C_{10}H_{10})_{0.01}\cdot(C_8H_8)_{0.70}\cdot(C_{10}H_{12}O)_{0.29}]$ (10.35 g, 35 mequiv), *p*-toluenesulfonyl chloride (8.4 g, 44 mequiv) and dry diisopropylamine (10 mL, 71 mequiv) were stirred together in 70 mL of carbon tetrachloride under nitrogen at room temperature and then heated to reflux for 6 h. The pale yellow suspension was filtered and the residue washed with acetone (1×), H_2O (3×), MEK (1×), CH_2Cl_2 (1×), and Et_2O (2×) and dried under vacuum overnight to yield 14.28 g of a very pale yellow-beige powder: IR (KBr) peaks absent at 3400 and 1046 cm^{-1} for alcohol precursor, peaks present at 1363 (s, SO–OC), 1180 (d, s, SO–OC), 1098 (m, C–O), 964 (s, S–O–C), 905 (m, S–O–C), 815 (m, S–O–C), 760 (m, S–O–C), 664 (m, Ar SO_3), and 555 cm^{-1} (s, Ar SO_3). Anal. Calcd for $(C_{10}H_{10})_{0.01}\cdot(C_8H_8)_{0.70}\cdot(C_{17}H_{18}SO_3)_{0.29}$: S, 5.74; N, 0. Found: S, 5.73; N, 0.

[2-(*m*-Nitrobenzoxy)ethyl]polystyrene (8b). Polymer **7** prepared above $[(C_{10}H_{10})_{0.01}\cdot(C_8H_8)_{0.68}\cdot(C_{17}H_{18}SO_3)_{0.31}]$ (0.50 g, 0.94 mequiv), *m*-nitrobenzoic acid (0.23 g, 1.4 mequiv), and anhydrous potassium carbonate (0.20 g, 1.4 mequiv) were stirred in 7.5 mL of dry dimethylformamide under nitrogen at 60 °C for 22 h. The mixture was filtered and the residue washed with H_2O (3×), MEK

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[28] Relles, H. M.; Schluenz, R. W. *J. Am. Chem. Soc.* **1974**, *96*, 6469.

[29] (a) A random copolymer of styrene and commercial divinylbenzene likely contaminated with <1% ethylstyrene. (b) For analytical purposes this ethylstyrene impurity is taken as styrene.

[30] Rigby, W. *Chem. Ind. (London)* **1969**, 1508.

(1×), CH_2Cl_2 (1×), and Et_2O (1×) and dried under vacuum overnight, yielding 0.51 g of very pale yellow powder: IR (KBr) peaks absent at 1363, 1180, 1098, 964, 905, 815, 760, 664, and 555 cm^{-1} for tosylate precursor and 1630 cm^{-1} for elimination side product, peaks present at 1727 (s, C=O), 1535 (s, Ar NO_2), 1351 (s, Ar NO_2), 1263 (m, CO–O), 1134 (m, CO–O), 720 cm^{-1} (m, Ar NO_2). Anal. Calcd for $(C_{10}H_{10})_{0.01}\cdot(C_8H_8)_{0.68}\cdot(C_{17}H_{15}NO_4)_{0.31}$: N, 2.64. Found: N, 2.45.

An alternate procedure involving cesium fluoride[31] instead of potassium carbonate also afforded excellent results.

(2-Chloroethyl)polystyrene (9). (2-Hydroxyethyl)polystyrene with DF = 0.24 $[(C_{10}H_{10})_{0.01}\cdot(C_8H_8)_{0.75}\cdot(C_{10}H_{12}O)_{0.24}]$ (3.03 g, 6.3 mequiv) was treated with thionyl chloride (1.5 mL, 21 mequiv) and dry pyridine (0.1 mL, 1 mequiv) in 30 mL of dry CCl_4 under nitrogen, and the suspension was stirred at reflux for 16 h. The orange suspension was filtered and the residue washed with H_2O (1×) (bleaching), MEK (1×), H_2O (3×), THF–concentrated HLc/H_2O (1:1, 1×), THF (1×), CH_2Cl_2 (1×), and CH_3OH (1×) and dried under vacuum overnight, yielding 3.15 g of a pale peach powder: IR (KBr) peaks absent at 3400 and 1046 cm^{-1} for alcohol precursor and at 1633, 1582 and 682 cm^{-1} for pyridinium side product; peaks present at 1245 (w, CH_2Cl), 657 cm^{-1} (w, C–Cl). Anal. Calcd for $(C_{10}H_{10})_{0.01}\cdot(C_8H_8)_{0.75}\cdot(C_{10}H_{11}Cl)_{0.24}$: C, 7.13. Found: Cl, 7.09.

(2-Bromoethyl)polystyrene (10). Method A. (2-Hydroxyethyl)polystyrene with DF = 0.31 $[(C_{10}H_{10})_{0.01}\cdot(C_8H_8)_{0.68}\cdot(C_{10}H_{12}O)_{0.31}]$ (0.49 g, 1.3 mequiv) and phosphorous tribromide (0.50 mL, 5.3 mequiv) were stirred together in dry ether for 18 h at 0 °C under nitrogen. The yellow suspension was quenched with methanol (fumes) and then filtered and the residue washed with CH_3OH (2×), H_2O (3×), MEK (1×), CH_2Cl_2 (1×), and CH_3OH (2×) and dried under vacuum overnight to yield 0.56 g of white powder: IR (KBr) peaks absent at 1046 cm^{-1} for alcohol precursor, peaks present at 1263 and 647 cm^{-1} attributable to product bromide, but other peaks at 1220 (m), 1068 (m), and 978 (m) cm^{-1} indicate some phosphite intermediate remaining in the polymer; this persisted even after a further wash with hydrobromic acid.

Method B. (2-Hydroxyethyl)polystyrene with DF = 0.31 $[(C_{10}H_{10})_{0.01}\cdot(C_8H_8)_{0.68}\cdot(C_{10}H_{12}O)_{0.31}]$ (2.00 g, 5.3 mequiv) hexadecyltributylphosphonium bromide (0.27 g, 0.5 mequiv), and 48% HBr/H_2O (8.0 mL, 70 mequiv) were stirred vigorously at slow reflux under nitrogen for 40 h. The suspension was then filtered and the residue washed with H_2O (3×), MEK (1×), CH_2Cl_2 (1×), and Et_2O (1×) and dried under vacuum overnight, yielding 2.30 g of pale yellow powder: IR (KBr) peaks absent at 1046 cm^{-1} for alcohol precursor, as well as P–O peaks seen in method A, peaks present at 1263 (m, CH_2Br) and 647 (w, C–Br) cm^{-1}. Anal. Calcd for $(C_{10}H_{10})_{0.01}\cdot(C_8H_8)_{0.68}\cdot(C_{10}H_{11}Br)_{0.31}$: Br, 18.01. Found: Br, 16.22.

Method C (Preferred Route). The tosylated polymer 7 with DF = 0.29 $[(C_{10}H_{10})_{0.01}\cdot(C_8H_8)_{0.70}\cdot(C_{17}H_{18}SO_3)_{0.29}]$ (5.00 g, 9.0 mequiv) was added to a solution of anhydrous magnesium bromide in ether, prepared from magnesium turnings (1.2 g, 50 mequiv) and 1,2-dibromoethane (2.2 mL, 25 mequiv) and decanted from excess solid, and then was allowed to stir at reflux under argon for 17 h. The pale brown suspension was filtered and the residue washed with acetone (1×), H_2O (3×), MEK (1×), CH_2Cl_2 (1×), and CH_3OH (2×) and dried under vacuum overnight, yielding 4.21 g of a very pale beige powder: IR (KBr) peaks absent at 1363, 1180, 1098, 964, 905, 815, 760, 664, and 555 cm^{-1} for tosylate precursor, peaks present are the same as those for **10** made by method B. Anal. Calcd for $(C_{10}H_{10})_{0.01}\cdot(C_8H_8)_{0.70}\cdot(C_{10}H_{11}Br)_{0.29}$: Br, 17.11. Found: Br, 17.18.

(2-Iodoethyl)polystyrene (11). (2-Hydroxyethyl)polystyrene with DF = 0.29 $[(C_{10}H_{10})_{0.01}\cdot(C_8H_8)_{0.70}\cdot(C_{10}H_{12}O)_{0.29}]$ (0.504 g, 1.3 mequiv), dry sodium iodide (0.412 g, 2.8 mequiv), chlorotrimethylsilane (0.35 mL, 2.8 mequiv), and 5 mL of dry acetonitrile were mixed and stirred under nitrogen at reflux for 8 h. The gold suspension was filtered and the residue washed with MEK (1×), H_2O (3×), MEK (1×), CH_2Cl_2 (1×), and CH_3OH (2×) and dried under vacuum overnight, yielding 0.654 g of a very pale beige-yellow powder: IR (KBr) peaks absent at 1046 cm^{-1} for alcohol precursor, peaks present at 1236 (m, CH_2I), 1168 (m, CH_2I), 867 cm^{-1} (s, C–I). Anal. Calcd for $(C_{10}H_{10})_{0.01}\cdot(C_8H_8)_{0.75}\cdot(C_{10}H_{11}I)_{0.24}$: I, 24.79. Found: I, 24.87.

(2-*N*-Pyridinioethyl)polystyrene Tosylate and (2-*N*-Pyridinioethyl)polystyrene Chloride (12). (2-Hydroxyethyl)polystyrene with DF = 0.24 $[(C_{10}H_{10})_{0.01}\cdot(C_8H_8)_{0.75}\cdot(C_{10}H_{12}O)_{0.24}]$ (4.99 g, 10.4 mequiv) and *p*-toluenesulfonyl chloride (5.0 g, 26 mequiv) were suspended in dry pyridine (60 mL, 700 mequiv) chilled in an ice bath at 0 °C under nitrogen. The mixture was allowed to warm to room temperature over 4 h, then refluxed for 2 h, then cooled, and filtered, and the residue was washed H_2O (3×), MEK (1×), CH_2Cl_2 (1×), CH_3OH (1×), and Et_2O (1×) and dried under vacuum overnight, yielding 6.72 g of a peach-colored powder (**12**, tosylate anion): IR (KBr) peaks absent at 1046 cm^{-1} for alcohol precursor, at 1363 and 1176 cm^{-1} for tosyl ester intermediate, and at 1245 (m) and 657 cm^{-1} (w) for alkyl chloride side product, peaks present at 3500 (s, br, absorbed H_2O), 1633 (m, pyr), 1582 (w, pyr), 1196 (s, SO–O^-), 1123 (s, SO–O^-), 1034 (s, SO–O^-), 1012 (s, SO–O^-), 682 (m, pyr^+), and 569 cm^{-1} (m, Ar SO_3^-). The product was then washed with concentrated hydrochloric acid, then HCl/H_2O–THF (1:1, 1×), HCl/H_2O–THF (1:4, 1×), H_2O (3×), MEK (1×), CH_2Cl_2 (1×), CH_3OH (1×), Et_2O (1×), and hexane (1×) and dried under vacuum overnight, yielding 5.99 g of beige powder (**12**, chloride anion): IR (KBr) peaks absent at 1196, 1123, 1034, 1012 and 569 cm^{-1} for tosylate anion, peaks still present at 1633, 1582 and 682 cm^{-1} for pyridinium nucleus. Anal. Calcd for $(C_{10}H_{10})_{0.01}\cdot(C_8H_8)_{0.75}\cdot(C_{15}H_{16}NCl)_{0.24}$: Cl, 6.15. Found: Cl, 6.19

(2-*N*-Pyrrolidinylethyl)polystyrene (13a). Method A (from 7 in Me_2SO). The tosylated polymer 7 with DF = 0.31 $[(C_{10}H_{10})_{0.01}\cdot(C_8H_8)_{0.68}\cdot(C_{17}H_{18}SO_3)_{0.31}]$ (0.195 g, 0.36 mequiv) was stirred with K_3PO_4 (0.10 g, 0.47 mequiv), K_2HPO_4 (0.05 g, 0.29 mequiv), and dry pyrrolidine (0.050 mL, 0.60 mequiv) in 3 mL of dry dimethyl sulfoxide under nitrogen at room temperature for 16 h and then at 40 °C for 18 h. The pale yellow-green suspension was filtered and the residue washed with acetone (1×), H_2O (3×), MEK (1×), CH_2Cl_2 (1×), and CH_3OH (1×) and dried under vacuum overnight, yeilding 0.171 g of pale beige powder: IR (KBr) peaks absent at 1363 and 1176 cm^{-1} for alcohol precursor, peaks present at 2785 cm^{-1} (m, CH_2) but also at 1630 cm^{-1} (w, C=C). Anal. Calcd for $(C_{10}H_{10})_{0.01}\cdot(C_8H_8)_{0.68}\cdot(C_{14}H_{19}N)_{0.31}$: N, 3.23. Found: N, 2.55. Other polymer pyrrolidines prepared in dimethyl sulfoxide, with or without added acid acceptor and/or heating, also display detectable peaks at 1630 cm^{-1}, attributed to elimination, and occasionally weak peaks at 1196, 1123, 1034, 1012, and 569 cm^{-1} due to tosylate anion, which persist even after washing with 5% methanolic NaOH. Very similar results were obtained with DMF as solvent instead of Me_2SO. Anal. Calcd: N, 3.07. Found: N, 2.85.

Method B (Direct Route: from 4 in Pyridine). (2-Hydroxyethyl)polystyrene with DF = 0.24 $[(C_{10}H_{10})_{0.01}\cdot(C_8H_8)_{0.75}\cdot(C_{10}H_{12}O)_{0.24}]$ (1.01 g, 2.1 mequiv) was stirred with *p*-toluenesulfonyl chloride (1.00 g, 5.2 mequiv) in dry pyridine (10 mL, 120 mequiv) under nitrogen at 0 °C for 23 h. To the red-orange suspension was added dry pyrrolidine (2.00 mL, 24 mequiv), and the mixture was allowed to stir at room temperature for 2 days, then heated to reflux for 4 h, and filtered and the residue washed with MEK (1×), CH_3OH (1×), H_2O (3×), 20% NaOH/H_2O–ethanol (1:5, 1×), H_2O (3×), EtOH (1×), MEK (1×), CH_2Cl_2 (1×), and CH_3OH (2×) and dried under vacuum overnight, yielding 1.12 g pale beige powder: IR (KBr) peaks absent at 1046 cm^{-1} for alcohol precursor, at 1363 and 1176 cm^{-1} for tosyl ester intermediate, at 1630 cm^{-1} for elimination side product, at 1196, 1123, 1034, 1012, and 569 cm^{-1} for tosylate anion, and at 1633, 1582 and 682 cm^{-1} for pyridinium side product, peaks present at 2785 cm^{-1} (CH_2). Anal. Calcd for $(C_{10}H_{10})_{0.01}\cdot(C_8H_8)_{0.75}\cdot(C_{14}H_{19}N)_{0.24}$: N, 2.63. Found: N, 2.69.

(2-*N*-Imidazolylethyl)polystyrene (13b). Anhydrous crystalline imidazole (0.724 g, 10.6 mequiv) dissolved in 5 mL of dimethylformamide was slowly added to a slurry of sodium hydride (0.23 g, 9.5 mequiv) in 15 mL of cooled dimethylformamide, and the mixture was stirred under nitrogen as it fizzed for 1 h before receiving tosylated polymer 7 $[(C_{10}H_{10})_{0.01}\cdot(C_8H_8)_{0.70}\cdot(C_{17}H_{18}SO_3)_{0.29}]$ (1.90 g, 3.4 mequiv) in portions. After being stirred at 10 °C for 18 h, the pale red-brown suspension was filtered and the residue washed with H_2O (3×), MEK (1×), CH_2Cl (1×), and CH_3OH (2×) and then dried under vacuum overnight, yielding

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[31] Clark, J. H.; Miller, J. M. *J. Am. Chem. Soc.* 1977, *99*, 498.

1.54 g of pale beige powder: IR (KBr) peaks absent at 1176 cm^{-1} for tosyl ester precursor, as well as at 1365 cm^{-1} (*N,N*-dialkylimidazolium nucleus) and 1196, 1123, 1034, 1012 and 569 cm^{-1} (tosylate anion) from quaternization, and 1630 cm^{-1} from elimination side products, peaks present at 3105 (w), 1508 (m), 1284 (m), 1231 (m), 1108 (m), 1076 (m), 905 (m), 663 (s), and 624 (m) cm^{-1} (all attributed to the *N*-alkylimidazole functionality). Anal. Calcd for $(C_{10}H_{10})_{0.01}\cdot(C_8H_8)_{0.70}\cdot(C_{13}H_{14}N_2)_{0.29}$: N, 6.17. Found: N, 5.87.

[2-(*N*-Methyl-*N*-(*p*-tolylsulfonyl)amino)ethyl]polystyrene (14). A mixture of tosylated polymer 7 $[(C_{10}H_{10})_{0.01}\cdot(C_8H_8)_{0.70}\cdot(C_{17}H_{18}SO_3)_{0.29}]$ (0.3894 g, 0,53 mequiv) with *N*-methyl-*p*-toluenesulfonamide (0.1373 g, 0.74 mmol) and anhydrous potassium carbonate (0.212 g, 1.53 mmol) in 4 mL of dry dimethyl sulfoxide containing 0.5 mL of HMPA was stirred overnight at 60 °C under nitrogen. After cooling, the beige suspension was filtered, and the residue was washed with acetone, H_2O (3×), MEK (1×), CH_2Cl_2 (1×), and CH_3OH (2×) and dried under vacuum overnight, yielding 0.3926 g of pale beige powder: IR (KBr) peaks absent at 1363 and 1176 cm^{-1} from tosyl ester precursor and at 1630 cm^{-1} from elimination byproduct, peaks present at 1344 (s, SO–NC), 1161 (s, SO–NC), 653 (m, Ar SO_2) and 549 cm^{-1} (m, Ar SO_2). Anal. Calcd for $(C_{10}H_{10})_{0.01}\cdot(C_8H_8)_{0.70}\cdot(C_{18}H_{21}NSO_2)_{0.29}$: N, 1.91; S, 4.53. Found: N, 1.98, S, 4.80.

An alternate procedure with sodium hydride in DMF at 10 °C was somewhat less satisfactory.

[2-(*N*-Methylamino)ethyl]polystyrene (15). Sodium metal (0.094 g, 4.1 mequiv) and naphthalene crystals (0.63 g, 4.9 mequiv) were stirred together in 4 mL of dry dimethoxyethane under nitrogen for 90 min, and then polymer 14 prepared above $[(C_{10}H_{10})_{0.01}\cdot(C_8H_8)_{0.70}\cdot(C_{18}H_{21}NSO_2)_{0.29}]$ (0.378 g, 0.68 mequiv) was added in portions. After being stirred at room temperature for 30 h, the dark brown solution was filtered and the residue washed with H_2O (3×), MEK (1×), CH_2Cl_2 (1×), and CH_3OH (2×) and then dried under vacuum overnight, yielding 0.348 g of pale yellow-green powder: IR (KBr) peaks absent at 1344, 1161, 653, and 549 cm^{-1} for precursor sulfonamide, peaks present at 1155 (w, C–N) and 1116 cm^{-1} (w, C–N). Anal. Calcd for $(C_{10}H_{10})_{0.01}\cdot(C_8H_8)_{0.70}\cdot(C_{18}H_{21}N)_{0.29}$: N, 3.36. Found: N, 2.43; S, 1.05.

(2-Aminoethyl)polystyrene (16). $(C_{10}H_{10})_{0.01}\cdot(C_8H_8)_{0.70}\cdot(C_{17}H_{18}SO_3)_{0.29}$ (0.200 g, 0.36 mequiv), phthalimide (0.062 g, 0.42 mequiv), and anhydrous potassium carbonate (0.0567 g, 0.41 mequiv) were stirred in 2.0 mL of dry DMF at 60 °C under nitrogen for 48 h. The pale yellow-green suspension was filtered and the residue washed with H_2O (3×), MEK (1×), CH_2Cl_2 (1×), and CH_3OH (2×) and then dried under vacuum overnight, yielding 0.198 g of pale beige-yellow powder: IR (KBr) peaks absent at 1363 and 1176 cm^{-1} for tosyl ester precursor and 1630 cm^{-1} for elimination side product, peaks present at 1774 (w, C=O), 1716 (s, C=O), 719 cm^{-1} (m, Ar C=O). Anal. Calcd for $(C_{10}H_{10})_{0.01}\cdot(C_8H_8)_{0.70}\cdot(C_{18}H_{15}NO_2)_{0.29}$: N, 2.63. Found: N, 2.54.

Part of the product (0.139 g, 0.26 mequiv) and 40% hydrazine/H_2O (0.10 mL, 1.3 mequiv) were stirred with 2 mL of ethanol at reflux for 5 h, then the white suspension was filtered, and the residue was washed with acetone (1×), H_2O (3×), 5% NaOH/EtOH (1×), H_2O (3×), EtOH (1×), MEK (1×), CH_2Cl (1×), and CH_3OH (2×) and dried under vacuum overnight, yielding 0.109 of white powder: IR (KBr) peaks absent at 1774, 1716, 719 cm^{-1} (as present above), peaks present at 3410 (m, NH_2) and 1098 (m, C–N) cm^{-1}. Anal. Calcd for $(C_{10}H_{10})_{0.01}\cdot(C_8H_8)_{0.70}\cdot(C_{10}H_{13}N_2)_{0.29}$: N, 3.48. Found: N, 2.61.

[2-(Butylthio)ethyl]polystyrene (17). Tosylated polymer 7 with DF = 0.31 $[(C_{10}H_{10})_{0.01}\cdot(C_8H_8)_{0.68}\cdot(C_{17}H_{18}SO_3)_{0.31}]$ (0.50 g, 0.94 mequiv), butanethiol (0.22 mL, 2.1 mequiv), hexadecyltributylphosphonium bromide (0.077 g, 0.15 mequiv) and anhydrous potassium carbonate (0.33 g, 2.4 mequiv) were stirred rapidly in 4.5 mL of refluxing toluene under nitrogen for 50 h, then the white suspension was filtered, and the residue was washed with H_2O (3×), MEK (1×), CH_2Cl_2 (1×), and CH_3OH (2X) and dried under vacuum overnight, yielding 0.44 g of white powder: IR (KBr) peaks absent at 1363 and 1176 cm^{-1} for tosyl ester precursor and 1630 cm^{-1} for elimination side product, peak present at 2853 cm^{-1} (m, CH_2). Anal. Calcd for $(C_{10}H_{10})_{0.01}\cdot(C_8H_8)_{0.68}\cdot(C_{14}H_{20}S)_{0.31}$: S, 7.08. Found: S, 5.76.

[2-(Diphenylphosphino)ethyl]polystyrene (18). A 25 wt % dispersion of lithium metal in mineral oil (0.10 g, 3.6 mequiv) was suspended in 5 mL of dry THF under argon; chlorodiphenylphosphine (0.30 mL, 1.7 mequiv) was added slowly, and the whole was stirred at room temperature for 3 h. The resulting red solution was then decanted through a double-ended needle onto tosylated polymer 7 (0.50 g, 0.94 mequiv), together with 0.5 mL of dry Me_2SO, and the mixture was stirred under argon at 25 °C for 24 h and then at 50 °C for 24 h. The red suspension was then filtered, and the residue was washed with acetone (1×), H_2O (3×), MEK (1×), benzene (1×), and CH_3OH (3×) and dried under vacuum overnight, yielding 0.51 g of pale beige powder: IR (KBr) peaks absent at 1363 and 1176 cm^{-1} for tosyl ester precursor, peaks present at 1435 (m, P–Ar), 1481 (w, P–Ar), and 999 cm^{-1} (w, P–Ar). Anal. Calcd for $(C_{10}H_{10})_{0.01}\cdot(C_8H_8)_{0.68}\cdot(C_{22}H_{21}P)_{0.31}$: P, 5.65. Found: P, 5.24.

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On the Stereochemistry and Mechanism of the Ozonation of Some Six-Membered Ring Vinyl Sulfides

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Allylic alcohols 3 and α,β-epoxy sulfoxides 6/7 were the partial cleavage products isolated from the ozonation of six-membered-ring vinyl sulfides 1 with respectively stoichiometric and double amounts of ozone. They were characterized by spectroscopic methods, including measurements of aromatic solvent induced shifts (ASIS). From careful examination of the resulting data, the stereochemistry of the ozone addition to vinyl sulfides seemed to derive from an initial, axial carbon–oxygen bond formation at the β-carbon. The intermediary epoxy sulfide 2 was correlated to a mechanism based on stereoelectronic control upon the fragmentation of a primary ozonide adduct, viz., the five-membered-ring 1,2,3-trioxolane IV.

Extensive interest has been shown in the ozone–olefins reactions, a topic which has been recently reviewed by Bailey.[1] Among the main reaction pathways in solution, ozonolysis is well-recognized as a versatile method for