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Functional Polymers from (Vinyl)polystyrene. Short Routes to Binding Functional Groups to Polystyrene Resin through a Dimethylene Spacer: Bromine, Sulfur, Phosphorus, Silicon, Hydrogen, Boron, and Oxygen

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Many spacer-containing functional polymers were produced by modifying beads of (vinyl)polystyrene, as obtained by free-radical suspension polymerization of a commercial 55:45 divinylbenzene: ethylstyrene mixture, or from commercial sources. Thus, in the presence of free-radical initiators, compounds HBr, HPR_2, $HP(OR)_2$, and HSR (R = various alkyl, aryl or acyl, some also containing further COOH/R, OH/R, SH/R, $N(H/R)_2$ groups) underwent anti-Markovnikov addition to the residual vinyl groups. Similar free-radical functionalization with various $HSiR_3$ also proved feasible but more difficult. Other products corresponding to formal anti-Markovnikov addition of H_2S, HSO_3^-, $HP(OH)_2$, H_2, HBR_2, HOH, and $HOSO_2R$ were obtained by other mechanisms, or after further modifications. FTIR spectra of the resulting functional polymers often showed complete or near-complete disappearance of initial vinyl groups and their replacement by the expected spacer-supported functionalities. The polymer products were also characterized by elemental analysis and solid-state NMR. Many of these functionalized beads, or their further derivatives upon functional group modification, could act as stable and effective solid-phase reagents, catalysts, sequestering agents, or protecting groups for solid-phase synthesis.

Over the years, cross-linked functional polymers have been much studied and widely employed as solid-phase reagents, catalysts, protecting groups, and sorbents.[1−5] Their advantages over corresponding soluble chemicals include easy separation from dissolved products by simple filtration, and multiple regeneration and reuse of the functional polymer to offset its initial cost. The special microenvironments inside polymer beads can also benefit the reactivities of functional groups there.[6−9]

For simplicity, versatility, controlled architecture, and even distribution and ready accessibility of functional groups, functional polymers are generally better prepared by modification of preexisting polymers, rather than by copolymerization with specialty monomers.[6,10−12] To date, chloromethylation of cross-linked polystyrene, followed by nucleophilic substitution, has been a very popular route.[13−15] However, serious problems arise from the carcinogenicity of the chloromethylation reagents; also, the stability of the polymer products is often limited, due to functional group heteroatoms being connected to the polymer backbone via only a weak benzylic bond that is subject to unwanted cleavage during many reaction or regeneration conditions.[16,17] More recently, other functional polymers have been reported that incorporate ethylene (dimethylene) spacers for more stable attachments through non-benzylic primary bonds.[16,17] Such distancing from the polymer backbone may also confer further advantages of more mobile[18] and accessible functional groups,[6,19,20] and thus greater catalytic or other activity of the functional polymer product.[7,21] However, their syntheses so far have required many steps and the use of toxic and/or expensive chemicals.

Here we describe a very general and direct way to make a wide variety of stable and effective spacer-

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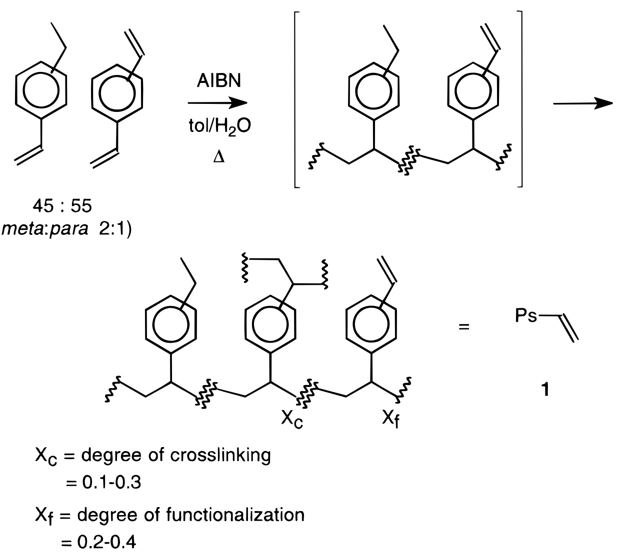
Scheme 1. Preparation of (Vinyl)polystyrene Intermediate 1



containing functional polymers, with mild conditions and good yields from a common precursor, **1**. Easily prepared, and even commercially available, **1** is essentially a cross-linked polystyrene matrix bearing residual vinyl groups, hence our term "(vinyl)polystyrene" and abbreviation "$PsCH{=}CH_2$" (Scheme 1). Upon radical or other anti-Markovnikov addition of a reagent "H−X" (Scheme 2), each such vinyl becomes a dimethylene spacer supporting a functional group, for an overall functional polymer "$PsCH_2CH_2X$" or "(X-ethyl)polystyrene)" (Scheme 3).

Results and Discussion

Preparation of $PsCH{=}CH_2$ Precursor. Free-radical suspension copolymerization of divinylbenzene with other styrenic monomers gives cross-linked macroporous resins of porosities and surface areas controlled by relative proportions of water, monomers, porogens, and suspending agents.[6,12,22−24] These have been shown to often still bear many unreacted pendant vinyl groups,[25,26] as detected by solid-phase NMR (δ 135 *C*H= and 110 =*C*H$_2$),[27,28] and quantitated by FTIR (1630 C=C and 990 C=*CH* cm^{-1}),[25,29,30] or, less conveniently and reliably,[27,29] by chemical assay with bromine[30] or other reagents.[11] A simple model of polymerization to account for this morphology would be (1) incorporation of divinylbenzene into propagating polymer chains, through reaction of one vinyl group as activated by the other; (2) further cross-linking reactions between those resulting polymer-bound vinyl groups that are actually adjacent, while others remain site isolated[20] and intact within the increasingly rigid cross-linked matrix. Thus, even after 24 h polymerization conditions from a "55% DVB" monomer mixture with toluene as porogen, ca. 0.20 of repeating units in the resulting (vinyl)polystyrene **1** still bore $CH{=}CH_2$ groups (degree of functionalization $X_f \cong 0.20$; Figure 1). Longer heating in toluene at 70 °C with AIBN did not significantly further consume vinyl groups, while 48 h reflux with di-*tert*-butyl peroxide (t-BPO) decreased X_f by only another 0.05;[11,31] few vinyls are reported to remain on further heating above 150 °C with a radical generator.[27] This eventual general reluctance for coupling between polymer-supported vinyls is in dramatic contrast to the analogous free molecules, i.e. styrene and its *m*/*p*-alkyl derivatives, in which vinyl polymerizations are often so rapid as to overshadow other possible reactions, so that even high reagent:alkene ratios yield telomers at best.[32] It also contrasts with the prevalence of interchain reactions in more lightly-cross-linked polystyrene matrices.[10,33,34]

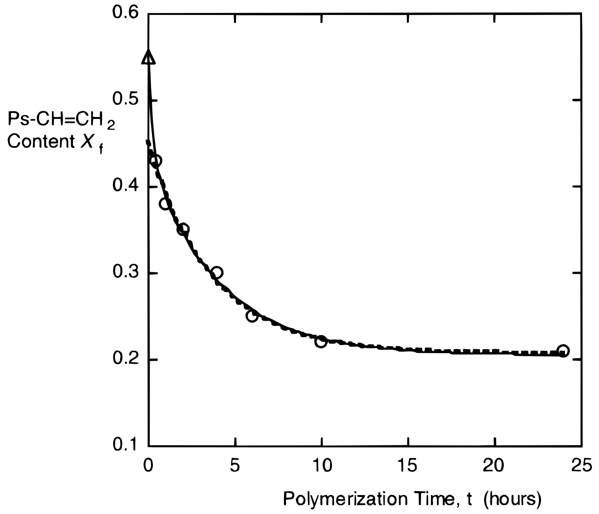


Figure 1. Effect of time on content of residual vinyl groups during preparation of (vinyl)polystyrene **1** by polymerization of divinylbenzene (see ExperimentalSection). (○) X_f measured by FTIR. (△) X_f reported by GC. (- - -) Curve fitted to FTIR points only: $X_f = 0.245e^{-0.273t} + 0.207$. (—) Curve fitted to all points: $X_f = 0.116e^{-3.56t} + 0.229e^{-0.246t} + 0.205$.

Table 1. Characteristics of the Several Batches of 1 Used in This Study[a]

batch no.	monomer mass (g)	yield (%)	vinyl content (X_f)	capacity (mmol/g)	particle diameter (μm)	particle area (m^2/g)	swell ratio (toluene)
1a	20	65	0.35	2.67	250−425	26.6	1.84
1b	100	50	0.43	3.28	250−425	20.9	1.96
1c	200	89	0.30	2.29	250−425	18.3	1.74
1d	250	88	0.30	2.29	250−425	16.7	1.59
1e	30	76	0.35	2.67	250−425	−	−
1f	30	83	0.35	2.67	250−425	−	−
1g	200	90	0.25	1.91	250−425	127.2	1.26
1h	200	60	0.35	2.67	250−425	77.2	1.85

[a] Proportions, conditions, and analyses as described in Experimental Section.

This study mostly used **1** from shorter polymerization times, typically at $X_f \cong 0.30{-}0.35$ after 2 h (Table 1). Even with such higher concentrations of vinyl groups or their derivatives, many of the later addition or other reactions of the individual functionalities were often able

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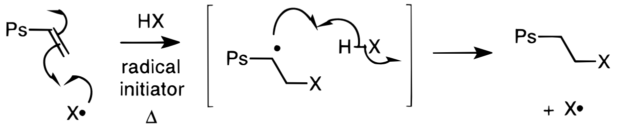
Scheme 2. Radical-Initiated Additions to 1



to compete with their further dimerization or other cross-linking to give functional group product of $X_f > 0.20$ (see below). Though we infer that significant further cross-linking could not be avoided at other times, still most such new cross-links would usually be chemically inert in themselves; moreover, cross-linking side-reactions are often also the rule for chloromethylation and other "traditional" functionalizations/functional group modifications on cross-linked polystyrene.[11,33]

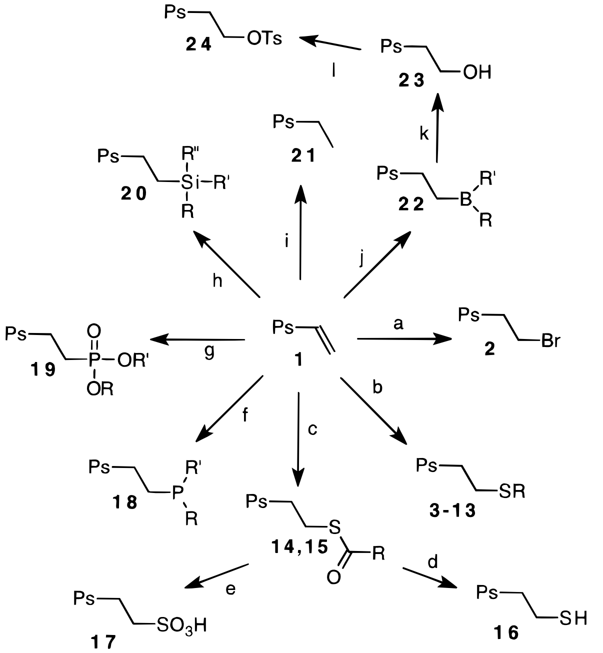
That surface area, and ability to swell in toluene, were both moderately large in the several batches of our **1** polymer particles (Table 1), implies both gellike and macroporous domains therein.[6] As noted elsewhere,[27,35] commercially-available (Rohm & Haas) "Amberlite XAD-4", "XAD-2", and "XAD-16" also contain residual vinyls as shown by FTIR spectra similar to our "benchtop" products and were presumably manufactured in a similar manner: further details on their characteristics and use as **1** to prepare other functional polymers will be reported elsewhere.[36] Preparations of (vinyl)polystyrene with much lower degrees of cross-linking (X_c) have also been reported from (chloromethyl)polystyrene[37,38] and by elimination of certain $PsCH_2CH_2X$ made in other ways.[17]

Chemical Modification of 1 to $PsCH_2CH_2X$. Though typically thought a nuisance in chloromethylation (undergoing cationic polymerization/cross-linking and other side-reactions)[12,39] and other "traditional" functionalizations, residual vinyl groups on cross-linked polystyrene have in the past been functionalized by graft copolymerization of functional monomers[11,40] and by bromination, epoxidation, and ozonolysis.[41] A few particular instances of addition of H−X have also been described, as will be mentioned below.

To achieve spacer-supported functional polymers $PsCH_2CH_2X$, addition of H−X to $PsCH{=}CH_2$ **1** must proceed exclusively with β or anti-Markovnikov orientation, such as occurs for several classes of compounds by a free-radical mechanism (Scheme 2).[42−44] The $PsCHX-CH_3$ α or Markovnikov product typical of electrophilic-type additions would be unwelcome for its functional group X being closer to the polymer backbone Ps and for having a secondary benzylic connection that is probably still less stable than the $PsCH_2-X$ bond from (chloromethyl)polystyrene.

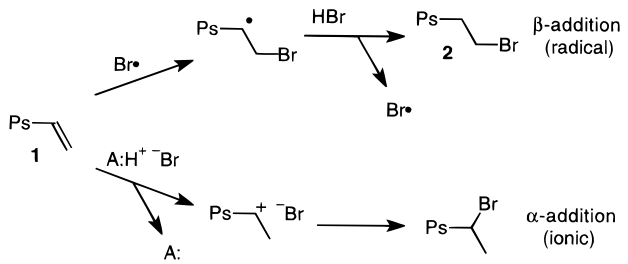
Bromide. Like $PsCH_2Cl$, $PsCH_2CH_2X$, in which X is a good leaving group like Br, would be a versatile intermediate for the synthesis of other dimethylene-spaced functional polymers by nucleophilic substitution, particularly with amines and other nitrogen species.[16,17,35] Preparations of $PsCH_2CH_2Br$ from PsH via $PsCH_2CH_2OH$ are known but complicated.[16,45]

Scheme 3. Functional Polymers With Dimethylene Spacers From 1[a]



[a] (a) LiBr, Me_3SiCl, H_2O, AIBN cat., Δ; (b) HSR, AIBN cat., Δ; (c) $HSCOCH_3$, AIBN cat., Δ; (d) HCl, H_2O, Δ; (e) CH_3CO_3H; (f) HPRR', AIBN cat., Δ; (g) HPO(OR)(OR'), AIBN cat., Δ; (h) HSiRR′R″, $(t\text{-}BuO)_2$ cat., Δ; (i) $HSiEt_3$, CF_3COOH; (j) 9-BBN-H; (k) H_2O_2, NaOH, H_2O; (l) TsCl, $i\text{-}Pr_2NH$, Δ.

Scheme 4. Two Modes of Addition of HBr to 1



It has become common wisdom that hydrogen bromide in the presence of radical generators such as peroxides will add across alkenes with anti-Markovnikov orientation. Even then, however, Markovnikov addition of this acidic substance often competes, particularly with even traces of aqueous or other oxygenated solvents that convert homolytically-cleavable covalent HBr to protonating $R'RHO^+$ ^-Br, and also particularly with styrene that has such a stabilized carbocation intermediate.[35,44,46−48]

Treatment of microparticulate (vinyl)polystyrene with aqueous hydrobromic acid in the absence of radical initiators that has previously been reported would thus likely be giving mostly α-addition product (Scheme 4).[41] More serious efforts for exclusive β-addition to residual vinyl groups of cross-linked polystyrene have also been

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described, using “carefully dried” hydrogen bromide gas in hydrocarbon solvent with AIBN, though even then some α-contaminant showed in the FTIR spectrum of the product.[35]

We found that after stirring **1** with AIBN catalyst in excess concentrated aqueous hydrobromic acid and toluene at 70−80 °C, most or all of its residual vinyl groups had disappeared, according to both FTIR (peaks gone at 1630 or 990 cm^{-1}) and ^{13}C CP-MAS NMR (peaks gone at δ 135 and 110) analyses. This disappearance of vinyl was mostly accompanied by uptake of Br (elemental analysis), mainly by β-addition of HBr (FTIR 1264 cm^{-1} $\mathit{CH_2}Br$, ^{13}C CP-MAS NMR δ 27 $\mathit{C}H_2Br$) but also by significant α-addition as well (FTIR 1180 cm^{-1} for $CHBr\mathit{CH_3}$, and ^{13}C CP-MAS NMR δ 27, persisting with 45 μs dipolar dephasing, for $CHBr\mathit{C}H_3$). In exploring conditions, we found this undesired side-reaction only increased with increasing temperature, to predominate at 125 °C, while still remaining important at lower temperatures; the addition of quaternary (e.g. trinonylmethyl) ammonium chloride at 80 °C gave α-product exclusively. Our own use of HBr gas confirmed previous reports[35] of greater but still not complete selectivity for β-addition. Somewhat unexpectedly, we found that this reaction with HBr being generated in situ by slow addition of a minimum of water to a mixture of chlorotrimethylsilane and anhydrous lithium bromide gave $PsCH_2CH_2Br$ **2** with even less (i.e. indiscernible amounts) of the α-product. Possibly these hygroscopic and otherwise dehydrating reagents and product (lithium chloride) quickly segregated even such traces of α-inducing free moisture as may have been present at the outset on polymer or glass surfaces. The use of preformed, commercial bromotrimethylsilane did not yield β nearly as selectively.

Sulfides and Sulfonates. $PsCH_2S(O)CH_3$ has been used to oxidize alkyl halides to aldehydes,[49] and polymer-supported thioethers to complex with borane for reductions.[50] Polymer-supported thiols have been used to make reagents for trifluoroacetylation[51] and to act as selective ion exchangers.[52] S-Linking to cross-linked polystyrene has been done by reaction of thiolate with (chloromethyl)polystyrene, often under phase-transfer conditions;[34] non-benzylic $PsCH_2CH_2SR$ have similarly been made by nucleophilic substitution of $PsCH_2CH_2OTs$.[16]

Thiols add directly to olefins with anti-Markovnikov orientation in the presence of free radicals; with these only weak acids, the Markovnikov reaction hardly competes. The thiol can be alkyl or aryl, primary, secondary, or tertiary, or containing OR, COOR, COR, F, Cl, NRR′, or SR including other SH; the reaction is also very general for alkenes to thus give an enormous variety of possible sulfides.[44] The reaction has been applied toward photoinitiated cross-linking of polyenes with polythiols.[53,54] In our experiments, radical additions of various HSR compounds across residual double bonds of (vinyl)polystyrene took place readily under mild conditions, usually at 70 °C, in toluene, with AIBN as radical initiator. Elemental analysis, FT-IR, and solid state ^{13}C CP-MAS NMR spectra of the resulting materials generally showed complete or nearly-complete disappearance of vinyl group after 1−2 days, with the appearance of the corresponding sulfide.

Most of these thiols were S-linked to polymer to over 0.20 degree of functionalization (X_f). The functionality of the product **4** from 1,1-dimethylethanethiol was a bit lower, possibly due to reduced accessibility of the thiol or its radical or by poorer penetration of this wider molecule into the polymer matrix. Cysteine ethyl ester hydrochloride for **12** also proved difficult to add under the standard conditions, presumably because of exclusion of this polar and ionic species from the toluene-like polymer phase. Its uptake was significantly improved by the use of more polar solvent systems and of 600 g/mol polyethylene glycol (PEG-600) as phase tranfer agent, as well as by grinding the solid phase to finer particle size, thus improving its surface-to-volume ratio and accessibility of its vinyl groups to the polar-enriched liquid phase.

The high sulfur analyses of the products from dithiols suggested that only one of the two SH groups of the dithiol had added to the double bond of (vinyl)polystyrene, to give $PsCH_2CH_2S(CH_2CH_2)_nSH$ **8**−**10** without cross-linking. This was confirmed by the peak at 2577 cm^{-1} of SH in the Raman spectrum and is thus evidence of site isolation of the starting vinyl groups and of all addition products therefrom. This contrasts with the cross-linking that occurs during many functional group modifications of 1−2% cross-linked (chloromethyl)polystyrene.[33,55]

Attempts to produce dimethylene spacer linked thiouronium salts $PsCH_2CH_2SCN_2H_5Br$ gave some α as well as β addition, as shown by FT-IR and solid-phase NMR of product **13**, possibly due to competing ionic reactions involving HBr coreagent.

$PsCH_2CH_2SH$ **16** could be obtained by the acid- or base-catalyzed hydrolysis[56] of a portion of $PsCH_2CH_2SCOCH_3$ **15** or other acyl sulfide. Oxidation of similar intermediates to the corresponding sulfonate $PsCH_2CH_2SO_3^-$ **17** was done using peracetic acid,[57] but with what appears to be some loss of functionality. The appearance in the FT-IR spectra of products corresponding to epoxides or alcohols may be explained by the elimination of sulfur having intermediate oxidation states, followed by epoxidation and hydrolysis.

Regarding microenvironment, an interesting behavior was observed from the solid-state ^{13}C NMR characterization (CP-MAS and CP-MAS-DD) of these materials. Results indicate that cross-linked polymer backbone behaves as a rigid network, while some S-linked moieties ($R = (CH_2)_3CH_3$ **3**, CH_2CH_2OH **6**, $(CH_2)_nSH$ **8**−**10**) show liquidlike flexibility even in the dry polymer, though others ($R = CH_2CH_2COOH$) were much less mobile. Such mobility of functional groups can be an important aspect of the polymer microenvironment, reflecting their accessibility and activity.[28]

Polymer-supported cysteine from **12**, being a zwitterion, has shown some ability to buffer solutions, as well as some metal-chelating properties. This polymer-supported amino acid may also be modified to an azlactone and can smoothly immobilize enzymes or other proteins

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out of buffer.[9] $PsCH_2CH_2SCH_2CHOHCH_2OH$ **7** may have application as a protecting group for carbonyls.[58,59]

Phosphines and Phosphonates. Polymer-supported phosphines have been synthesized previously and are succesful as transition-metal supports for catalytic hydrogenation, reducing agents,[60,61] and as reagents for the enormously versatile Wittig and Mitsunobu reactions. These solid-phase reagents have been shown to be easily recyclable from the phosphine oxide using trichlorosilane.[2] Polymer-supported phosphines are usually synthesized via nucleophillic substitution on the polymer ring by costly organometallic intermediates.[15,16]

Formation of carbon−phosphorus bonds through free radical addition is a well known process.[44] Free radical addition of diphenylphosphine across the C=C bond of (vinyl)polystyrene to **18** took place under mild conditions (AIBN, 70 °C in toluene), but required a slightly longer time for complete reaction than did most thiols. IR spectra showed nearly-complete disappearance of double bond after 3 days, and solid phase ^{31}P solid-state NMR showed only one peak, which was consistent with analogous small molecules.[62]

Polymer-supported phosphonic acids may find application in ion extraction processes.[63] $HPO(OR)_2$ also added to (vinyl)polystyrene in the presence of AIBN at 70 °C to obtain the corresponding phosphonate such as **19**, also exclusively in the β position. Subsequent acid-catalyzed hydrolysis of these phosphonate esters[64] yielded the corresponding mixture of phosphonic acids and phosphonic acid monoesters.

Silanes. The versatility of organosilicon reagents in synthetic organic chemistry has been firmly established, yet polymer-supported versions, though potentially very useful, have not been used extensively except for some recent advances in oligosaccharide synthesis using $PsSi(Ph)_2Cl$.[65] $PsSiMe_2Cl$ has been prepared but was not easily regenerable because of Ph−Si cleavage with Lewis acidic reagents.[66] $Ps(CH_2)_3SiMe_2Cl$ was made in several steps and proved regenerable with trifluoroacetic anhydride and thionyl chloride.[67,68] The grafting of polysiloxanes to (vinyl)polystyrene using platinum catalysts has previously been explored as a route to functional polymers.[39] The difficulties in free-radical hydrosilylation of polymers and smaller analogs has been extensively studied and established.[69,70] Similarly free-radical hydrostannylation has been reported, of (vinyl)polystyrene prepared by Wittig reaction of $PsCH_2Cl$.[38]

Free radical addition of HSi to (vinyl)polystyrene proved difficult and required a higher temperature (t-BPO, 125 °C) than for the other elements in this study. For dimethylphenylsilane, the double bond nearly disappeared after stirring for 3 days. Solid-state ^{29}Si NMR of the resulting **20** showed a single peak at the expected position. Ash analysis (SiO_2) indicated uptake of 0.51 mmol Si/g, for $X_f = 0.20$. Similar radical-catalyzed additions of chlorodimethylsilane, chlorodiisoproplysilane, and chlorodi-*tert*-butysilane to (vinyl)polystyrene were not successful and many double bonds of (vinyl)polystyrene remained. This may have to do with the volatility of the silanes, steric hindrance from some of the large R groups, or that the propagation was more difficult due to dialkylchlorosilyl radicals being less easily formed than dialkylphenyl. Their addition using organometallic catalysts, to give polymer-supported silyl halides able to function as recyclable solid-phase protecting groups for solid-phase synthesis, will be reported elsewhere.[71]

Hydride. If needed, a convenient way of removing residual vinyl groups is hydrogenation using $HSi(Et)_3 + CF_3COOH$,[72] two compounds which are soluble in the polymeric matrix and whose excess is easily removed. More common ways of reducing alkenes, requiring solid or colloidal transition metals and/or hydride salts, were not expected to significantly affect the residual groups in the solid polymer due to their inability to penetrate the matrix. Reduction of these residual vinyls using diimide chemistry did not work in our hands. The hydrogenation of the residual vinyl groups in this cross-linked polymer was partially effected (10% residual vinyl groups remaining) using this silane method . Though residual C=C will not interefere with most applications, nevertheless this reaction is a good model for hydrogenation in a solid phase.

Boranes, Hydroxyl, and Tosylate. Besides free-radical addition, hydroboration is another convenient way to synthesize β-addition intermediates. Hydroboration of (vinyl)polystyrene with BH_3 and further modification have been reported previously,[41] but we found that this reaction gave a mixture of α and β addition products, as is reported for styrene.[73] Styrene is known to react readily at room temperature with 9-borabicyclo(3.3.1)-nonane (9-BBN) to place the boron at the terminal position with a selectivity of at least 99.9%.[74] Thus, hydroboration of (vinyl)polystyrene with 9-BBN in THF gave a borane intermediate **22**, upon which addition of aqueous NaOH and H_2O_2 solution converted it to (hydroxyethyl)polystyrene **23**, identical by FTIR to $PsCH_2CH_2OH$ prepared by two other techniques.[16] Further reaction of **23** with a refluxing solution of toluenesulfonyl chloride and diisopropylamine[16] gave $PsCH_2CH_2OTs$ **24**, a versatile alternative to $PsCH_2CH_2Br$ as intermediate.

Conclusions. Several stable, highly cross-linked and reactive classes of functionalized resins containing dimethylene spacers have been prepared by facile and convenient routes from (vinyl)polystyrene, often in near-quantitative conversion. Some analyses of the hydrosulfurated polymers in particular also indicated that this method of polymer modification is generally efficient in producing site-isolated functional groups. We are cur-

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rently investigating the application of several of these polymers as themselves or general intermediates toward solid-phase protecting groups, reagents, chiral auxilliaries, chelating groups, and catalysts and the beneficial effects of the dimethylene spacer in these applications.

Experimental Section

General. "Reagent-grade" solid and liquid chemicals were obtained from commercial suppliers as indicated and used as received except where indicated. IR spectra of polymer samples ground into KBr were recorded using Bomem Michelson 100 (transmittance) and Bruker FT-88 (diffuse reflectance) FTIR spectrophotometers. ^{13}C, ^{31}P, and ^{29}Si CP/MAS (cross-polarization/magic angle spinning) as well as ^{13}C CP-MAS-DD (cross-polarization/magic angle spinning/dipolar dephasing; dephasing time $\tau = 45\ \mu$s) solid-phase NMR spectra were obtained on a Chemagnetics Inc. 25.1 MHz M-100 spectrometer.[28] Elemental analyses were done by Guelph Chemical Laboratories (ON, Canada) and Robertson Microlit Laboratories (NJ), except for some sulfur analyses that were done on-site by a modified Schöninger flask method.[75] Surface area measurements[6] were done on a Quantchrome Quantasorb BET apparatus; swelling in toluene was volumetrically gauged on a sample in a small graduated cylinder. Polymer particles were generally collected from suspensions by filtration through 75 μm poly(tetrafluoroethylene) mesh (Spectrum Inc.).

(Vinyl)polystyrene (1a). In a 125 mL Erlenmeyer flask was weighed hydroxypropyl methylcellulose dispersing agent (Methocel K100LV, Dow Inc., 100 mg), 50 mL of boiling water was added, and the mixture was rapidly stirred as it cooled to room temperature and then poured into a 500 mL, three-necked round-bottom flask equipped with a mechanical stirrer, condenser, septum, and nitrogen inlet, rinsing with an additional 150 mL of water and stirring for an additional 15 min. Divinylbenzene (Aldrich or Dow "technical grade", 20.00 g, 153 mmol), azobis(isobutyronitrile) (AIBN, 0.20 g 1.22 mmol), and toluene (20 mL) were then added and stirring (about 1000 rpm) begun, while the atmosphere within the vessel was replaced by nitrogen and the temperature was raised to 70 °C. After 2 h, benzoquinone (0.4 g, 3.7 mmol) in toluene (10 mL) was added, the mixture was stirred without heating for another 5 min and then filtered, and the residue was washed with hot water (2 × 100 mL) and then acetone (2 × 100 mL) and then subjected to Soxhlet extraction with ethanol overnight. Vacuum drying overnight yielded 13.11 g of **1a** as white beads: FT-IR (KBr) 1630, 1603, 1510, 1486, 1444, 990, 904, 835, 795, 709 cm^{-1}, calculations on which[29] indicated $X_f = 0.35$ for PsCH=CH$_2$ (2.67 mmol CH=CH$_2$/g); ^{13}C CP-MAS NMR δ 145 (DD), 135, 127, 110, 40, 28, 15 (DD).[28] The dried beads had a surface area of 26.6 m^2/g and a swelling ratio in toluene of 1.84.

Another reaction on similar scale was allowed to proceed for 24 h, while sampling the suspension at intervals to generate the data for Figure 1. Polymers **1b**–**g** (Table 1) were prepared under the same conditions but with proportionately larger quantities of all reagents and solvents.

In general, further reactions of the (vinyl)polystyrene was preceded by thorough degassing in the reaction flasks by placing these under vacuum for 20–30 min, followed by purging with nitrogen.

Preparation of PsCH$_2$CH$_2$Br. Attempt Using Aqueous Hydrobromic Acid (2a). A suspension of (vinyl)polystyrene **1b** [$(C_{10}H_{12})_{0.45}(C_{10}H_{10})_{0.20}(C_8H_7CH{=}CH_2)_{0.35}$ (0.40 g, 1.07 mmol C=C)] in 5 mL of toluene was stirred under N$_2$ and then heated to 80 °C. AIBN (6.5 mg, 0.040 mmol) in 0.5 mL of toluene and 48% HBr/H$_2$O (2.5 mL, 22 mmol) were injected. After stirring for 21 h under N$_2$ at 75–80 °C, the suspension was cooled to room temperature and filtered. The residue was then washed with acetone several times and dried under vacuum overnight, yielding 0.45 g of **2a** as a light yellow powder: FTIR (KBr) 1264 (CH_2Br) and 1180 (w, CHBrCH_3) cm^{-1}, with peaks weak or absent at 1630 and 990 cm^{-1}; ^{13}C CP-MAS NMR (100 MHz; "DD" = peak also seen in spectrum with $\tau = 45\ \mu$s dipolar dephasing) δ 145 (DD), 127, 40, 27 (DD, CHBrCH$_3$), 15 (DD, CH$_2$$CH_3$), with peaks absent at δ 135 and 110. Anal. Calcd for $(C_{10}H_{12})_{0.45}(C_{10}H_{10})_{0.32}(C_{10}H_{11}Br)_{0.23}$ (66% conversion, 1.54 mmol Br/g): Br, 12.30. Found: Br, 12.26.

Preparation of PsCH$_2$CH$_2$Br (2b). (Vinyl)polystyrene **1b** [2.67 mmol C=C/g $(C_{10}H_{12})_{0.45}(C_{10}H_{10})_{0.20}(C_8H_7CH{=}CH_2)_{0.35}$ (1.00 g, 2.67 mmol C=C)] was suspended in 10 mL of toluene and stirred under N$_2$. Anhydrous lithium bromide (0.5 g, 6 mmol), chlorotrimethylsilane (0.72 mL, 6.7 mmol), water (0.06 mL, 3 mmol), and then AIBN (0.1 g, 0.6 mmol) were added, and the mixture was stirred at 70 °C for 24 h. The suspension was then filtered and the residue washed several times with hot acetonitrile and then ether and dried in vacuo overnight, yielding 1.15 g of **2b** as a light brown powder: ^{13}C CP-MAS NMR δ 145 (DD), 127, 40, 28, 15 (DD), with peaks absent at δ 135 and 110, and 27 in the DD spectrum; FT-IR (KBr) 1264 (PsCH$_2$$CH_2$Br),[16] peak absent at 1180 cm^{-1}. Anal. Calcd for $(C_{10}H_{12})_{0.45}(C_{10}H_{10})_{0.25}(C_{10}H_{11}Br)_{0.30}$ (86% conversion): Br, 15.4. Found: Br, 15.0.

General Preparation of PsCH$_2$CH$_2$SR Compounds. To a mixture of (vinyl)polystyrene such as **1f** [$(C_{10}H_{12})_{0.45}(C_{10}H_{10})_{0.20}(C_8H_7CH{=}CH_2)_{0.35}$ (1–2 g, 2.7–5.3 mmol of C=C)] and a thiol compound (15–30 mmol) in 8–10 mL of hexanes (**3**, **4**) or toluene (**5**–**11**, **14**, **15**) was added AIBN (1 mol % of C=C). The suspension was then heated to 70 °C under N$_2$ for 1–2 days and then the polymer isolated by filtration and subjected to Soxhlet extraction with acetone overnight. After being dried in vacuo overnight, the PsCH$_2$CH$_2$SR product (**3**–**11**, **14**) was characterized by ^{13}C CP-MAS NMR, FTIR, and elemental analysis.

PsCH$_2$CH$_2$S(CH$_2$)$_3$CH$_3$ (3). From **1f**. ^{13}C CP-MAS NMR δ 145 (DD), 127, 33, 40, 28, 23 (DD), 15 (DD). Anal. Calcd for $(C_{10}H_{12})_{0.45}(C_{10}H_{10})_{0.30}(C_{10}H_{11}SC_4H_9)_{0.25}$ (71% conversion): S, 5.25. Found: S, 5.27.

PsCH$_2$CH$_2$SC(CH$_3$)$_3$ (4). From **1e**. ^{13}C CP-MAS NMR δ 145 (DD), 127, 42, 40, 34 (DD), 28, 15 (DD). Anal. Calcd for $(C_{10}H_{12})_{0.45}(C_{10}H_{10})_{0.42}(C_{10}H_{11}SC_4H_9)_{0.13}$ (37% conversion): S, 2.74. Found: S, 2.73.

PsCH$_2$CH$_2$SC$_6$H$_5$ (5). From **1e**. ^{13}C CP-MAS NMR δ 145 (DD), 131, 127, 40, 28, 15 (DD). Anal. Calcd for $(C_{10}H_{12})_{0.45}(C_{10}H_{10})_{0.36}(C_{10}H_{11}SC_6H_5)_{0.19}$ (54% conversion): S, 4.00. Found: S, 3.97.

PsCH$_2$CH$_2$SCH$_2$CH$_2$OH (6). From **1f**. ^{13}C CP-MAS NMR δ 145 (DD), 127, 64, 40, 35, 28, 15 (DD). Anal. Calcd for $(C_{10}H_{12})_{0.45}(C_{10}H_{10})_{0.26}(C_{10}H_{11}SC_2H_5O)_{0.29}$ (83% conversion): S, 6.01. Found: S, 6.02.

PsCH$_2$CH$_2$SCH$_2$CH(OH)CH$_2$OH (7). From **1f**. ^{13}C CP-MAS NMR δ 145, 127, 72, 65, 40, 28, 15. Anal. Calcd for $(C_{10}H_{12})_{0.45}(C_{10}H_{10})_{0.22}(C_{10}H_{11}SC_3H_7O_2)_{0.33}$ (95% conversion): S, 6.29. Found: S, 6.27.

PsCH$_2$CH$_2$S(CH$_2$)$_2$SH (8). From **1f**. ^{13}C CP-MAS NMR δ 145 (DD), 127, 40, 35, 28, 25, 15 (DD). Anal. Calcd for $(C_{10}H_{12})_{0.45}(C_{10}H_{10})_{0.27}(C_{10}H_{11}S_2C_2H_5)_{0.28.}$ (80% conversion): S, 11.55. Found: S, 11.54.

PsCH$_2$CH$_2$S(CH$_2$)$_3$SH (9). From **1f**. ^{13}C CP-MAS NMR δ 145 (DD), 127, 40, 36, 34, 28, 25, 15 (DD). Anal. Calcd for $(C_{10}H_{12})_{0.45}(C_{10}H_{10})_{0.26}(C_{10}H_{11}S_2C_3H_7)_{0.29}$ (83% conversion): S, 11.33. Found: S, 11.32.

PsCH$_2$CH$_2$S(CH$_2$)$_4$SH (10). From **1f**. ^{13}C CP-MAS NMR δ 145 (DD), 127, 40, 34, 30, 28, 24, 15 (DD). Anal. Calcd for $(C_{10}H_{12})_{0.45}(C_{10}H_{10})_{0.30}(C_{10}H_{11}S_2C_4H_9)_{0.25}$ (71% conversion): S, 9.96. Found: S, 9.96.

PsCH$_2$CH$_2$S(CH$_2$)$_2$COOH (11). From **1f**. ^{13}C CP-MAS NMR δ 180 (DD), 145 (DD), 127, 40, 28, 15 (DD). Anal. Calcd for $(C_{10}H_{12})_{0.45}(C_{10}H_{10})_{0.36}(C_{10}H_{11}SC_3H_5O_2)_{0.19}$ (89% conversion): S, 6.00. Found: S, 6.00.

PsCH$_2$CH$_2$SCOCH$_3$ (14). From **1f**. ^{13}C CP-MAS NMR δ 193 (DD), 145 (DD), 127, 40, 30, 28, 15 (DD); FT-IR (KBr) 1692 cm^{-1} (C=O). Anal. Calcd for $(C_{10}H_{12})_{0.45}(C_{10}H_{10})_{0.32}(C_{10}H_{11}SC_2H_3O)_{0.23}$ (66% conversion): S, 5.01. Found: S, 5.00.

PsCH$_2$CH$_2$SCOPh (15). From 10.00 g of **1h**. Yields 12.87 g of pink beads of **15**: FT-IR (KBr) 1667, 1203, 1175, 990 (w), 771 cm^{-1}. Anal. Calcd for $(C_{10}H_{12})_{0.45}(C_{10}H_{10})_{0.27}(C_{10}H_{11}SC_7H_5O)_{0.28}$ (80% conversion): S, 5.41. Found: S, 5.41.

Preparation of PsCH$_2$CH$_2$SCH$_2$CH(NH$_2$)COOEt·HCl (12). Cysteine ethyl ester hydrochloride (2.00 g, 10.7 mmol) in 5 mL of ethanol was added to (vinyl)polystyrene **1h** [$(C_{10}H_{12})_{0.45}(C_{10}H_{10})_{0.20}(C_8H_7CH{=}CH_2)_{0.35}$ (4.00 g, 10.7 mmol of

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C=C)], that had been ground to 45−63 μm diameter in 5 mL of toluene. AIBN (0.1 g, 0.60 mmol) was then added along with "PEG-600" polyethylene glycol 600 g/mol (0.1 g, 0.17 mmol) as phase tranfer agent. The mixture was heated to 70 °C under nitrogen for 24 h. The beads were then filtered and washed liberally with hot ethanol and then ether and dried in vacuo at 50 °C to give 5.1 g of **12** as a pale yellow powder: ^{13}C CP-MAS NMR δ 170 (DD), 145 (DD), 127, 75, 40, 15 (DD); FT-IR (KBr) 1746, 3000−3500 cm^{-1}(RNH$_3^+$). Reaction of a portion with 0.25% ninhydrin solution quickly colored the solid deep violet to black, similar to reaction with amino acids. Anal. Calcd for $(C_{10}H_{12})_{0.45}(C_{10}H_{10})_{0.33}$ $(C_{10}H_{11}SC_5H_{11}NO_2Cl)_{0.22}$ (63% conversion): S, 4.01. Found: S, 4.00.

A second reaction under the same conditions gave a product of X_f 0.21. Without grinding (106−250 μm diameter particles), degree of functionalization dropped to 0.18, while products from reactions in THF:H$_2$O 1:1 and dioxane:H$_2$O 1:1 (this from **1c**), using unground beads and without PEG 600, finished with amino ester contents of X_f 0.10 and 0.12, respectively.

Preparation of PsCH$_2$CH$_2$SCN$_2$H$_4$·HBr (13). (Vinyl)polystyrene **1g** $[(C_{10}H_{12})_{0.45}(C_{10}H_{10})_{0.30}(C_8H_7CH{=}CH_2)_{0.25}$ (9.25 g, 17.6 mmol of C=C)] was swollen with 25 mL of dioxane. Then thiourea (8.00 g, 105 mmol), 48% HBr/H$_2$O (20 mL, 180 mmol HBr), and AIBN (0.1g, 0.6 mmol) were added, and the mixture was heated at 70 °C under N$_2$ 48 h. The beads were filtered, washed with dioxane, toluene (4×), and ethanol (4×), and then dried in vacuo at 70 °C 24 h, yielding 10.95 g of **13** as white beads: ^{13}C CP-MAS NMR δ 165, 145, 127, 40, 20, 15; FT-IR (KBr) 3000−3500 (NH$_2^+$), 1646 (C=N), 1341 cm^{-1} (PsCHSR-*CH$_3$*). Anal. Calcd for $(C_{10}H_{12})_{0.45}(C_{10}H_{10})_{0.38}(C_{10}H_{11}SCN_2H_5Br)_{0.17}$ (72% conversion): S, 3.70. Found: S, 3.67.

Preparation of PsCH$_2$CH$_2$SH (16). PsCH$_2$CH$_2$SCOCH$_3$ **14** $[(C_{10}H_{12})_{0.45}(C_{10}H_{10})_{0.32}(C_{10}H_{10}SC_2H_3O)_{0.23}$ (1 g, 1.88 mmol of SCOCH$_3$)] was stirred in a mixture of 6 mL of dioxane and 37% HCl/H$_2$O (3 mL, 40 mmol of HCl, 130 mmol of H$_2$O) under nitrogen at 70 °C for 2 days and then filtered and extracted with acetone by Soxhlet overnight, and the residue was dried at 60 °C for 2 days giving 0.90 g of **15**: IR and Raman (KBr) peaks absent at 1667, present at 2577 cm^{-1} (S−H). Anal. Calcd for $(C_{10}H_{12})_{0.45}(C_{10}H_{10})_{0.36}(C_{10}H_{11}SH)_{0.19}$ (83% conversion): S, 4.54. Found: S, 4.53.

Preparation of PsCH$_2$CH$_2$SO$_3$H (17). PsCH$_2$CH$_2$SCOPh **15** $[(C_{10}H_{12})_{0.45}(C_{10}H_{10})_{0.27}(C_{10}H_{11}SC_7H_5O)_{0.28}$ (5.00 g, 8.5 mmol of SCOPh)] was swollen with 6 mL of toluene and then cold 32 wt % peracetic acid in acetic acid (40 mL, 190 mmol of COOOH) was added slowly, and then the suspension stirred at room temperature for 18 h. The yellow-brown suspension was then filtered and the residue washed with toluene (3×) and then ether (6×) and then dried in vacuo 24 h at 75 °C, giving 5.43 g of **17** as dark brown beads: FT-IR (KBr) 1206, 1175, 1040 cm^{-1}. Anal. Calcd for $(C_{10}H_{12})_{0.45}(C_{10}H_{10})_{0.33}(C_{10}H_{11}SO_3H)_{0.12}\cdot 2.24H_2O$: C, 64.2; S, 2.29. Found: C, 64.25; S, 2.28.

Preparation of PsCH$_2$CH$_2$P(C$_6$H$_5$)$_2$ (18). To a mixture of (vinyl)polystyrene **1f** $[(C_{10}H_{12})_{0.45}(C_{10}H_{10})_{0.20}(C_8H_7CH{=}CH_2)_{0.35}$ (2.13 g, 5.69 mmol of C=C)], AIBN (0.0239 g, 0.146 mmol), and 5 mL of hexanes was added diphenylphosphine (4.97 g, 26.6 mmol) under N$_2$ with stirring. The mixture was then heated to 70 °C under N$_2$ for 2−3 days and then filtered, and the residue was subjected to Soxhlet extraction with hexanes overnight. Vacuum drying overnight gave 2.45 g of **18** as white beads: ^{13}C CP-MAS NMR δ 145 (DD), 127, 40, 28, 15 (DD); ^{31}P solid-state NMR δ −15.8; FT-IR (KBr) 1097 cm^{-1} (P*Ph*). Anal. Calcd for $(C_{10}H_{12})_{0.45}(C_{10}H_{10})_{0.25}(C_{10}H_{11}PC_{12}H_{10})_{0.30}$ (86% conversion): P, 5.21. Found: P, 5.18.

Preparation of PsCH$_2$CH$_2$PO(OMe)$_2$ (19). (Vinyl)polystyrene **1g** $[(C_{10}H_{12})_{0.45}(C_{10}H_{10})_{0.30}(C_8H_7CH{=}CH_2)_{0.25}$ (9.25 g, 17.6 mmol of C=C)] was swollen with 25 mL of toluene and dimethyl phosphite (8.00 mL, 87.2 mmol). AIBN (0.1 g, 0.6 mmol) was added and the mixture heated at 70 °C under N$_2$ for 48 h. The suspension was then filtered and the residue washed with toluene (4×) and ethanol (4×) and then dried in vacuo at 70 °C for 24 h, yielding 10.95 g of **19** as white beads: ^{31}P solid-state NMR δ 32.5; FT-IR (KBr) 1181, 1018 cm^{-1}. Anal. Calcd for $(C_{10}H_{12})_{0.45}(C_{10}H_{10})_{0.37}(C_{10}H_{10}PC_20_3H_7)_{0.18}$ (72% conversion): P, 3.70. Found: P, 3.67.

Preparation of PsCH$_2$CH$_2$Si(CH$_3$)$_2$C$_6$H$_5$ (20). To a suspension of (vinyl)polystyrene **1g** $[(C_{10}H_{12})_{0.45}(C_{10}H_{10})_{0.30}(C_8H_7CH{=}CH_2)_{0.25}$ (3.22 g, 6.14 mmol of C=C)] in 6 mL of toluene were injected dimethylphenylsilane (4.72 g, 34.6 mmol) and *tert*-butyl peroxide (60 μL, 0.4 mmol) under N$_2$ with stirring. The mixture was kept at 125 °C under N$_2$ for 3 days, during which further aliquots of t-BPO were added at the end of the first (30 μL) and second (40 μL) days. The mixture was then filtered, and the residue was subjected to Soxhlet extraction with acetone overnight. Vacuum drying overnight gave 3.55 g of **20** as white beads: ^{13}C CP-MAS NMR δ 145 (DD), 127, 40, 28, 15 (DD), −2 (DD); ^{29}Si solid-state NMR (300 MHz) δ −4.9; FT-IR (KBr) 1251 (Si−CH$_3$), 1113 cm^{-1} (Si−Ph). Anal. Calcd for $(C_{10}H_{12})_{0.45}(C_{10}H_{10})_{0.35}(C_{10}H_{11}SiC_8H_{11})_{0.20}$ (80% conversion): Si, 3.49. Found (ash): Si, 3.46.

Reduction to PsCH$_2$CH$_3$ (21). (Vinyl)polystyrene **1h** $[(C_{10}H_{12})_{0.45}(C_{10}H_{10})_{0.20}(C_8H_7CH{=}CH_2)_{0.35}$ (0.55 g, 1.46 mmol of C=C)] was suspended in 3 mL of toluene. Trifluoroacetic acid (0.60g, 5.2 mmol) was added along with triethylsilane (0.45 g, 3.9 mmol), and the mixture was stirred under nitrogen for 48 h. The beads were then filtered and washed with toluene (3×) and then ether. Drying in vacuo overnight yielded 0.54 g of **21** as pale yellow beads: ^{13}C CP-MAS NMR δ 145 (DD), 135, 127, 109, 40, 28, 15 (DD); FT-IR showed residual C=C peaks at 1630 and 990 cm^{-1} for $(C_{10}H_{12})_{0.70}(C_{10}H_{10})_{0.20}(C_8H_7CH{=}CH_2)_{0.10}$ (71% conversion).

Preparation of PsCH$_2$CH$_2$OH (23). (Vinyl)polystyrene **1e** $[(C_{10}H_{12})_{0.45}(C_{10}H_{10})_{0.20}(C_8H_7CH{=}CH_2)_{0.35}$ (1.04 g, 2.77 mmol of C=C)] was placed in a 25 mL dry flask which was then purged with N$_2$ for a few minutes. 9-BBN (0.5 M) in THF (12 mL, 6 mmol) was injected over 10 min, and the mixture was stirred for 23 h under N$_2$ at room temperature. H$_2$O (2 mL, 111 mmol) was then added to the flask, followed by the addition of 5 mL of 3 M aqueous NaOH (15 mmol) solution. After the mixture was stirred for 5 min, 30% H$_2$O$_2$/H$_2$O (3 mL, 30 mmol) was introduced slowly with stirring over 4 h. The suspension was filtered and the residue washed with water and acetone several times and then extracted with acetone. Drying under vacuum overnight yielded 1.05 g of **23** as white beads: ^{13}C CP-MAS NMR δ 145 (DD), 127, 64, 40, 28, 15 (DD); FT-IR (KBr) 1046 cm^{-1} (PsCH$_2$*CH$_2$OH*).[16]

Preparation of PsCH$_2$CH$_2$OTs (24). (Hydroxyethyl)polystyrene **23** (0.50 g), toluenesulfonyl chloride (1.00 g, 5.24 mmol), and dry diisopropylamine (0.90 g, 8.90 mmol) were stirred together in 6 mL of CCl$_4$ under N$_2$ at room temperature and then heated to reflux for 23 h. The pale yellow suspension was filtered, and the residue was washed thoroughly with acetone and water. After drying at 50 °C at 20 mmHg overnight, 0.56 g of **23** as a pale yellow product was obtained: ^{13}C CP-MAS NMR δ 145 (DD), 127, 72 (DD), 40, 28, 15 (DD); FT-IR (KBr) 1361, 1188, 1176, 1097, 964, 898, 664, 554 cm^{-1} (ROSO$_2$R′), peak absent at 1046 cm^{-1}. Anal. Calcd for $(C_{10}H_{12})_{0.45}(C_{10}H_{10})_{0.43}(C_{10}H_{11}OSO_2C_7H_7)_{0.12}$: S, 2.38. Found: S, 2.36.

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