Functional Polymers from (Vinyl)polystyrene. Recyclable Polymer-Supported Organosilicon Protecting Groups for Solid-Phase Synthesis

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Dicobalt octacarbonyl catalyzed the hydrosilylation of residual vinyl groups on insoluble porous beads of divinylbenzene-rich copolymer, exclusively with β orientation, by either dialkylhalosilanes or alkyldihalosilanes. The resulting silyl halide functionalities, now bound to a cross-linked polystyrene matrix through stable dimethylene spacers, could then be used to protect and immobilize hydroxyl-containing free molecules for their further modification in the course of solid-phase synthesis. The reaction proved selective for primary hydroxyls in the presence of secondary, and secondary over tertiary. Together with product free alcohols, later cleavage of these silyl ethers with aqueous acid or base also released the corresponding silanol groups, while HF, under particularly mild and selective conditions, left silyl fluorides that themselves could then be very conveniently regenerated by BCl_3/CH_2Cl_2 back to the polymer-supported silyl chlorides. For a variety of possible applications, these solid-phase protecting groups offer control, yield, recovery, and reusability, as well as other possible advantages involving site-site isolation of functional groups within the cross-linked polystyrene matrix.

For many conceivable organic applications involving protecting groups, the use of insoluble supports bearing organosilyl halide moieties would, by analogy with other types of solid-phase synthesis, greatly ease product separation, improve yields, allow automation, and possibly show other benefits from site separation and a polymer microenvironment. However, to become widely adopted as tools for organic synthesis, such materials would have to be easy enough to prepare, or regenerate for reuse, or both. Thus, though halosilyl-functionalized cross-linked polystyrene Ps−SiRR′−X (R = R′ = Me or Ph; X = Cl or other leaving group) has already proven useful,[1] the difficulty and expense of its preparation using organolithium reagents, and the inefficiency of its regeneration due to the lability of its aryl−silicon linkage toward the Lewis acid reagents needed for its regeneration,[2] have limited its application. In common with many other functional polymers from (chloromethyl)polystyrene, the alternative Ps−CH_2−SiRR′−X would have a benzylic bond that is still fragile toward other species (i.e., fluoride).[3,4] Functional polymers with longer spacers would be chemically much more robust: but, though Ps−$CH_2CH_2CH_2$−SiRR′−X has been prepared and regenerated from the silanol,[5,6] the preparation was involved, and the regeneration conditions did not apply to the silyl fluoride of greater practical interest.

Controlled polymerization of technical-grade divinylbenzene:ethylstyrene results in macroporous beads of cross-linked polystyrene that bear many residual vinyl groups (typical X_f = degree of functionalization = 0.20 to over 0.40 mol of functional groups per mole of polymer repeating units). Anti-Markovnikov addition of various small molecules HZ to such (vinyl)polystyrene Ps-CH=CH_2 (also commercially available as Amberlite XAD-2 and XAD-4) gives many useful spacer-containing functional polymers Ps−CH_2CH_2−Z, in which functional groups are accessible, stably-linked, and mobile.[7−9] Hydrosilylation of alkenes is a well-known means for preparing organosilicon compounds,[10] and by this reaction, as catalyzed by dicyclopentadienylplatinum(II) chloride, poly(methylhydrosiloxane) has been grafted onto commercial (vinyl)polystyrene.[11] However, many such organoplatinum catalysts cause mixed α and β addition to vinylarenes or, from being colloids, cannot penetrate a cross-linked polymer matrix.[11,12] Procedures using an alternative, free-radical mechanism, though able to add $HSiCl_3$ and $HSiMe_2Ph$ to Ps−CH=CH_2, proved ineffective

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Scheme 1

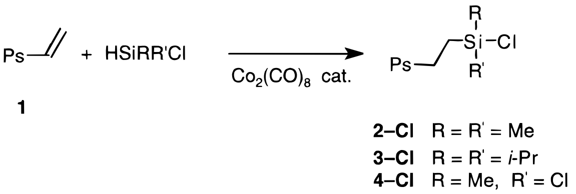


Table 1. Modification of Resin 1 by $Co_2(CO)_8$-Catalyzed Hydrosilylation

mass of **1** (g)	X_f of **1**	product	X_f of product	% conversion
1	0.43	**2−Cl**	0.23	53
50	0.30	**2−Cl**	0.15	50
1	0.25	**3−Cl**	0.12	48
30	0.30	**3−Cl**	0.14	47
25	0.30	**4−Cl**	0.10	33

with such silanes as $HSiMe_2Cl$, which cannot as easily form radical intermediates.[9]

Dicobalt octacarbonyl $Co_2(CO)_8$ has been established as an effective, homogeneous catalyst for the exclusive β-hydrosilylation of various substituted styrenes.[13−15] Following its application to our analogous polymer modification, we can now report on a quite facile method for preparing solid-phase organosilicon protecting groups, along with equally straightforward procedures for their application and regeneration.[16]

Results and Discussion

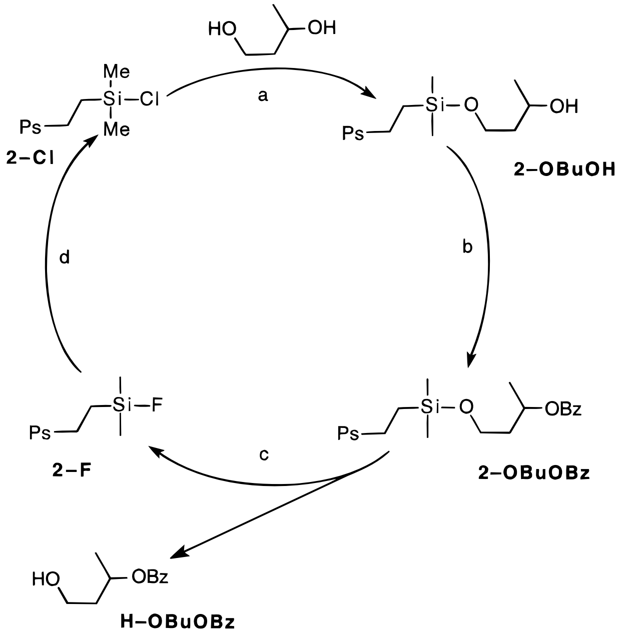
The action of an excess of several HSiRR′Cl on (vinyl)polystyrene in the presence of 2−4 mol % $Co_2(CO)_8$ gave, after a few days, exclusive β−hydrosilylation of polymer vinyls, as determined by FT-IR, solid-phase ^{13}C and ^{29}Si NMR, and elemental analysis (Scheme 1, Table 1). Supported on a hydrophobic polymer matrix, the resulting silyl chloride groups were found to be relatively stable in air, with only a little hydrolysis from atmospheric moisture after several weeks in the open.

The resulting solid-phase trialkylchlorosilanes were reacted with alcohols in the presence of pyridine or triethylamine, in a suitable solvent, to form the corresponding trialkylsilyl ethers. Elemental analysis of the product from a nitrogen-containing alcohol confirmed spectral analyses showing complete reaction. Solid-phase ^{13}C NMR experiments on $Ps-CH_2CH_2-Si(CH_3)_2-O(CH_2)_3CH_3$ (**2−OBu**) showed, by retention of the peak corresponding to $Si-O-CH_2$ in the dipolar dephased (DD) spectrum, that the protected and supported alcohol moiety was very mobile (liquid-like), thus unhindered, thus probably accessible.[7] The use of alcohol mixtures showed selective protection of primary hydroxyls in the presence of secondary, and secondary over tertiary (Table 2).

Table 2. Selectivity of Resin 2−Cl for Alcohols

alcohols added	alcohols protected
EtOH:*i*-PrOH 1:1	EtOH only
i-PrOH:*t*-BuOH 1:1	*i*-PrOH only
EtOH:*i*-PrOH:*t*-BuOH 1:1:1	EtOH only

Scheme 2



[a] Key: (a) Pyr, CH_2Cl_2; (b) BzCl, pyr, CH_2Cl_2; (c) HF, H_2O, MeCN; (d) BCl_3, CH_2Cl_2.

1,3-Butanediol, bearing both primary and secondary hydroxyls on the same molecule, normally reacts with an excess of acylating agent to give mixtures of 1-monoacylated and 1,3-diacylated products. In a demonstration of solid-phase synthesis, its addition to **2−Cl**, followed by wash, excess benzoyl chloride + base, wash, then cleavage of silyl ether, gave only the 3-monobenzoylated product in high isolated yield, and none of the dibenzoylated or the 1-monobenzoylated products (Scheme 2). The small quantity of starting material that was also recovered can be explained by diprotection of the starting diol, through reaction with two insufficiently-separated[17] Si−Cl groups within the **2−Cl** resin. This side reaction, further cross-linking the polymer matrix as well as decreasing final yields of desired product, could arise from primary hydroxyls of diol molecules still diffusing into the resin, having to compete with certain secondary hydroxyls of diol already bound. This model is supported by the observation that a greater excess of diol as starting material (from 1.2- to 1.5- to 3.5-fold) actually results in less diol appearing as side product at reaction's end (from 15% to 12% to 10%, respectively). Use of more hindered silyl halide groups for still better selectivity of primary > secondary hydroxyl, and of lower-functionalized resin for better site-isolation, should help even more.

Somewhat similar to certain small-molecule studies,[13,14] except for using better-swelling solvents than methanol or ethanol, conditions were explored for acid- and base-catalyzed hydrolysis and fluoride-induced cleavage of sample polymeric menthyl silyl ethers **2−OMen** and **3−OMen** (Table 3). Because of deviations from pseudo-first-order kinetics (probably due to reaction heterogeneity and site variability), and for other practical reasons, the relative stability of each was here expressed as the time needed for its apparent 100% deprotection and release of menthol (t_{100}).

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Table 3. Time for Complete Release of Menthol from Polymeric Menthyl Silyl Ethers (t_{100}) under Various Conditions

condns[a]	**2−OMen**	**3−OMen**
1.0 M HCl	<30 s[b]	30 min[c]
1.0 M $Me_4N^{+-}OH$	2 h[c]	no reaction after 48 h[d]
0.22 M HF	10 min	30 min

[a] 1.0 mmol of substrate, 5 mL of 9:1 dioxane:water, 22−24 °C. [b] Desilylation was so fast that t_{100} could not be determined accurately. [c] Kinetics curves of triplicate experiments matched to ±10%. [d] Subsequent addition of 1 equiv of HF_{aq} released all menthol within 30 min.

Table 4. Effect of Recycling on Analysis of 2/3−*p*-OCH$_2$CH$_2$PhNO$_2$

	from **2−Cl**		from **3−Cl**	
no. of recycles	% Si	% N	% Si	% N
0 (“fresh”)	2.54	1.30	2.30	1.17
1	2.55	1.30	2.30	1.17
2	2.54	1.25	2.28	0.84

After hydrolysis and drying, the spent resin **2−OH** was found to also contain Si−O−Si groups, according to solid-phase ^{29}Si NMR, further demonstrating that site isolation was not complete. Possibly because of greater steric hindrance, such siloxane cross-linking appeared negligible under all conditions for producing **3−OH**.

Fluoride cleaved all polymer-bound silyl ethers and other silyl derivatives to the corresponding **2−F**, **3−F**, or **4−F**, showing slight or no disiloxane formation by ^{29}Si NMR. Such reaction generally proved slower with tetrabutylammonium fluoride (TBAF) than with hydrofluoric acid (>18 h vs. 30 min, for **3−OMen**), perhaps owing to the more bulky and ionic nature of the former reagent that hindered its penetration into the hydrophobic polymer matrix, and to greater assistance by protons with the latter. In surprisingly convenient fashion, boron trichloride was then able to convert the solid-phase silyl fluoride resins back to the starting silyl chlorides, a reaction presumably driven by the conversion of admittedly strong Si−F bonds to even stronger B−F and evolution of gaseous BF_3 side product. Elemental and solid-phase NMR analyses, and experiments with [(fluorodimethylsilyl)ethyl]benzene as a small molecule analogue, confirmed that transformation was clean and complete. Alternative regeneration of the fluoride through triethylamine-catalyzed halogen exchange with Me_3SiCl[18] proved much less successful. The same BCl_3 also converted SiOR and SiOH to SiCl, presumably with borate ester or anhydride as side products, whereas similar reactions with $SOCl_2$ or $MeSO_2Cl$ did not proceed to completion.

Elemental analysis showed **2−*p*-OCH$_2$CH$_2$PhNO$_2$** to be the same whether produced from “fresh” or once- or twice-recycled **2−Cl** (Table 4), and the polymer showed no spectral changes after two further such cycles. **3−Cl**, however, after recycling twice, could not be completely regenerated even after 3 days, thus showing some loss of active functionality.

On the basis of these results, we eventually took to treating these organosilicon functional polymers with aqueous hydrogen fluoride immediately after their preparation by hydrosilylation, thus transforming them to the inert silyl fluoride forms most suitable for long-term storage, while also washing out any remaining traces of dicobaltoctacarbonyl catalyst. As needed, portions could later be weighed into a reaction vessel and then “activated” in situ to the silyl chloride form by treatment with a commercial dichloromethane solution of boron trichloride, which also dried the solid powder of any remaining adsorbed atmospheric moisture. Subsequent application of vacuum, or flushing with dry nitrogen gas, then removed BCl_3 reagent, CH_2Cl_2 solvent, and BF_3 side product, all of them volatile, leaving a dry powder ready for use in organic synthesis.

We continue to investigate these silyl-bearing polymers and their further derivatives for application as solid-phase reagents and catalysts, as well as protecting groups for other solid-phase syntheses.

Experimental Section

Where specified “dry” below, aromatic solvents were distilled from calcium hydride and other solvents and reagents stored over molecular sieves. Otherwise, chemicals were used as received. Organohalosilanes came from Hüls America and dicobalt octacarbonyl from Johnson Matthey. (Vinyl)polystyrene (**1**) was prepared as previously described.[7] Transmittance FT-IR spectra were recorded of samples ground and pressed into dry KBr pellets or spread onto IR-transparent silicon wafers. ^{13}C and ^{29}Si CP-MAS (cross polarization/magic angle spinning) and ^{13}C CP-MAS-DD (cross polarization/magic angle spinning/dipolar-dephasing, $\tau = 45\ \mu s$; in the lists following, peaks labeled “DD” persist here) solid-phase NMR spectra were obtained on a Chemagnetics Inc. M-100 spectrometer. Elemental analyses were done by Robertson Microlit Laboratories (NJ).

***β*-Hydrosilylation of (vinyl)polystyrene (general procedure).** (Vinyl)polystyrene (**1**), of X_f 0.20−0.45 (25−50 g, 55−111 mmol CH=CH$_2$), was oven-dried for 2 days and then transferred to a flame-dried, two-neck round-bottom flask, which was then purged with nitrogen. To this was added 100 mL of dry toluene, and the suspension was heated on an oil bath with slow stirring at 60 °C. A dialkylchlorosilane (4−8-fold excess) or alkyldichlorosilane (4-fold excess) was then slowly injected. Dicobalt octacarbonyl (2−4 mol %) was finally added portionwise, whereupon the mixture turned deep blue to brown. Stirring continued for 5 days, with 0.2−0.3 g of suspended solids being sampled after 2 and 4 days for FT-IR assay. The suspension was then filtered under nitrogen and the residue placed in a Soxhlet extractor, extracted with dry benzene or toluene until the filtrate was colorless, and then dried in a vacuum oven at 40 °C for 24 h to give **2−Cl**, **3−Cl**, and **4−Cl** as pale blue beads.

[(Chlorodimethylsilyl)ethyl]polystyrene (2−Cl). From **1** $(C_{10}H_{12})_{0.45}(C_{10}H_{10})_{0.25}(C_8H_7CH{=}CH_2)_{0.30}$. Product **2−Cl**: FTIR (KBr) 1262 (Si*CH*$_3$), 1078 (*SiO*), 472 cm^{-1} (*SiCl*); solid-phase ^{29}Si NMR (300 MHz) δ 29.9 (CH$_2$*Si*Me$_2$Cl), 6.3 ppm (w, *Si*O*Si*); ^{13}C CP-MAS NMR (100 MHz) δ 146 (DD), 129, 43, 31, 16 (DD), 3 ppm (DD, Si*CH*$_3$). Anal. Calcd for $(C_{10}H_{12})_{0.45}(C_{10}H_{10})_{0.40}(C_{12}H_{17}SiCl)_{0.15}$ (50% conversion): Si, 2.90. Found: Si, 2.88.

[(Chlorodiisopropylsilyl)ethyl]polystyrene (3−Cl). From **1** $(C_{10}H_{12})_{0.45}(C_{10}H_{10})_{0.25}(C_8H_7CH{=}CH_2)_{0.30}$. Product **3−Cl**: FTIR (KBr) 1453, 1364, 1062, 997, 888, 572 cm^{-1}; solid-phase ^{29}Si NMR (300 MHz) δ 33.9 ppm (*Si*Cl), 5.1 ppm (w, *Si*O*Si*). Anal. Calcd for $(C_{10}H_{12})_{0.45}(C_{10}H_{10})_{0.41}(C_{16}H_{25}SiCl)_{0.14}$ (47% conversion): Si, 2.58. Found: Si, 2.56.

[(Dichloromethylsilyl)ethyl]polystyrene (4−Cl). From **1** $(C_{10}H_{12})_{0.45}(C_{10}H_{10})_{0.25}(C_8H_7CH{=}CH_2)_{0.30}$. Product **4−Cl**: FTIR (Si wafer) 1264, 1078, 997, 888, 551 cm^{-1}; solid-phase ^{29}Si NMR (300 MHz) δ 30.6 ppm (*Si*Cl); CP-MAS ^{13}C NMR (100 MHz) δ 146 (DD), 129, 43, 31, 16 (DD), 5 ppm (DD; Si*CH*$_3$). Anal. Calcd for $(C_{10}H_{12})_{0.45}(C_{10}H_{10})_{0.45}(C_{15}H_{22}SiCl_2)_{0.10}$ (33% conversion): Si, 2.58. Found: Si, 2.56.

[[[(*p*-Nitrophenethyl)oxy]dimethylsilyl]ethyl]polystyrene (2−*p*-OCH$_2$CH$_2$PhNO$_2$). Resin **2−Cl** $(C_{10}H_{12})_{0.45}(C_{10}H_{10})_{0.40}(C_{12}H_{17}SiCl)_{0.15}$ (0.50 g, 0.51 mmol Cl) was placed in a 25 mL round-bottom flask containing *p*-nitrophenethyl alcohol (0.20 g, 1.2 mmol) and dry CH_2Cl_2:pyridine 5:1 (6 mL, 12 mmol pyr). The reaction was stirred for 8 h at room

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temperature under N_2 and filtered and the residue extracted in a Soxhlet overnight with $CHCl_3$ and then dried in vacuo 24 h to yield 0.51 g of **2−*p***-$OCH_2CH_2PhNO_2$ as pale gray beads: ^{29}Si solid-phase NMR (300 MHz) δ 14.3 ppm. Anal. Calcd for $(C_{10}H_{12})_{0.45}(C_{10}H_{10})_{0.40}(C_{20}H_{24}SiNO_3)_{0.15}$ (100% conversion): Si, 2.55; N, 1.27. Found: Si, 2.54; N, 1.30.

[[[(*p*-Nitrophenethyl)oxy]diisopropylsilyl]ethyl]polystyrene (3−*p*-$OCH_2CH_2PhNO_2$). Resin **3−Cl** $(C_{10}H_{12})_{0.45}(C_{10}H_{10})_{0.41}(C_{16}H_{25}SiCl)_{0.14}$ (0.50 g, 0.46 mmol Cl) was treated as for **2−*p*-$OCH_2CH_2PhNO_2$** to yield 0.50 g of **3−*p*-$OCH_2CH_2PhNO_2$** as light gray beads: FTIR (KBr) 1610, 1455, 1342, 1255, 1062, 918 cm^{-1}; ^{29}Si NMR δ 13.8 (*Si*OCH_2), 7.6 ppm (w, *Si*O*Si*). Anal. Calcd for $(C_{10}H1_{2})_{0.45}$ $(C_{10}H_{12})_{0.41}(C_{24}H_{32}SiNO_3)_{0.14}$ (100% conversion): Si, 2.30; N, 1.15. Found: Si, 2.30; N, 1.17.

[(Butoxydimethylsilyl)ethyl]polystyrene (2−OBu). Resin **2−Cl** $(C_{10}H_{12})_{0.45}(C_{10}H_{10})_{0.40}(C_{12}H_{17}SiCl)_{0.15}$ (0.50 g, 0.51 mmol Cl) was reacted as in **2−*p*-$OCH_2CH_2PhNO_2$**, with *n*-butyl alcohol (0.20 g, 1.2 mmol): ^{13}C NMR δ 146, 130 (DD), 61 (DD), 43, 31 (DD), 18 (DD), 15 (DD), 1 ppm (DD).

[(Menthoxydimethylsilyl)ethyl]polystyrene (2−OMen). Resin **2−Cl** $(C_{10}H_{12})_{0.45}(C_{10}H_{10})_{0.40}(C_{12}H_{17}SiCl)_{0.15}$ (5.00 g, 5.1 mmol Cl) was added to (−)-menthol (2.00 g, 12.7 mmol) in CH_2Cl_2:pyridine 5:1 (10 mL, 20 mmol pyr) and the mixture stirred at room temperature 12 h. The beads were then filtered and extracted in a Soxhlet for 12 h with $CHCl_3$ and then dried in vacuo overnight, yielding 5.16 g of **2−OMen** as light gray beads: FTIR (Si wafer) 1455, 1342, 1255, 1062, 918 cm^{-1}; solid-phase ^{29}Si NMR (300 MHz) δ 13.2 ppm (*Si*OCH<), 7.8 ppm (w, *Si*O*Si*).

[(Menthoxydiisopropylsilyl)ethyl]polystyrene (3−OMen). Resin **3−Cl** $(C_{10}H_{12})_{0.45}(C_{10}H_{10})_{0.41}(C_{16}H_{25}SiCl)_{0.14}$ (4.60 g, 4.30 mmol Cl) was treated as in the preparation of **2−Cl**, giving 5.00 g of **3−OMen**: solid-phase ^{29}Si NMR (300 MHz) δ 12.1 ppm.

Selectivity in forming silyl ethers from 2−Cl. Resin **2−Cl** $(C_{10}H_{12})_{0.45}(C_{10}H_{10})_{0.40}(C_{12}H_{17}SiCl)_{0.15}$ (0.50 g, 0.51 mmol Cl) was reacted with mixed alcohols (0.1 mL, ca. 2.5 mmol) in toluene:triethylamine 14:1 (6 mL, 3 mmol R_3N) as for **2−*p*-$OCH_2CH_2PhNO_2$**. The suspended solid products were then recovered by filtration (0.35 g, 0.35 mmol **2−OR**), washed with toluene, treated with 1 M TBAF in THF (2 mL, 2 mmol) overnight, and extracted with 2 mL of ether, and the filtrate was analyzed for relative content of each alcohol by gas chromatography.

Use of 2−Cl in the Solid-Phase Synthesis of 3-Hydroxy-1-methylpropyl Benzoate (H−OBuOBz). Resin **2−Cl** $(C_{10}H_{12})_{0.45}(C_{10}H_{10})_{0.40}(C_{12}H_{17}SiCl)_{0.15}$ (25.01 g, 25 mmol Cl) was added to 1,3-butanediol (6.00 g, 67 mmol) in CH_2Cl_2:pyridine 5:1 (50 mL, 100 mmol of pyr), and the mixture was rapidly stirred overnight. The suspension was then filtered and the residue washed with warm $CHCl_3$; FTIR of a dried small portion showed a strong peak at 3550 cm^{-1}. The remaining beads were then resuspended in a solution containing benzoyl chloride (7.01 g, 50 mmol) in CH_2Cl_2:pyridine 5:1, refluxed 24 h, and then recovered by filtration and washed with $CHCl_3$; another small dried portion showed a different strong FTIR peak at 1746 cm^{-1}. The remaining polymer was suspended in a mixture of 52% hydrofluoric acid (10 mL, 270 mmol HF) and 50 mL of MeCN for 3 h, the suspension was then filtered, and the filtrate was extracted with ethyl acetate (2 × 100 mL), GC analysis of which showed 10% starting 1,3-butanediol, besides a single other product peak. Evacuation of the solvent and Kugelrohr distillation (12 mm Hg, 130−140 °C) afforded 3.6 g of **H−OBuOBz** as a clear oil (90% isolated yield): ^{1}H NMR (CD_3OD, TMS) δ 8.1 (dd 2H), 7.5 (m 3H), 5.4 (m 1H), 3.5 (q 2H), 1.9 (dd 2H), 1.7 ppm (d 3H); ^{13}C NMR (270 MHz, CD_3OD, TMS) δ 167, 133, 130, 129, 128, 68, 57, 40, 20 ppm.

Kinetics of Cleavage of Polymer-Supported Silyl Ethers 2−OMen and 3−OMen. Resins **2−OMen** or **3−OMen** (1 g, ca. 1 mmol of −OR) were added to 1 M HCl or 1 M $(Me)_4N^{+-}OH$ (5 mL, 5 mmol) in dioxane:water 9:1, with 1 mM triglyme as internal standard, at 22−24 °C, and the release of menthol into the liquid phase was monitored by gas chromatography. The rates were obtained by comparison with 1 mmol of each substrate hydrolyzed with 52% hydrofluoric acid (0.04 mL, 1.1 mmol HF) in dioxane:water 9:1 with 1 mM triglyme as internal standard, where complete conversion after 0.5 h was confirmed by ^{29}Si solid-state NMR on the **2−F** and **3−F** products.

[(Fluorodimethylsilyl)ethyl]polystyrene (2−F). Resin **2−Cl** $(C_{10}H_{12})_{0.45}(C_{10}H_{10})_{0.40}(C_{12}H_{17}SiCl)_{0.15}$ (12.21 g, 12.3 mmol Cl) was placed in a 50 mL polypropylene tube and swollen with 25 mL of MeCN. Hydrofluoric acid 52% (5 mL, 145 mmol of HF) was added and the tube shaken for 3 h. The suspension was then filtered and the residue washed with 200 mL of MeCN and then dried in vacuo at 60 °C for 24 h, yielding 12.17 g of **2−F** as light gray beads: FTIR 1256 (Si*CH_3*), 875 cm^{-1} (*SiF*); solid-phase ^{29}Si NMR (300 MHz) δ 29.3 (d, *Si*F), 6.3 (w, *Si*O*Si*). Anal. Calcd for $(C_{10}H_{12})_{0.45}(C_{10}H_{10})_{0.40}((C_{12}H_{17}Si)_2O)_{0.015}(C_{12}H_{17}SiF)_{0.12}$ (80% conversion, remainder siloxane): F, 1.60. Found: F, 1.64.

[(Fluorodiisopropylsilyl)ethyl]polystyrene (3−F). Resin **3−Cl** $(C_{10}H_{12})_{0.45}(C_{10}H_{10})_{0.41}(C_{16}H_{25}SiCl)_{0.14}$ (1.02 g, 0.96 mmol Cl) was placed in a 50 mL polypropylene tube with 20 mL of dioxane and hydrofluoric acid 52% (5 mL, 145 mmol of HF). The suspension was then shaken 12 h and filtered and the residue washed 5× with 20 mL acetone and dried in vacuo at 65 °C for 24 h, yielding 0.99 g **3−F** as light gray beads: FTIR (KBr) 1610, 1342, 998, 880 cm^{-1}; solid-phase ^{29}Si NMR (300 MHz) δ 26.7 (d, *Si*F), 2.5 ppm (w, *Si*O*Si*). Anal. Calcd for $(C_{10}H_{12})_{0.45}(C_{10}H_{12})_{0.41}(C_{16}H_{25}SiF)_{0.14}$ (100% conversion): F, 1.47. Found: F, 1.40.

Regeneration of [(Chlorodimethylsilyl)ethyl]polystyrene (2−Cl). Resin **3−F** $(C_{10}H_{12})_{0.45}(C_{10}H_{10})_{0.40}((C_{12}H_{17}Si)_2O)_{0.015}(C_{12}H_{17}SiF)_{0.12}$ (1.26 g, 1.29 mmol F) was added to a polypropylene tube in an ice bath and purged with N_2, 1 M BCl_3 in CH_2Cl_2 (5 mL, 5 mmol) was added slowly, and the mixture was then stirred for 3 h. The ice bath was then removed, and N_2 was passed over the suspension until all liquids had disappeared. The remaining beads were rinsed with CH_2Cl_2 under N_2 and then vacuum dried for 12 h, yielding 1.21 g of **2−Cl** as light brown beads: FTIR (KBr in air) 1258, 1079 cm^{-1} (w); solid-phase ^{29}Si NMR (300 MHz) δ 30.1 ppm; ^{13}C CP-MAS NMR (100 MHz) δ 146 (DD), 129, 43, 31, 16 (DD), 3 ppm (DD). Anal. Calcd for $(C_{10}H_{12})_{0.45}(C_{10}H_{10})_{0.40}(C_{12}H_{17}SiCl)_{0.15}$ (100% conversion): Cl, 3.51. Found: Cl, 3.48.

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