



(72) DARLING, Graham D., CA

(72) STRANIX, Brent R., CA

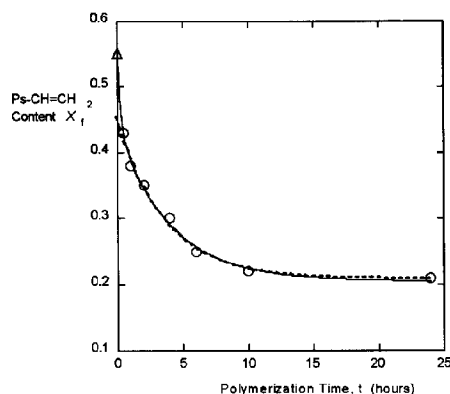
(71) DARLING, Graham D., CA

(71) STRANIX, Brent R., CA

(51) Int.Cl.<sup>6</sup> C08F 8/00

(54) **POLYMERES RENFERMANT DES GROUPEMENTS  
FONCTIONNELS ET PORTANT DES DERIVES OXYACIDES  
NON METALLIQUES SUR DES GROUPEMENTS  
DIMETHYLENES DE SEPARATION**

(54) **FUNCTIONAL POLYMERS BEARING NON-METAL OXYACID  
DERIVATIVES ON DIMETHYLENE SPACERS**



-----  
Effect of time on content of residual vinyl groups during preparation of (vinyl)polystyrene **1** by polymerization of divinylbenzene (see Experimental).  $\circ$   $X_f$  measured by FTIR.  $\square$   $X_f$  reported by GC. --- Curve fitted to FTIR points only:  $X_f = 0.245e^{-0.213t} + 0.207$ .  $\dot{\cdot}$  Curve fitted to all points:  $X_f = 0.116e^{-3.56t} + 0.229e^{-0.246t} + 0.205$ .

(57) Many spacer-containing functional polymers were produced by modifying beads of (vinyl)polystyrene, as obtained by free-radical suspension polymerization of commercial 55:45 divinylbenzene:ethylstyrene mixture, or from commercial sources. Thus, in the presence of free-radical initiators, compounds HBr, HPR<sub>2</sub>, HP(OR)<sub>2</sub> and HSR (R = various alkyl, aryl or acyl, some also containing further -COOH/R, -OH/R, -SH/R, -N(H/R)<sub>2</sub> groups) underwent anti-Markovnikov addition to the residual vinyl groups. Similar free-radical functionalization with various HSiR<sub>3</sub> also proved feasible but more difficult. Other products corresponding to formal anti-Markovnikov addition of H<sub>2</sub>S, HSO<sub>3</sub><sup>-</sup>, HP(OH)<sub>2</sub>, H<sub>2</sub>, HBR<sub>2</sub>, HOH and HOSO<sub>2</sub>R 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.



**Abstract**

Many spacer-containing functional polymers were produced by modifying beads of (vinyl)polystyrene, as obtained by free-radical suspension polymerization of commercial 55:45 divinylbenzene:ethylstyrene mixture, or from commercial sources. Thus, in the presence of free-radical initiators, compounds HBr, HPR<sub>2</sub>, HP(OR)<sub>2</sub> and HSR (R = various alkyl, aryl or acyl, some also containing further -COOH/R, -OH/R, -SH/R, -N(H/R)<sub>2</sub> groups) underwent anti-Markovnikov addition to the residual vinyl groups. Similar free-radical functionalization with various HSiR<sub>3</sub> also proved feasible but more difficult. Other products corresponding to formal anti-Markovnikov addition of H<sub>2</sub>S, HSO<sub>3</sub><sup>-</sup>, HP(OH)<sub>2</sub>, H<sub>2</sub>, HBR<sub>2</sub>, HOH and HOSO<sub>2</sub>R 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.

## Functional Polymers Bearing Non-metal Oxyacid Derivatives On Dimethylene Spacers

### Introduction

Over the years, crosslinked functional polymers have been much studied and widely employed as solid-phase reagents, catalysts, protecting groups and sorbents.<sup>1-5</sup> 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.<sup>6-9</sup>

For simplicity, versatility, controlled architecture, and even distribution and ready accessibility of functional groups, functional polymers are generally better prepared by modification of pre-existing polymers, rather than by copolymerization with specialty monomers.<sup>6,10-12</sup> To date, chloromethylation of crosslinked polystyrene, followed by nucleophilic substitution, has been a very popular route.<sup>1-3</sup> However, serious problems arise from the carcinogenicity of the chloromethylation reagents; too, 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.<sup>4,5</sup> More recently, other functional polymers have been reported that incorporate ethylene (dimethylene) spacers for more stable attachments through non-benzylic primary bonds.<sup>4,5</sup> Such distancing from the polymer backbone may also confer further advantages of more mobile<sup>6</sup> and accessible functional groups,<sup>6,19,20</sup> and thus greater catalytic or other activity of the functional polymer product.<sup>7,8</sup> 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-containing functional polymers, with mild conditions and good yields from a common precursor, **1**. Easily prepared, and even commercially available, **1** is essentially a crosslinked

polystyrene matrix bearing residual vinyl groups, hence our term "(vinyl)polystyrene", and abbreviation "Ps-CH=CH<sub>2</sub>" (Figure 2). Upon radical or other anti-Markovnikov addition of a reagent "H-X" (Figure 3), each such vinyl becomes a dimethylene spacer supporting a functional group, for an overall functional polymer "Ps-CH<sub>2</sub>CH<sub>2</sub>-X" or "(X-ethyl)polystyrene)" (Figure 4).

## Results and Discussion

**Preparation of Ps-CH=CH<sub>2</sub> Precursor.** Free-radical suspension copolymerization of divinylbenzene with other styrenic monomers gives crosslinked macroporous resins, of porosities and surface areas controlled by relative proportions of water, monomers, porogens and suspending agents.<sup>9,10</sup> These have been shown to often still bear many unreacted pendant vinyl groups,<sup>25,26</sup> as detected by solid-phase NMR ( $\delta$  135 CH= and 110 =CH<sub>2</sub>),<sup>27,28</sup> and quantitated by FTIR (1630 C=C and 990 C=CH cm<sup>-1</sup>),<sup>9,11,12</sup> or, less conveniently and reliably,<sup>11,13</sup> by chemical assay with bromine<sup>12</sup> or other reagents.<sup>14</sup> 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 crosslinking reactions between those resulting polymer-bound vinyl groups that are actually adjacent, while others remain site isolated<sup>20</sup> and intact within the increasingly rigid crosslinked 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<sub>2</sub> 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-*t*-butyl peroxide (t-BPO) decreased  $X_f$  by only another 0.05;<sup>1,31</sup> few vinyls are reported to remain on further heating above 150 °C with radical generator.<sup>13</sup> 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.<sup>15</sup> It also

contrasts with the prevalence of inter-chain reactions in more lightly-crosslinked polystyrene matrices.<sup>16-18</sup>

This study mostly used **1** from shorter polymerization times, typically at  $X_f \cong 0.30-0.35$  after 2 hours (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 to compete with their further dimerization or other crosslinking, to give functional group product of  $X_f > 0.20$  (see below). Though we infer that significant further crosslinking could not be avoided at other times, still most such new crosslinks would usually be chemically inert in themselves; moreover, crosslinking side-reactions are often also the rule for chloromethylation and other "traditional" functionalizations/functional group modifications on crosslinked polystyrene.<sup>14,16</sup>

**Table 1. Characteristics of the several batches of **1** used in this study.<sup>a</sup>**

Batch #	Monomer mass (g)	Yield (%)	Vinyl content ( $X_f$ )	Capacity (mmol/g)	Particle diameter (Åm)	Partic earea (m <sup>2</sup> /g)	Swell ratio (toluene )
<b>1a</b>	20	65	0.35	2.67	250-425	26.6	1.84
<b>1b</b>	100	50	0.43	3.28	250-425	20.9	1.96
<b>1c</b>	200	89	0.30	2.29	250-425	18.3	1.74
<b>1d</b>	250	88	0.30	2.29	250-425	16.7	1.59
<b>1e</b>	30	76	0.35	2.67	250-425	-	-
<b>1f</b>	30	83	0.35	2.67	250-425	-	-
<b>1g</b>	200	90	0.25	1.91	250-425	127.2	1.26
<b>1h</b>	200	60	0.35	2.67	250-425	77.2	1.85

<sup>a</sup>Proportions, conditions and analyses as described in Experimental.

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 gel-like and macroporous domains therein.<sup>6</sup> As noted elsewhere,<sup>13,19</sup> commercially-available (Rohm & Haas) Amberlite XAD-4<sup>TM</sup>, XAD-2<sup>TM</sup> and XAD-16<sup>TM</sup> 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.<sup>20</sup> Preparations of (vinyl)polystyrene with much lower degrees of crosslinking ( $X_c$ ) have also been reported from (chloromethyl)polystyrene<sup>21,22</sup> and by elimination of certain Ps-CH<sub>2</sub>CH<sub>2</sub>-X made in other ways.<sup>5</sup>

**Chemical Modification of 1 to Ps-CH<sub>2</sub>CH<sub>2</sub>-X.** Though typically thought a nuisance in chloromethylation (undergoing cationic polymerization/crosslinking and other side-reactions)<sup>23,24</sup> and other "traditional" functionalizations, residual vinyl groups on crosslinked polystyrene have in the past been functionalized by graft copolymerization of functional monomers,<sup>11,40</sup> and by bromination, epoxidation and ozonolysis.<sup>41</sup> A few particular instances of addition of H-X have also been described, as will be mentioned below.

To achieve spacer-supported functional polymers Ps-CH<sub>2</sub>CH<sub>2</sub>-X, addition of H-X to Ps-CH=CH<sub>2</sub> **1** must proceed exclusively with  $\beta$  or anti-Markovnikov orientation, such as occurs for several classes of compounds by a free-radical mechanism (Figure 3).<sup>42-44</sup> The Ps-CHX-CH<sub>3</sub>  $\alpha$  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's probably still less stable than Ps-CH<sub>2</sub>-X bond from (chloromethyl)polystyrene.

**Bromide.** Like PsCH<sub>2</sub>Cl, Ps-CH<sub>2</sub>CH<sub>2</sub>-X 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.<sup>4,5,19</sup> Preparations of Ps-CH<sub>2</sub>CH<sub>2</sub>-Br from Ps-H via Ps-CH<sub>2</sub>CH<sub>2</sub>-OH are known but complicated.<sup>4,25</sup>

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 H-Br to protonating  $R'RHO^+{}^aBr$ , and also particularly with styrene that has such a stabilized carbocation intermediate.<sup>26,19,26-29</sup>

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  $\alpha$ -addition product (Figure 5).<sup>41</sup> More serious efforts for exclusive  $\beta$ -addition to residual vinyl groups of crosslinked polystyrene have also been described, using "carefully dried" hydrogen bromide gas in hydrocarbon solvent with AIBN, though even then some  $\alpha$ -contaminant showed in the FTIR spectrum of the product.<sup>19</sup>

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  $\delta$  135 and 110) analyses. This disappearance of vinyl was mostly accompanied by uptake of Br (elemental analysis), mainly by  $\beta$ -addition of HBr (FTIR 1264  $cm^{-1}$   $CH_2Br$ ,  $^{13}C$  CP-MAS NMR  $\delta$  27  $CH_2Br$ ) but also by significant  $\alpha$ -addition as well (FTIR 1180  $cm^{-1}$  for  $CHBrCH_3$ , and  $^{13}C$  CP-MAS NMR  $\delta$  27, persisting with 45  $\mu s$  dipolar dephasing, for  $CHBrCH_3$ ). 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  $\alpha$ -product exclusively. Our own use of HBr gas confirmed previous reports<sup>19</sup> of greater but still not complete selectivity for  $\beta$ -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  $Ps-CH_2CH_2-Br$  **2** with even less (i.e. indiscernible amounts) of the  $\alpha$ -product. Possibly these hygroscopic and otherwise dehydrating reagents and product (lithium chloride) quickly segregated even such traces of  $\alpha$ -inducing free moisture as may have been present at the

outset on polymer or glass surfaces. The use of pre-formed, commercial bromotrimethylsilane did not yield  $\beta$  nearly as selectively.

**Sulfides and sulfonates.**  $\text{PsCH}_2\text{S(O)CH}_3$  has been used to oxidize alkyl halides to aldehydes,<sup>30</sup> and polymer-supported thioethers to complex with borane for reductions.<sup>31</sup> Polymer-supported thiols have been used to make reagents for trifluoroacetylation,<sup>32</sup> and to act as selective ion exchangers.<sup>33</sup> S-linking to crosslinked polystyrene has been done by reaction of thiolate with (chloromethyl)polystyrene, often under phase-transfer conditions;<sup>18</sup> non-benzylic  $\text{Ps-CH}_2\text{CH}_2\text{-SR}$  have similarly been made by nucleophilic substitution of  $\text{Ps-CH}_2\text{CH}_2\text{-OTs}$ .<sup>4</sup>

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.<sup>26</sup> The reaction has been applied towards photoinitiated crosslinking of polyenes with polythiols.<sup>34,35</sup> In our experiments, radical additions of various H-SR 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 <sup>13</sup>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 *tert*-butanethiol 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 transfer 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  $\text{Ps-CH}_2\text{CH}_2\text{-S(CH}_2\text{CH}_2)_n\text{SH}$  **8-10** without crosslinking. This was confirmed by the peak at  $2577\text{ cm}^{-1}$  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 crosslinking that occurs during many functional group modifications of 1-2% crosslinked (chloromethyl)polystyrene.<sup>16,36</sup>

Attempts to produce dimethylene spacer linked thiuronium salts  $\text{Ps-CH}_2\text{CH}_2\text{-S-CN}_2\text{H}_3\text{Br}$  gave some  $\alpha$  as well as  $\beta$  addition, as shown by FT-IR and solid phase NMR of product **13**, possibly due to competing ionic reactions involving HBr co-reagent.

$\text{Ps-CH}_2\text{CH}_2\text{-SH}$  **16** could be obtained by the acid or base catalyzed hydrolysis<sup>37</sup> of a portion of  $\text{Ps-CH}_2\text{CH}_2\text{-SCOCH}_3$  **15** or other acyl sulfide. Oxidation of similar intermediates to the corresponding sulfonate  $\text{Ps-CH}_2\text{CH}_2\text{-SO}_3^-$  **17** was done using peracetic acid,<sup>38</sup> 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  $^{13}\text{C}$  NMR characterization (CP-MAS and CP-MAS-DD) of these materials. Results indicate that crosslinked polymer backbone behaves as a rigid network, while some S-linked moieties (-R =  $-(\text{CH}_2)_3\text{CH}_3$  **3**,  $-\text{CH}_2\text{CH}_2\text{OH}$  **6**,  $-(\text{CH}_2)_n\text{SH}$  **8-10**) show liquid-like flexibility even in the dry polymer, though others (-R =  $-\text{CH}_2\text{CH}_2\text{COOH}$ ) were much less mobile. Such mobility of functional groups can be an important aspect of the polymer micro-environment, reflecting their accessibility and activity.<sup>28</sup>

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 out of buffer.  $^{39}\text{Ps-CH}_2\text{CH}_2\text{SCH}_2\text{CHOHCH}_2\text{OH}$  **7** may have application as a protecting group for carbonyls.<sup>58, 40</sup>

**Phosphines and phosphonates.** Polymer-supported phosphines have been synthesized previously and are successful as transition-metal supports for catalytic hydrogenation, reducing agents,<sup>41,42</sup> 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.<sup>43</sup> Polymer supported phosphines are usually synthesized via nucleophilic substitution on the polymer ring by costly organometallic intermediates.<sup>3,4</sup>

Formation of carbon-phosphorous bonds through free radical addition is a well known process.<sup>26</sup> 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 <sup>31</sup>P solid-state NMR showed only one peak, which was consistent with analogous small molecules.<sup>44</sup> Polymer-supported phosphonic acids may find application in ion extraction processes.<sup>45</sup> HPO(OR)<sub>2</sub> 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-catalysed hydrolysis of these phosphonate esters<sup>46</sup> 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 Ps-Si(Ph)<sub>2</sub>Cl.<sup>47</sup> Ps-SiMe<sub>2</sub>Cl has been prepared but was not easily regenerable because of Ph-Si cleavage with Lewis-acidic reagents.<sup>48</sup> Ps(CH<sub>2</sub>)<sub>3</sub>SiMe<sub>2</sub>Cl was made in several steps and proved regenerable with trifluoroacetic anhydride and thionyl chloride.<sup>49,50</sup> The grafting of polysiloxanes to (vinyl)polystyrene using platinum catalysts has previously been explored as a route to functional polymers.<sup>23</sup> The difficulties in free-radical hydrosilylation of polymers and smaller analogs has been extensively studied and established.<sup>69,70</sup> Similarly free-radical hydrostannylation has been reported, of (vinyl)polystyrene prepared by Wittig reaction of Ps-CH<sub>2</sub>Cl.<sup>22</sup>

Free radical addition of H-Si 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  $^{29}\text{Si}$  NMR of the resulting **20** showed a single peak at the expected position. Ash analysis ( $\text{SiO}_2$ ) indicated uptake of 0.51 mmol Si/g, for  $X_f = 0.20$ . Similar radical-catalyzed additions of chlorodimethylsilane, chlorodiisopropylsilane and chlorodi-*t*-butylsilane 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, or 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.<sup>51</sup>

**Hydride.** If needed, a convenient way of removing residual vinyl groups is hydrogenation using  $\text{HSi}(\text{Et})_3 + \text{CF}_3\text{COOH}$ ,<sup>52</sup> 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 crosslinked polymer was partially effected (10% residual vinyl groups remaining) using this silane method. Though residual C=C will not interfere 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  $\beta$ -addition intermediates. Hydroboration of (vinyl)polystyrene with  $\text{BH}_3$  and further modification have been reported previously,<sup>41</sup> but we found that this reaction gave a mixture of  $\alpha$  and  $\beta$  addition products, as is reported for styrene.<sup>53</sup> 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%.<sup>54</sup> Thus, hydroboration of (vinyl)polystyrene with 9-BBN in THF gave a borane intermediate **22**, which addition of aqueous

NaOH and H<sub>2</sub>O<sub>2</sub> solution converted to (hydroxyethyl)polystyrene **23**, identical by FTIR to Ps-CH<sub>2</sub>CH<sub>2</sub>OH prepared by two other techniques.<sup>4</sup> Further reaction of **23** with a refluxing solution of toluenesulfonyl chloride and diisopropylamine<sup>4</sup> gave Ps-CH<sub>2</sub>CH<sub>2</sub>-OTs **24**, a versatile alternative to Ps-CH<sub>2</sub>CH<sub>2</sub>-Br as intermediate.

**Conclusions.** Several stable, highly crosslinked 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 currently investigating the application of several of these polymers as themselves, or general intermediates towards, solid-phase protecting groups, reagents, chiral auxiliaries, 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. <sup>13</sup>C, <sup>31</sup>P and <sup>29</sup>Si CP/MAS (cross-polarization/magic angle spinning), as well as <sup>13</sup>C CP-MAS-DD (cross-polarization/magic angle spinning/dipolar dephasing; dephasing time  $\tau = 45 \mu\text{s}$ ), solid-phase NMR spectra were obtained on a Chemagnetics Inc. 25.1 MHz M-100 spectrometer.<sup>28</sup> Elemental analyses were done by Guelph Chemical Laboratories (ON, Canada) and Robertson Microlit Laboratories (NJ, USA), except for some sulfur analyses that were done on-site by a modified Schöniger flask method.<sup>55</sup> Surface area measurements<sup>6</sup> 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  $\mu\text{m}$  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), then 50 mL of boiling water was added and the mixture rapidly stirred as it cooled to room temperature, then poured into a 500 mL, 3-necked round flask equipped with a mechanical stirrer, condenser, septum and nitrogen inlet, rinsing with 150 mL more water, and stirring for 15 more minutes. 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 hours, benzoquinone (0.4 g, 3.7 mmol) in toluene (10 mL) was added and the mixture was stirred without heating for another 5 minutes, then filtered and the residue washed with hot water (2 ∞ 100 mL) then acetone (2 ∞ 100 mL), 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<sup>-1</sup>, calculations on which<sup>11</sup> indicated  $X_f = 0.35$  for Ps-CH=CH<sub>2</sub> (2.67 mmol -CH=CH<sub>2</sub>/g); <sup>13</sup>C CP-MAS NMR δ 145 (DD), 135, 127, 110, 40, 28, 15 (DD).<sup>28</sup> The dried beads had a surface area of 26.6 m<sup>2</sup>/g and a swelling ratio in toluene of 1.84.

Another reaction on similar scale was allowed to proceed for 24 hours, while sampling the suspension at intervals to generate the data for Figure 1. Polymers **1b-g** (Table I) 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 Ps-CH<sub>2</sub>CH<sub>2</sub>-Br. Attempt using aqueous hydrobromic acid (2a).** A suspension of **1b** (vinyl)polystyrene (C<sub>10</sub>H<sub>12</sub>)<sub>0.45</sub>(C<sub>10</sub>H<sub>10</sub>)<sub>0.20</sub>(C<sub>8</sub>H<sub>7</sub>CH=CH<sub>2</sub>)<sub>0.35</sub> (0.40 g, 1.07 mmol C=C) in 5 mL toluene was stirred under N<sub>2</sub>, then heated to 80 °C. AIBN (6.5 mg, 0.040 mmol) in 0.5 mL toluene, and 48% HBr/H<sub>2</sub>O (2.5 mL, 22 mmol) were injected. After stirring for 21 h under N<sub>2</sub> 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 ( $\text{CH}_2\text{Br}$ ) and 1180 (w,  $\text{CHBrCH}_3$ )  $\text{cm}^{-1}$ , with peaks weak or absent at 1630 and 990  $\text{cm}^{-1}$ ;  $^{13}\text{C}$  CP-MAS NMR (100 MHz; "DD" = peak also seen in spectrum with  $\tau = 45 \mu\text{s}$  dipolar dephasing)  $\delta$  145 (DD), 127, 40, 27 (DD,  $\text{CHBrCH}_3$ ), 15 (DD,  $\text{CH}_2\text{CH}_3$ ), with peaks absent at  $\delta$  135 and 110. Anal. Calcd for  $(\text{C}_{10}\text{H}_{12})_{0.45}(\text{C}_{10}\text{H}_{10})_{0.32}(\text{C}_{10}\text{H}_{11}\text{Br})_{0.23}$  (66% conversion, 1.54 mmol Br/g): Br, 12.30. Found: Br, 12.26.

**Preparation of Ps- $\text{CH}_2\text{CH}_2\text{-Br}$  (2b).** (Vinyl)polystyrene **1b** 2.67 mmol C=C/g  $(\text{C}_{10}\text{H}_{12})_{0.45}(\text{C}_{10}\text{H}_{10})_{0.20}(\text{C}_7\text{H}_7\text{CH}=\text{CH}_2)_{0.35}$  (1.00 g, 2.67 mmol C=C) was suspended in 10 mL toluene and stirred under  $\text{N}_2$ . Anhydrous lithium bromide (0.5 g, 6 mmol), chlorotrimethylsilane (0.72 mL, 6.7 mmol), water (0.06 mL, 3 mmol) then AIBN (0.1 g, 0.6 mmol) were added and the mixture stirred at 70 °C for 24 h. The suspension was then filtered and the residue washed several times with hot acetonitrile, then ether and dried in vacuo overnight, yielding 1.15g of **2b** as a light brown powder:  $^{13}\text{C}$  CP-MAS NMR  $\delta$  145 (DD), 127, 40, 28, 15 (DD), with peaks absent at  $\delta$  135 and 110, and 27 in the DD spectrum; FT-IR (KBr) 1264 ( $\text{Ps-CH}_2\text{-CH}_2\text{Br}$ ),<sup>4</sup> peak absent at 1180  $\text{cm}^{-1}$ . Anal. Calcd for  $(\text{C}_{10}\text{H}_{12})_{0.45}(\text{C}_{10}\text{H}_{10})_{0.25}(\text{C}_{10}\text{H}_{11}\text{-Br})_{0.30}$  (86% conversion): Br, 15.4. Found: Br, 15.0.

**General preparation of Ps- $\text{CH}_2\text{CH}_2\text{-SR}$  compounds.** To a mixture of (vinyl)polystyrene such as **1f**  $(\text{C}_{10}\text{H}_{12})_{0.45}(\text{C}_{10}\text{H}_{10})_{0.20}(\text{C}_7\text{H}_7\text{CH}=\text{CH}_2)_{0.35}$  (1-2 g, 2.7-5.3 mmol C=C) and a thiol compound (15-30 mmol) in 8-10 mL 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  $\text{N}_2$  for 1-2 days, then the polymer isolated by filtration and subjected to Soxhlet extraction with acetone overnight. After being dried in vacuo overnight, the Ps- $\text{CH}_2\text{CH}_2\text{-SR}$  product (**3-11,14**) was characterized by  $^{13}\text{C}$  CP-MAS NMR, FTIR and elemental analysis.

**-S(CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub> (3).** From **1f**.  $^{13}\text{C}$  CP-MAS NMR  $\delta$  145 (DD), 127, 33, 40, 28, 23 (DD), 15 (DD).

Anal. Calcd for  $(\text{C}_{10}\text{H}_{12})_{0.45}(\text{C}_{10}\text{H}_{10})_{0.30}(\text{C}_{10}\text{H}_{11}\text{-SC}_4\text{H}_9)_{0.25}$  (71% conversion): S, 5.25. Found: S, 5.27.

**-SC(CH<sub>3</sub>)<sub>3</sub> (4).** From **1e**.  $^{13}\text{C}$  CP-MAS NMR  $\delta$  145 (DD), 127, 42, 40, 34 (DD), 28, 15 (DD).

Anal. Calcd for  $(\text{C}_{10}\text{H}_{12})_{0.45}(\text{C}_{10}\text{H}_{10})_{0.42}(\text{C}_{10}\text{H}_{11}\text{-SC}_4\text{H}_9)_{0.13}$  (37%conversion): S, 2.74. Found: S, 2.73.

**-SC<sub>6</sub>H<sub>5</sub> (5).** From **1e**. <sup>13</sup>C CP-MAS NMR δ 145 (DD), 131, 127, 40, 28, 15 (DD). Anal. Calcd for (C<sub>10</sub>H<sub>12</sub>)<sub>0.45</sub>(C<sub>10</sub>H<sub>10</sub>)<sub>0.36</sub>(C<sub>10</sub>H<sub>11</sub>-SC<sub>6</sub>H<sub>5</sub>)<sub>0.19</sub> (54% conversion): S, 4.00. Found: S, 3.97.

**-SCH<sub>2</sub>CH<sub>2</sub>OH (6).** From **1f**. <sup>13</sup>C CP-MAS NMR δ 145 (DD), 127, 64, 40, 35, 28, 15 (DD). Anal. Calcd for (C<sub>10</sub>H<sub>12</sub>)<sub>0.45</sub>(C<sub>10</sub>H<sub>10</sub>)<sub>0.26</sub>(C<sub>10</sub>H<sub>11</sub>-SC<sub>2</sub>H<sub>5</sub>O)<sub>0.29</sub> (83% conversion): S, 6.01. Found: S, 6.02.

**-SCH<sub>2</sub>CH(OH)CH<sub>2</sub>OH (7).** From **1f**. <sup>13</sup>C CP-MAS NMR δ 145, 127, 72, 65, 40, 28, 15. Anal. Calcd for (C<sub>10</sub>H<sub>12</sub>)<sub>0.45</sub>(C<sub>10</sub>H<sub>10</sub>)<sub>0.22</sub>(C<sub>10</sub>H<sub>11</sub>-SC<sub>3</sub>H<sub>7</sub>O<sub>2</sub>)<sub>0.33</sub> (95% conversion): S, 6.29. Found: S, 6.27.

**-S(CH<sub>2</sub>)<sub>2</sub>SH (8).** From **1f**. <sup>13</sup>C CP-MAS NMR δ 145 (DD), 127, 40, 35, 28, 25, 15 (DD). Anal. Calcd for (C<sub>10</sub>H<sub>12</sub>)<sub>0.45</sub>(C<sub>10</sub>H<sub>10</sub>)<sub>0.27</sub>(C<sub>10</sub>H<sub>11</sub>-S<sub>2</sub>C<sub>2</sub>H<sub>5</sub>)<sub>0.28</sub> (80% conversion): S, 11.55. Found: S, 11.54.

**-S(CH<sub>2</sub>)<sub>3</sub>SH (9).** From **1f**. <sup>13</sup>C CP-MAS NMR δ 145 (DD), 127, 40, 36, 34, 28, 25, 15 (DD). Anal. Calcd for (C<sub>10</sub>H<sub>12</sub>)<sub>0.45</sub>(C<sub>10</sub>H<sub>10</sub>)<sub>0.26</sub>(C<sub>10</sub>H<sub>11</sub>-S<sub>2</sub>C<sub>3</sub>H<sub>7</sub>)<sub>0.29</sub> (83% conversion): S, 11.33. Found: S, 11.32.

**-S(CH<sub>2</sub>)<sub>4</sub>SH (10).** From **1f**. <sup>13</sup>C CP-MAS NMR δ 145 (DD), 127, 40, 34, 30, 28, 24, 15 (DD). Anal. Calcd for (C<sub>10</sub>H<sub>12</sub>)<sub>0.45</sub>(C<sub>10</sub>H<sub>10</sub>)<sub>0.30</sub>(C<sub>10</sub>H<sub>11</sub>-S<sub>2</sub>C<sub>4</sub>H<sub>9</sub>)<sub>0.25</sub> (71% conversion): S, 9.96. Found: S, 9.96.

**-S(CH<sub>2</sub>)COOH (11).** From **1f**. <sup>13</sup>C CP-MAS NMR δ 180 (DD), 145 (DD), 127, 40, 28, 15 (DD). Anal. Calcd for (C<sub>10</sub>H<sub>12</sub>)<sub>0.45</sub>(C<sub>10</sub>H<sub>10</sub>)<sub>0.36</sub>(C<sub>10</sub>H<sub>11</sub>-SC<sub>3</sub>H<sub>5</sub>O<sub>2</sub>)<sub>0.19</sub> (89% conversion): S, 6.00. Found: S, 6.00.

**-SCOCH<sub>3</sub> (14).** From **1f**. <sup>13</sup>C CP-MAS NMR δ 193 (DD), 145 (DD), 127, 40, 30, 28, 15 (DD); FT-IR (KBr) 1692 cm<sup>-1</sup> (C=O). Anal. Calcd for (C<sub>10</sub>H<sub>12</sub>)<sub>0.45</sub>(C<sub>10</sub>H<sub>10</sub>)<sub>0.32</sub>(C<sub>10</sub>H<sub>11</sub>-SC<sub>2</sub>H<sub>5</sub>O)<sub>0.23</sub> (66% conversion): S, 5.01. Found: S, 5.00.

**-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<sup>-1</sup>. Anal. Calc. for (C<sub>10</sub>H<sub>12</sub>)<sub>0.45</sub>(C<sub>10</sub>H<sub>10</sub>)<sub>0.27</sub>(C<sub>10</sub>H<sub>11</sub>-SC<sub>7</sub>H<sub>5</sub>O)<sub>0.28</sub> (80% conversion): S, 5.41. Found: S, 5.41.

**Preparation of Ps-CH<sub>2</sub>CH<sub>2</sub>-SCH<sub>2</sub>CH(NH<sub>2</sub>)COOEt•HCl (12).** Cysteine ethyl ester hydrochloride (2.00 g, 10.7 mmol) in 5 mL ethanol was added to (vinyl)polystyrene **1h** (C<sub>10</sub>H<sub>12</sub>)<sub>0.45</sub>(C<sub>10</sub>H<sub>10</sub>)<sub>0.20</sub>(C<sub>8</sub>H<sub>7</sub>CH=CH<sub>2</sub>)<sub>0.35</sub> (4.00 g, 10.7 mmol C=C), that had been ground to 45-63 Åm diameter, in 5 mL toluene. AIBN (0.1g, 0.60 mmol) was then added along with "PEG-600" polyethyleneglycol 600 g/mol (0.1g, 0.17 mmol) as phase transfer agent. The mixture was heated to 70 °C under nitrogen for 24 h. The beads were then filtered and washed liberally with hot ethanol then ether and dried in vacuo at 50 °C to give 5.1 g of **12** as a pale yellow powder: <sup>13</sup>C

CP-MAS NMR  $\delta$  170 (DD), 145 (DD), 127, 75, 40, 15 (DD); FT-IR (KBr) 1746, 3000-3500  $\text{cm}^{-1}$  ( $\text{RNH}_3^+$ ). Reaction of a portion with 0.25% ninhydrin solution quickly coloured the solid deep violet to black, similar to reaction with amino acids. Anal. Calcd for  $(\text{C}_{10}\text{H}_{12})_{0.45}(\text{C}_{10}\text{H}_{10})_{0.33}(\text{C}_{10}\text{H}_{11}\text{-SC}_2\text{H}_4\text{NO}_2\text{Cl})_{0.22}$  (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  $\mu\text{m}$  diameter particles), degree of functionalization dropped to 0.18, while products from reactions in THF:H<sub>2</sub>O 1:1 and dioxane:H<sub>2</sub>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 Ps-CH<sub>2</sub>CH<sub>2</sub>-SCN<sub>2</sub>H<sub>4</sub>•HBr (13).** (Vinyl)polystyrene **1g**

$(\text{C}_{10}\text{H}_{12})_{0.45}(\text{C}_{10}\text{H}_{10})_{0.30}(\text{C}_2\text{H}_7\text{CH}=\text{CH}_2)_{0.25}$  (9.25 g, 17.6 mmol C=C) was swollen with 25 mL dioxane, then thiourea (8.00 g, 105 mmol) and 48% HBr/H<sub>2</sub>O (20 mL, 180 mmol HBr), then AIBN (0.1g, 0.6 mmol) were added and the mixture heated at 70 °C under N<sub>2</sub> 48 h. The beads were filtered, washed with dioxane, toluene 4X and ethanol 4X, then dried in vacuo at 70 °C 24 h, yielding 10.95 g of **13** as white beads: <sup>13</sup>C CP-MAS NMR  $\delta$  165, 145, 127, 40, 20, 15; FT-IR (KBr) 3000-3500 ( $\text{NH}_2^+$ ), 1646 (C=N) and 1341  $\text{cm}^{-1}$  (Ps-CHSR-CH<sub>3</sub>). Anal. Calcd for  $(\text{C}_{10}\text{H}_{12})_{0.45}(\text{C}_{10}\text{H}_{10})_{0.34}(\text{C}_{10}\text{H}_{11}\text{-SCN}_2\text{H}_4\text{Br})_{0.17}$  (72% conversion): S, 3.70. Found: S, 3.67.

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

**Preparation of Ps-CH<sub>2</sub>CH<sub>2</sub>SO<sub>3</sub>H (17).** PsCH<sub>2</sub>CH<sub>2</sub>SCOPh  $(\text{C}_{10}\text{H}_{12})_{0.45}(\text{C}_{10}\text{H}_{10})_{0.27}(\text{C}_{10}\text{H}_{11}\text{-SC}_7\text{H}_3\text{O})_{0.28}$  **15** (5.00 g, 8.5 mmol -SCOPh) was swollen with 6 mL toluene, then cold 32wt.% peracetic acid in acetic acid (40 mL, 190 mmol COOOH) was added slowly, then the suspension stirred at room temperature 18 h. The yellow-brown suspension was then filtered and the residue washed with toluene 3X then ether 6X, 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  $\text{cm}^{-1}$ . Anal. Calc. for  $(\text{C}_{10}\text{H}_{12})_{0.45}(\text{C}_{10}\text{H}_{10})_{0.33}(\text{C}_{10}\text{H}_{11}\text{-SO}_3\text{H})_{0.12} \cdot 2.24 \text{H}_2\text{O}$ : C, 64.2; S, 2.29. Found: C, 64.25; S, 2.28.

**Preparation of Ps-CH<sub>2</sub>CH<sub>2</sub>-P(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub> (18).** To a mixture of (vinyl)polystyrene **1f**  $(\text{C}_{10}\text{H}_{12})_{0.45}(\text{C}_{10}\text{H}_{10})_{0.20}(\text{C}_6\text{H}_5\text{CH=CH}_2)_{0.35}$  (2.13 g, 5.69 mmol C=C), AIBN (0.0239 g, 0.146 mmol) and 5 mL hexanes, diphenylphosphine (4.97 g, 26.6 mmol) was added under N<sub>2</sub> with stirring. The mixture was then heated to 70 °C under N<sub>2</sub> for 2-3 days, then filtered and the residue subjected to Soxhlet extraction with hexanes overnight. Vacuum drying overnight gave 2.45 g of **18** as white beads: <sup>13</sup>C CP-MAS NMR  $\delta$  145 (DD), 127, 40, 28, 15 (DD); <sup>31</sup>P solid-state NMR  $\delta$  -15.8; FT-IR (KBr) 1097  $\text{cm}^{-1}$  (P-Ph). Anal. Calcd for  $(\text{C}_{10}\text{H}_{12})_{0.45}(\text{C}_{10}\text{H}_{10})_{0.22}(\text{C}_{10}\text{H}_{11}\text{-PC}_{12}\text{H}_{10})_{0.30}$  (86% conversion): P, 5.21. Found: P, 5.18.

**Preparation of Ps-CH<sub>2</sub>CH<sub>2</sub>-PO(OMe)<sub>2</sub> (19).** (Vinyl)polystyrene **1g**  $(\text{C}_{10}\text{H}_{12})_{0.45}(\text{C}_{10}\text{H}_{10})_{0.30}(\text{C}_6\text{H}_5\text{CH=CH}_2)_{0.25}$  (9.25 g, 17.6 mmol C=C) was swollen with 25 mL toluene and dimethylphosphite (8.00 mL, 87.2 mmol). AIBN (0.1 g, 0.6 mmol) was added and the mixture heated at 70 °C under N<sub>2</sub> 48 h. The suspension was then filtered and the residue washed with toluene 4X and ethanol 4X, then dried in vacuo at 70 °C 24 h, yielding 10.95 g of **19** as white beads: <sup>31</sup>P solid-state NMR  $\delta$  32.5 ppm; FT-IR (KBr) 1181, 1018  $\text{cm}^{-1}$ . Anal. Calcd for  $(\text{C}_{10}\text{H}_{12})_{0.45}(\text{C}_{10}\text{H}_{10})_{0.37}(\text{C}_{10}\text{H}_{10}\text{-PC}_2\text{O}_3\text{H}_7)_{0.18}$  (72% conversion): P, 3.70. Found: P, 3.67.

**Preparation of Ps-CH<sub>2</sub>CH<sub>2</sub>-Si(CH<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>5</sub> (20).** To a suspension of (vinyl)polystyrene **1g**  $(\text{C}_{10}\text{H}_{12})_{0.45}(\text{C}_{10}\text{H}_{10})_{0.30}(\text{C}_6\text{H}_5\text{CH=CH}_2)_{0.25}$  (3.22 g, 6.14 mmol C=C) in 6 mL toluene, were injected dimethylphenylsilane (4.72 g, 34.6 mmol) and *t*-butyl peroxide (60  $\mu\text{L}$ , 0.4 mmol) under N<sub>2</sub> with stirring. The mixture was kept at 125 °C under N<sub>2</sub> for 3 days, during which further aliquots of *t*-BPO were added at the end of the first (30  $\mu\text{L}$ ) and second (40  $\mu\text{L}$ ) 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: <sup>13</sup>C CP-MAS NMR  $\delta$  145 (DD), 127, 40, 28, 15 (DD), -2 (DD); <sup>29</sup>Si solid-state NMR (300 MHz)  $\delta$  -4.9; FT-IR (KBr) 1251 (Si-CH<sub>3</sub>), 1113  $\text{cm}^{-1}$  (Si-Ph). Anal. Calcd for  $(\text{C}_{10}\text{H}_{12})_{0.45}(\text{C}_{10}\text{H}_{10})_{0.35}(\text{C}_{10}\text{H}_{11}\text{-SiC}_6\text{H}_{11})_{0.20}$  (80% conversion): Si, 3.49. Found (ash): Si, 3.46.

**Reduction to Ps-CH<sub>2</sub>-CH<sub>3</sub> (21).** (Vinyl)polystyrene **1h** (C<sub>10</sub>H<sub>12</sub>)<sub>0.45</sub>(C<sub>10</sub>H<sub>10</sub>)<sub>0.20</sub>(C<sub>2</sub>H<sub>3</sub>CH=CH<sub>2</sub>)<sub>0.35</sub> (0.55 g, 1.46 mmol C=C) was suspended in 3 mL 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 48 h. The beads were then filtered and washed with toluene 3X then ether. Drying in vacuo overnight yielded 0.54 g of **21** as pale yellow beads: <sup>13</sup>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<sup>-1</sup> for (C<sub>10</sub>H<sub>12</sub>)<sub>0.70</sub>(C<sub>10</sub>H<sub>10</sub>)<sub>0.20</sub>(C<sub>2</sub>H<sub>3</sub>CH=CH<sub>2</sub>)<sub>0.10</sub> (71 % conversion).

**Preparation of Ps-CH<sub>2</sub>CH<sub>2</sub>-OH (23).** (Vinyl)polystyrene **1e** (C<sub>10</sub>H<sub>12</sub>)<sub>0.45</sub>(C<sub>10</sub>H<sub>10</sub>)<sub>0.20</sub>(C<sub>2</sub>H<sub>3</sub>CH=CH<sub>2</sub>)<sub>0.35</sub> (1.04 g, 2.77 mmol C=C) was placed in a 25 mL dry flask which was then purged with N<sub>2</sub> for a few minutes. 9-BBN 0.5M in THF (12 mL, 6 mmol) was injected over 10 min and the mixture was stirred for 23 h under N<sub>2</sub> at room temperature. H<sub>2</sub>O (2 mL, 111 mmol) was then added to the flask, followed by the addition of 5 mL of 3M aqueous NaOH (15 mmol) solution. After the mixture was stirred for 5 min, 30% H<sub>2</sub>O<sub>2</sub>/H<sub>2</sub>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, then extracted with acetone. Drying under vacuum overnight yielded 1.05 g of **23** as white beads: <sup>13</sup>C CP-MAS NMR δ 145 (DD), 127, 64, 40, 28, 15 (DD); FT-IR (KBr) 1046 cm<sup>-1</sup> (Ps-CH<sub>2</sub>-CH<sub>2</sub>OH).<sup>4</sup>

**Preparation of Ps-CH<sub>2</sub>CH<sub>2</sub>-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 CCl<sub>4</sub> under N<sub>2</sub> at room temperature, 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@20 mm Hg overnight, 0.56 g of **23** as a pale yellow product was obtained: <sup>13</sup>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<sup>-1</sup> (ROSO<sub>2</sub>R'), peak absent at 1046 cm<sup>-1</sup>. Anal. Calcd for (C<sub>10</sub>H<sub>12</sub>)<sub>0.45</sub>(C<sub>10</sub>H<sub>10</sub>)<sub>0.45</sub>(C<sub>10</sub>H<sub>11</sub>-OSO<sub>2</sub>C<sub>7</sub>H<sub>7</sub>)<sub>0.12</sub>: S, 2.38. Found: S, 2.36.

## References

- (1) Fréchet, J. M. J. In *Chemistry of Crosslinked Polymers*; Labana, S. S., Ed.; Academic Press: New York, 1977, p 59.
- (2) Akelah, A.; Sherrington, D. C. *Chem. Rev.* **1981**, *81*, 557.
- (3) O'Brien, R. A., Chen, T., Rieke, R.D. *J.Org. Chem.* **1992**, *57*, 2667-2677.
- (4) Darling, G. D.; Fréchet, J. M. J. *J. Org. Chem.* **1986**, *51*, 2270-2276.
- (5) Darling, G. D.; Fréchet, J. M. J. In *Chemical Reactions on Polymers*; Benham, J. L., Kinstle, J. F., Eds.; American Chemical Society: Washington, DC, 1988; Vol. 364, p 24-36.
- (6) Gao, J. P.; Barghi, R.; Darling, G. D. , 33rd IUPAC International Symposium on Macromolecules, July 8-13, Montreal, QC, Canada, ; , 1990; Session 1.7.5.
- (7) Deratani, A.; Darling, G. D.; Fréchet, J. M. J. *Polymer* **1987**, *28*, 825-830.
- (8) Vogl, O. *J. Macromol. Sci. Chem.* **1984**, *21*, 1217.
- (9) Malinski, J.; Klaban, J.; Dusek, K. *J. Macromol. Sci. Chem.* **1971**, *5*, 1071-1085.
- (10) Kwant, P. W. *J. Polym. Sci., Polym. Chem. Ed.* **1979**, *17*, 1331.
- (11) Bartholin, M.; Boissier, G.; Dubois, J. *Makromol. Chem.* **1981**, *182*, 2075-2085.
- (12) Okubo, M.; Nakagawa, T. *Coll. Polym. Sci.* **1992**, *270*, 853-858.
- (13) Periyasamy, M.; Ford, W. T.; McEnroe, F. J. *J. Polym. Sci. Polym. Chem.* **1989**, *27*, 2357-2366.
- (14) Brunelet, T.; Bartholin, M.; Guyot, A. *Angew. Makromol. Chem.* **1982**, *106*, 79-90.
- (15) Walling, C.; Huyser, E. S. *Org. React.* **1963**, *13*, 91-149.
- (16) Farrell, M. J.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **1978**, *100*, 7998.
- (17) Ford, W. T. In *Polymeric Reagents and Catalysts*; Ford, W. T., Ed.; American Chemical Society: Washington, DC, 1986; Vol. 308, p 247-285.
- (18) Szabó, L. F.; Tétényi Jr., P.; Pecher, J. *Reactive Polym.* **1989**, *11*, 47-56.

- (19) Faber, M. C.; van de Berg, H. J.; Challa, G.; Pandit, U. K. *Reactive Polym.* **1988**, *11*, 117-126.
- (20) Stranix, B. R.; Darling, G. D.; , m. i. p. .
- (21) Fréchet, J. M. J.; Eichler, E. *Polym. Bull.* **1982**, *7*, 345.
- (22) Neumann, W. P.; Peterseim, M. *Reactive Polym.* **1993**, *20*, 189-205.
- (23) Bootsma, J. P. C.; Eling, B.; Challa, G. *Reactive Polym.* **1984**, *3*, 17.
- (24) Guyot, A. *Reactive Polym.* **1989**, *10*, 113-129.
- (25) Farrall, M. J.; Fréchet, J. M. J. *J. Org. Chem.* **1976**, *41*, 3877-3882.
- (26) Stacey, F. W.; Harris Jr., J. F. *Org. React.*; John Wiley & Sons, Inc.: New York, 1963; Vol. 13.
- (27) Rhone-Poulenc, S. d. u. c. , 1935.
- (28) Walling, C.; Kharasch, M. S.; Mayo, F. R. *J. Am. Chem. Soc.* **1939**, *61*, 2693-2696.
- (29) Thaler, W. A. *Methods Free-Radical Chem.* **1969**, *2*, 121-227, 182-195.
- (30) Davies, J. A.; Sood, A. *Makromol. Chem. Rapid Commun.* **1983**, *4*, 777.
- (31) Crosby, G. A. U.S. Patent 3 928 293, 1975.
- (32) Svirskaya, P. I.; Leznoff, C. C. *J. Org. Chem.* **1987**, *52*, 1362-1364.
- (33) Parrish, J. R. *Chem. Ind. (London)* **1956**, 137.
- (34) Boutevin, B.; Fleury, E.; Parisi, J. P.; Pietrasanta, Y. *Macromol. Chem. Phys.* **1989**, *190*, 2363-2372.
- (35) Jacobine, A. F.; Glaser, D. M.; Nakos, S. T. In *Radiation curing of polymer materials.*; Hoyle, C. E., Kinstle, J. F., Eds.; American Chemical Society: Washington, D.C., 1990, p 160-175.
- (36) Fyles, T. M.; Leznoff, C. C.; Weatherston, J. *Can. J. Chem.* **1978**, *56*, 1031.
- (37) Morse, B. K.; Tarbell, D. S. *JACS* **1952**, *74*, 416-419.
- (38) Showell, J. S.; Russell, J. R.; Swern, D. *J. Org. Chem.* **1962**, *27*, 2853-2858.
- (39) Stranix, B. R., Darling, G.D. *Biotechnol. Tech.* **1995**, *9*, 75-80.
- (40) Leznoff, C. C.; Synawyk, W. *J. Org. Chem.* **1977**, *42*, 3203.

- (41) Garrou, P. E. In *Polymeric Reagents and Catalysts*; Ford, W. T., Ed.; American Chemical Society: Washington, DC, 1986; Vol. 308, p 84-106.
- (42) Amaratunga, W.; Fréchet, J. M. J. *Polym. Prepr. Am. Chem. Soc. Div. polym. Chem.* **1981**, *22*, 151.
- (43) Akelah, A., Moet A. *Functionalized polymers and their applications.*; Chapman and Hall: New York, 1990.
- (44) Verkade, J. G., Quin, L.D. *Phosphorous-31 NMR Spectroscopy in Stereochemical analysis*; VCH Publishers Inc., 1987; Vol. 8.
- (45) Alexandratos, S. D., Quillen, D.R. *Reactive Polym.* **1990**, 255-265.
- (46) Sundell, M. J., Nasman, J.H. *Chemtech* **1993**, 16-23.
- (47) Danishefsky, S. J., McClure, K.F., Randolph, J.T., Ruggeri, R.B. *Science* **1993**, *260*, 1307-1309.
- (48) Chan, T. H., Huang, W.Q. *Chem. Commun.* **1985**, 909-912.
- (49) Fréchet, J. M. J.; Darling, G. D.; Itsuno, S.; Lu, P. Z.; Meftahi, M. V. d.; Rolls Jr., W. A. *Pure & Appl. Chem.* **1988**, *60*, 353-364.
- (50) Stover, H.; Lu, D. H.; Zhi, P.; Fréchet, J. M. J. *Polymer Bull.* **1991**, 575-582.
- (51) Stranix, B. R., Liu, H.Q., Darling, G.D. **in prep.**
- (52) Loim N.M. *Synthesis* **1974**, 633-651.
- (53) Brown, H. C.; Zweifel *J. Am. Chem. Soc.* **1960**, *82*, 4708.
- (54) Srebnik, M.; Cole, T. E.; Brown, H. C. *J. org. Chem.* **1990**, *55*, 5051-5058.
- (55) Budesinsky, B. *Anal. Chem.* **1965**, *9*, 1159.

We claim:

1. A functional polymer bearing nonmetal oxyacid derivatives on dimethylene spacers, comprising repeat units that are nonmetal oxyacid derivatives, of the form  $-\text{CH}[\text{Ph}-\text{CH}_2\text{CH}_2-\text{X}(\text{O})_m\text{R}^1_n\text{R}^2_p]-\text{CH}_2-$ , where:

a)  $\text{X} = \text{S}$ ,  $m = 2$ ,  $n = 0$ ,  $p = 1$  and  $\text{R}^2$  is selected from  $\text{Cl}$ ,  $\text{Br}$ ,  $\text{O}^-$  and  $\text{OH}$ , or

b)  $\text{X} = \text{P}$ ,  $m = 1$ ,  $n = 1$ ,  $p = 1$ ,  $\text{R}^1$  is selected from  $\text{Cl}$ ,  $\text{Br}$ ,  $\text{O}^-$ ,  $\text{OH}$ ,  $\text{R}^3$ ,  $\text{OR}^3$ ,  $\text{NH}_2$ ,  $\text{NHR}^4$  and  $\text{NR}^4\text{R}^5$ , and  $\text{R}^2$  is selected from  $\text{Cl}$ ,  $\text{Br}$ ,  $\text{O}^-$ ,  $\text{OH}$ ,  $\text{OR}^6$ ,  $\text{NH}_2$ ,  $\text{NHR}^7$  and  $\text{NR}^7\text{R}^8$  where  $\text{R}^3$ ,  $\text{R}^4$ ,  $\text{R}^5$ ,  $\text{R}^6$ ,  $\text{R}^7$  and  $\text{R}^8$  are selected from methyl, ethyl, *n*-propyl, *i*-propyl, *n*-butyl, *i*-butyl, *s*-butyl, *t*-butyl, 2-ethylhexyl, hexadecyl, 2-chloroethyl, 2-bromoethyl, 2,2,2-trifluoroethyl, 2-hydroxyethyl, 2-butoxyethyl, 2-aminoethyl, cyclohexyl, phenyl, benzyl, 4-nitrobenzyl, tolyl, and cyclic  $-(\text{CH}_2)_q-$  where  $q$  is selected from 2 to 4.

2. A functional polymer of claim 1., that is derived from a polymer comprising 1-(vinylphenyl)ethylene repeat units.

3. A functional polymer of claim 2., wherein said polymeric 1-(vinylphenyl)ethylene repeat units arise from copolymerization of a monomer mixture that includes divinylbenzene.

4. A functional polymer of claim 1., wherein  $\text{X} = \text{S}$ ,  $m = 2$ ,  $n = 0$ ,  $p = 1$  and  $\text{R}^2$  is  $\text{O}^-$ .

5. A functional polymer of claim 1., wherein  $\text{X} = \text{P}$ ,  $m = 1$ ,  $n = 1$ ,  $p = 1$  and  $\text{R}^1$  and  $\text{R}^2$  are both  $\text{OCH}_3$ .

6. A functional polymer of claim 1., wherein  $\text{X} = \text{P}$ ,  $m = 1$ ,  $n = 1$ ,  $p = 1$  and  $\text{R}^1$  and  $\text{R}^2$  are both  $\text{OH}$ .

7. A functional polymer of claim 1., wherein  $\text{X} = \text{P}$ ,  $m = 1$ ,  $n = 1$ ,  $p = 1$ ,  $\text{R}^1$  is  $\text{OH}$  and  $\text{R}^2$  is  $\text{OCH}_3$ .

8. A method of preparing a functional polymer bearing nonmetal oxyacid derivatives on dimethylene spacers, wherein polymeric 1-(vinylphenyl)ethylene repeat units are treated with  $\text{HX}(\text{O})_m\text{R}^1_n\text{R}^2_p$  in the presence of free radicals, where:

a)  $\text{X} = \text{S}$ ,  $m = 2$ ,  $n = 0$ ,  $p = 1$  and  $\text{R}^2$  is selected from  $\text{O}^-$  or  $\text{OH}$ .

b)  $\text{X} = \text{P}$ ,  $m = 1$ ,  $n = 1$ ,  $p = 1$ ,  $\text{R}^1$  is selected from  $\text{Cl}$ ,  $\text{Br}$ ,  $\text{O}^-$ ,  $\text{OH}$ ,  $\text{R}^3$ ,  $\text{OR}^3$ ,  $\text{NH}_2$ ,  $\text{NHR}^4$  and  $\text{NR}^4\text{R}^5$ , and  $\text{R}^2$  is selected from  $\text{Cl}$ ,  $\text{Br}$ ,  $\text{O}^-$ ,  $\text{OH}$ ,  $\text{OR}^6$ ,  $\text{NH}_2$ ,  $\text{NHR}^7$  and  $\text{NR}^7\text{R}^8$ ,

where  $R^3$ ,  $R^4$ ,  $R^5$ ,  $R^6$ ,  $R^7$  and  $R^8$  are selected from methyl, ethyl, *n*-propyl, *i*-propyl, *n*-butyl, *i*-butyl, *s*-butyl, *t*-butyl, 2-ethylhexyl, hexadecyl, 2-chloroethyl, 2-bromoethyl, 2,2,2-trifluoroethyl, 2-hydroxyethyl, 2-butoxyethyl, 2-aminoethyl, cyclohexyl, phenyl, benzyl, 4-nitrobenzyl, tolyl, and cyclic  $-(CH_2)_q-$  where  $q$  is selected from 2 to 4.

9. A method of preparing a functional polymer bearing nonmetal oxyacid derivatives on dimethylene spacers, wherein polymeric repeat units  $-CH[Ph-CH_2CH_2-X(O)_mR^nR^p]-CH_2-$  are treated with peracetic acid or other oxidizing agent so as to increase the oxidation state of X, where:

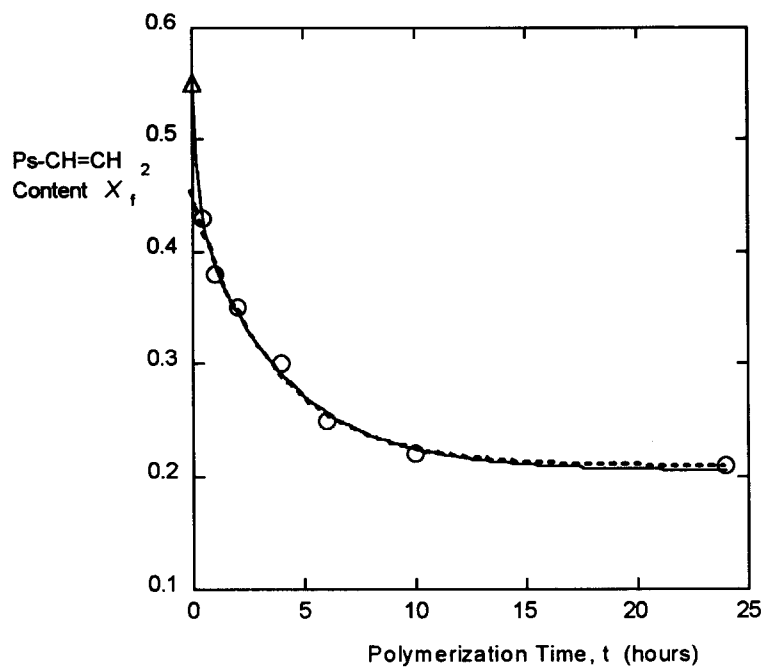
a)  $X = S$ ,  $m = 0$ ,  $n = 0$ ,  $p = 1$  and  $R^2$  is selected from H,  $SO_3^-$ ,  $C(NH_2)_2^+$ ,  $CH(NMe_2)^+$ ,  $C(CH_3)(NH_2)^+$ , CN, SH, and  $COR^3$  where  $R^3$  is selected from hydrogen, methyl, ethyl, *n*-propyl, *i*-propyl, *n*-butyl, *i*-butyl, *s*-butyl, *t*-butyl, cyclohexyl, phenyl and tolyl.

b)  $X = P$ ,  $m$  is selected from 0 or 1,  $n = 1$ ,  $p = 1$ ,  $R^1$  is selected from H, Cl, Br, O $\cdot$ , OH,  $R^3$ ,  $OR^3$ ,  $NH_2$ ,  $NHR^4$  and  $NR^4R^5$ , and  $R^2$  is selected from H, Cl, Br, O $\cdot$ , OH,  $OR^6$ ,  $NH_2$ ,  $NHR^7$  and  $NR^7R^8$ , where  $R^3$ ,  $R^4$ ,  $R^5$ ,  $R^6$ ,  $R^7$  and  $R^8$  are selected from methyl, ethyl, *n*-propyl, *i*-propyl, *n*-butyl, *i*-butyl, *s*-butyl, *t*-butyl, 2-ethylhexyl, hexadecyl, 2-chloroethyl, 2-bromoethyl, 2,2,2-trifluoroethyl, 2-hydroxyethyl, 2-butoxyethyl, 2-aminoethyl, cyclohexyl, phenyl, benzyl, 4-nitrobenzyl, tolyl, and cyclic  $-(CH_2)_q-$  where  $q$  is selected from 2 to 4.

10. A method of preparing a functional polymer bearing nonmetal oxyacid derivatives on dimethylene spacers, wherein polymeric repeat units  $-CH[Ph-CH_2CH_2-X(O)_mR^nR^p]-CH_2-$  are treated with either  $HR^9$  or  $R^9$  reagents so as to replace either  $R^1$  or  $R^2$  or both by  $R^9$ , where:

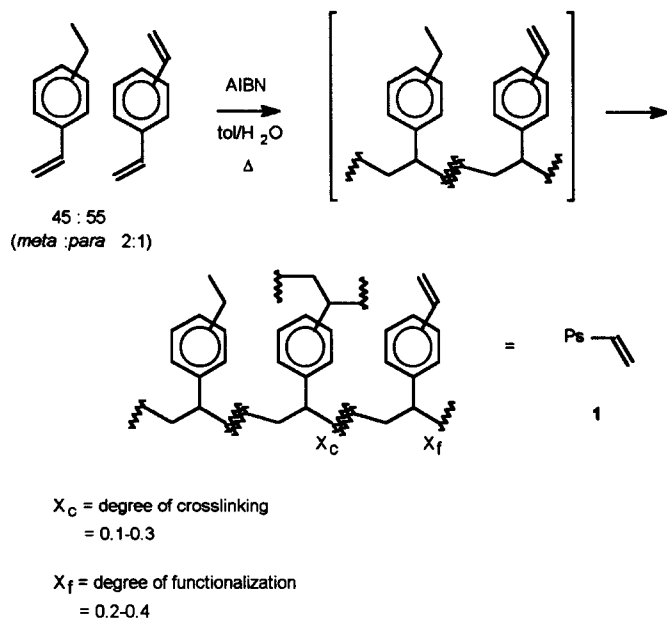
a)  $X = S$ ,  $m = 2$ ,  $n = 0$ ,  $p = 1$ , and  $R^2$  and  $R^9$  are selected from Cl, Br, O $\cdot$  and OH, or

b)  $X = P$ ,  $m = 1$ ,  $n = 1$ ,  $p = 1$ ,  $R^1$  is selected from Cl, Br, O $\cdot$ , OH,  $R^3$ ,  $OR^3$ ,  $NH_2$ ,  $NHR^4$  and  $NR^4R^5$ , and  $R^2$  is selected from Cl, Br, O $\cdot$ , OH,  $OR^6$ ,  $NH_2$ ,  $NHR^7$  and  $NR^7R^8$  where  $R^3$ ,  $R^4$ ,  $R^5$ ,  $R^6$ ,  $R^7$ ,  $R^8$  and  $R^9$  are selected from methyl, ethyl, *n*-propyl, *i*-propyl, *n*-butyl, *i*-butyl, *s*-butyl, *t*-butyl, 2-ethylhexyl, hexadecyl, 2-chloroethyl, 2-bromoethyl, 2,2,2-trifluoroethyl, 2-hydroxyethyl, 2-butoxyethyl, 2-aminoethyl, cyclohexyl, phenyl, benzyl, 4-nitrobenzyl, tolyl, and cyclic  $-(CH_2)_q-$  where  $q$  is selected from 2 to 4.

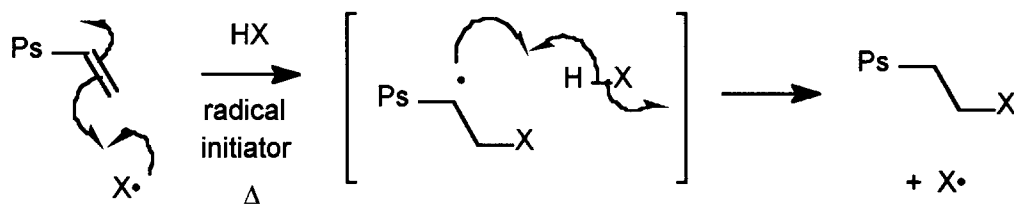


-----

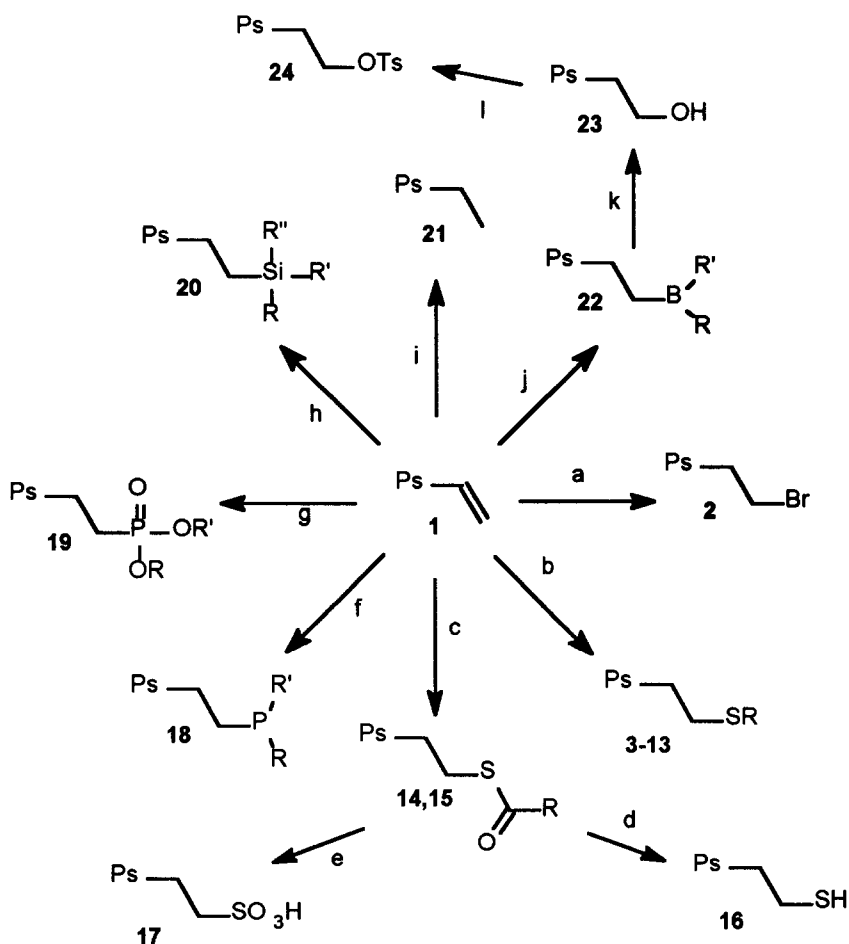
**Figure 1.** Effect of time on content of residual vinyl groups during preparation of (vinyl)polystyrene **1** by polymerization of divinylbenzene (see Experimental).  $\circ$   $X_f$  measured by FTIR.  $\triangle$   $X_f$  reported by GC. --- Curve fitted to FTIR points only:  $X_f = 0.245e^{-0.273t}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



**Figure 2. Preparation of (Vinyl)polystyrene Intermediate 1**

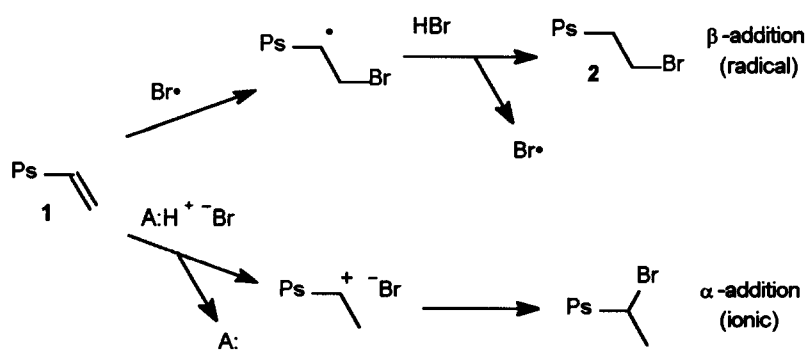


**Figure 3 Radical-Initiated Additions to 1**

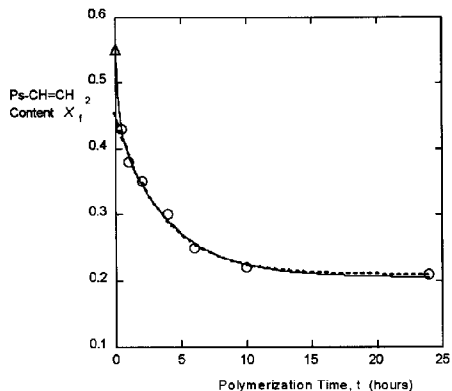


**Figure 4. Functional Polymers With Dimethylene Spacers From 1<sup>a</sup>**

<sup>a</sup> (a) LiBr, Me<sub>3</sub>SiCl, H<sub>2</sub>O, AIBN cat., Δ; (b) HSR, AIBN cat., Δ; (c) HSCOH<sub>3</sub>, AIBN cat., Δ; (d) HCl, H<sub>2</sub>O, Δ; (e) CH<sub>3</sub>CO<sub>3</sub>H; (f) HPRR', AIBN cat., Δ; (g) HPO(OR)(OR'), AIBN cat., Δ; (h) HSiRR'R'', *t*(-BuO)<sub>2</sub> cat., Δ; (i) HSiEt<sub>3</sub>, CF<sub>3</sub>COOH; (j) 9-BBN-H; (k) H<sub>2</sub>O<sub>2</sub>, NaOH, H<sub>2</sub>O; (l) TsCl, *i*-Pr<sub>2</sub>NH, Δ.



**Figure 5. Two Modes of Addition of HBr to 1.**



-----

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