Heteroatom Chemistry
Volume 9, Number 2, 1998

Hydrovinylsilanes in Sequential Reactions: A Route to Graft Copolymers [1]

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Received 9, July 1997; revised 8, August 1997

ABSTRACT

The radical copolymerization of styrene or methyl methacrylate and diphenylvinylsilane **1** *led to Si–H functionalized polyolefins* **5–7** *and* **8–10,** *respectively. The efficiency of incorporation of* **1** *was low. In addition, the molecular weights were inversely proportional to the concentration of* **1,** *indicating that, while the silane behaves as a monomer (Si–CH=CH$_2$), its primary role was as a chain termination and a chain transfer (Si–H) agent. The copolymers contained about 1 mol% Si–H groups: the methacrylate derivatives also contained Si-vinyl groups. The residual Si–H groups in the copolymers remained chemically active. It was thus possible to graft vinylsilicones onto* **9** *using transition metal catalyzed hydrosilation to give* **11,** *or vinylanthracene onto* **9** *using radically induced hydrosilation to give* **12.** © 1998 John Wiley & Sons, Inc. Heteroatom Chem 9:241–251, 1998

INTRODUCTION

Silicon-based polymers possess a variety of interesting properties. Silicones, the most important class of such polymers, have very low glass transition temperatures, are exceptionally hydrophobic, and possess high thermal stability, and electrical resistance and permeability to gases such as oxygen [2]. There is, of course, much interest in other silicon-containing polymers including polysilanes [3].

To a degree, the properties possessed by silicon-based homopolymers can be transferred to carbon-based polymers if a sufficient amount (often very little) of the silane component is present. Several synthetic approaches for such incorporation exist, including block copolymers formed by anionic polymerization (silicone/polystyrene [4], polysilane/poly(methyl methacrylate) [5]) and by hydrosilation (silicone/polyethylene oxide) [6]. Alternatively, radical copolymerizations of vinylsilanes with olefin monomers can be performed.

The radical copolymerization of vinylsilanes such as vinylsilicones [7–9], vinylhalosilanes, vinylalkoxysilanes, vinylsiloxanes [10], vinylalkylsilanes [11], and vinylhydrosilanes with a variety of monomers including methyl and butyl methacrylate, styrene, dichlorostyrene [12], and acrylonitrile have been described. In the cases reported, homopolymerization of the hydrocarbon monomer was more efficient than the copolymerization of the same olefin with the vinylsilane. An absence of polymerization, lower molecular weights, lower yields, and low incorporation of the vinylsilane monomer were consistently observed in these copolymerization reactions.

The incidence of these effects was found to be proportional to the relative amount of the vinylsilane comonomer in the polymerization. The efficiency of vinylsilane incorporation was also dependent upon the nonparticipating groups on silicon. Thus, triethoxyvinylsilane, unlike trichlorovinylsilane, underwent copolymerization with ethyl maleate and maleic anhydride to give triethoxyvinylsilane-maleic anhydride copolymers with molecular weights up to

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CCC 1042-7163/98/020241-11

3000 [13,14]. Vinylsilanes only poorly undergo homopolymerization [15].

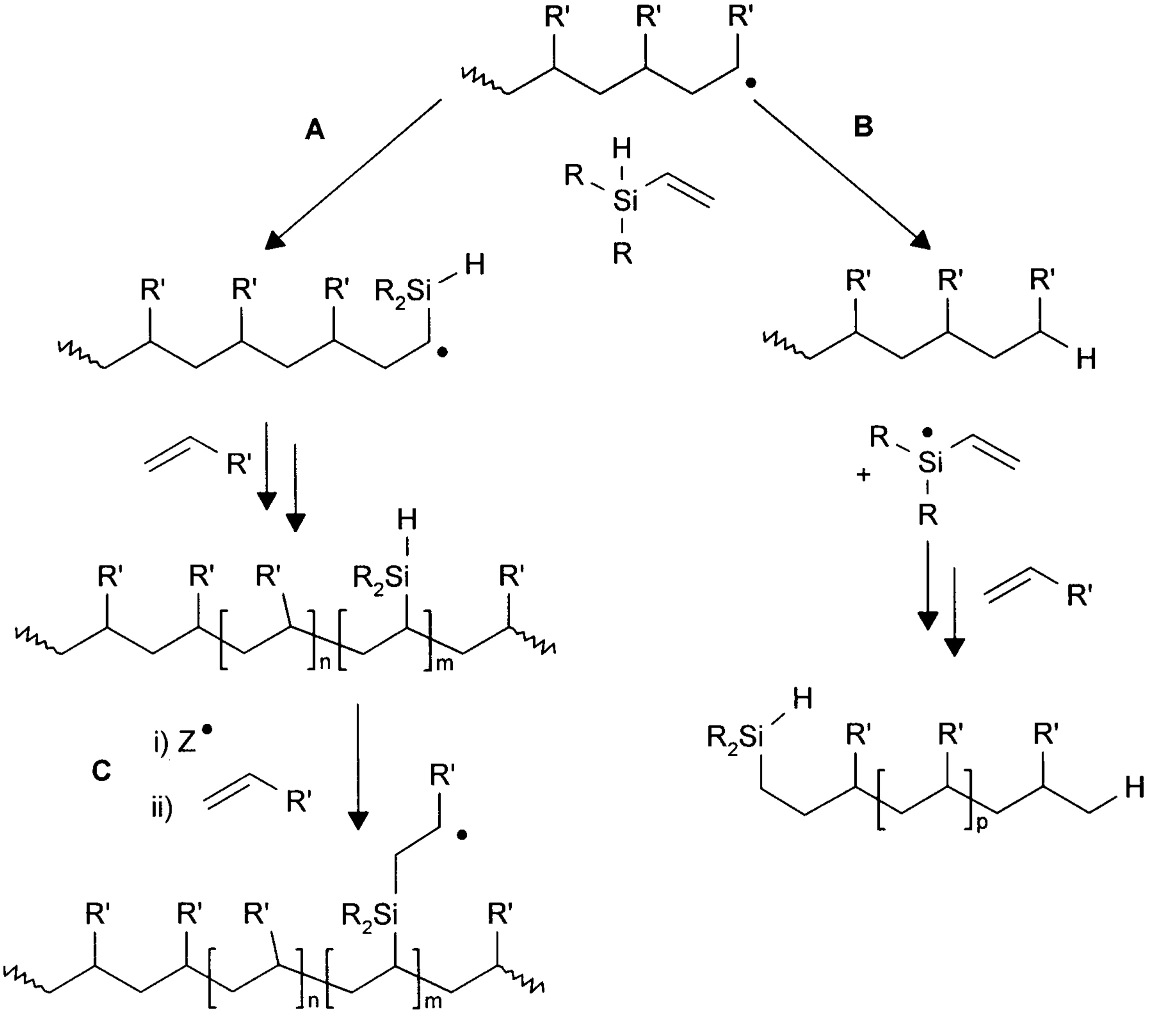
Hydrovinylsilanes are a special class of silicon species in that both the Si-vinyl and Si–H groups can react under transition metal catalyzed or radical conditions [16]. When such compounds are polymerized, the vinyl group can participate in the olefin polymerization and/or hydrosilation/chain transfer of the Si–H group and may occur to the exclusion of the vinyl group (Scheme 1) [17]. The homopolymerization of $Ph_2HSiCH=CH_2$ **1** led to preferential consumption of the vinyl groups to give low oligomers containing both types of functional groups that could subsequently be used for further elaboration (Scheme 2).

We wished to examine if the copolymerization of such compounds with reactive vinyl compounds would lead to functional polymers. Residual vinyl and Si–H groups could provide anchors for further synthetic chemistry, including cross-linking, and/or change the nature of the hydrophobicity of the copolymer when compared to the homopolymer resulting from the reactive olefin (Scheme 1). We also wished to establish the relative efficacy of the Si–H and Si-vinyl groups, when on the same silicon, under radical conditions. Our examination of the copolymerization of methyl methacrylate or styrene with **1** is presented in the following section.

RESULTS

$Ph_2SiHCH=CH_2$ [18] was utilized in this study because of the convenience in following its reactions by UV and IR spectroscopy and the opportunity to modify the electronic demands of the phenyl groups: **1** was prepared from Ph_2SiClH in high yield using vinylmagnesium bromide in THF.

The homopolymerization of **1** led to low molecular weight oligomers ($\bar{M}_n \approx 800$, trimers—penta-



SCHEME 1

mers primarily) containing both vinyl and Si–H groups. Some of the lower molecular weight fragments that were isolated include compounds **2** and **3** (Scheme 2). The oligomeric mixture contained residual Si–H groups and Si-vinyl groups in a ratio of about 2:1.

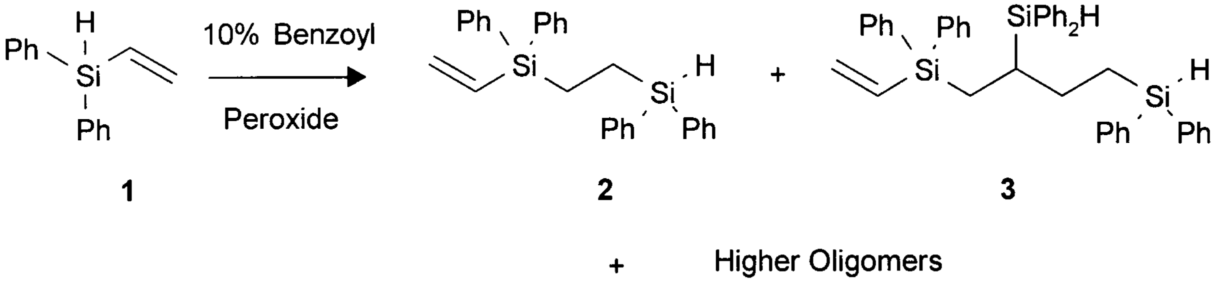
Styrene and methyl methacrylate, respectively, were copolymerized with **1** in several mole ratios. Refluxing benzene was used as the solvent with benzoyl peroxide as the initiator. The results of these radical copolymerizations are shown in Table 1.

The data in Table 1 show that the reactivity of **1** in the radical copolymerization with styrene or methyl methacrylate is low. The copolymers were comprised mainly of the hydrocarbon monomer irrespective of the initial mole ratio of silicon monomer to hydrocarbon monomer. As the amount of **1** was increased in the initial monomer mixture, the copolymer yield and the molecular weight of the resultant copolymers decreased (Figure 1, Table 1). Running the reaction at a higher concentration, 0.6 to 2.0 M for methyl methacrylate: **1** (2:1 ratio), for instance, did not significantly increase the silicon content in the copolymers.

The relative reactivity of the Si–H and Si–$CH=CH_2$ groups in the copolymerizations is shown in Table 2. With styrene copolymerizations, complete consumption of the vinyl group occurred. A small proportion of Si–H groups survived the polymerization. In the polymerizations with methyl methacrylate, however, both residual Si–H and Si-vinyl groups were observed in about a 1:1 ratio. Thus, the rates of consumption are similar, unlike the case of homopolymerization of **1** in which the vinyl was consumed about twice as fast as the Si–H groups.

GRAFTING REACTIONS

The copolymers **5–10** obtained in this work (Scheme 3) contained, in small quantity, constituents of monomer **1**. These groups possessed residual Si–H functional groups, as shown from infrared absorptions (**5–7** styrene:**1** 2115 cm^{-1}, **8–10** MMA:**1** 2135 cm^{-1}) and ^1H NMR signals between 4.00 and 5.00 ppm. As shown in Table 1, the copolymer contained approximately 1 mol% of Si–H groups along the backbone of the copolymer. To determine whether these residual Si–H groups remained reactive, grafting reactions catalyzed by transition metal and rad-



SCHEME 2

TABLE 1 The Products of Copolymerization of **1** with Styrene and MMA

Monomer (molarity)[a]	*Ratio of Monomer:* **1** *in Reaction Mixture*	*Copolymer Yield (%)*	*Ratio of Monomer:* **1** *in Copolymer Product*	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$
Styrene (0.6)[b,c]	5:1	34	ND[d]	9,700	1.8
Styrene (0.6)	2:1	22	ND	8,500	1.8
Styrene (0.6)	1:1	13	ND	4,500	1.8
MMA (0.6 M)[e]	5:1	75	96:4	10,000	2.3
MMA (0.6 M)	2:1	65	96:4	6,900	2.2
MMA (2.0 M)	2:1	66	ND	6,000	3.0
MMA (0.6 M)	1:1	54	94:6	4,500	1.8

[a] Total monomer concentration (olefin + **1**).
[b] Polymerization of 0.6 M styrene in the absence of **1**: $\bar{M}_n$ = 10,000 and $\bar{M}_w/\bar{M}_n$ was 1.9.
[c] There were no residual vinyl signals in the styrene copolymers.
[d] ND: not determined.
[e] Polymerization of 0.6 M MMA in the absence of **1**: $\bar{M}_n$ = 17,750 and $\bar{M}_w/\bar{M}_n$ = 2.3; of 2.0 M MMA in the absence of **1**: $\bar{M}_n$ = 21,000 and $\bar{M}_w/\bar{M}_n$ = 3.0.

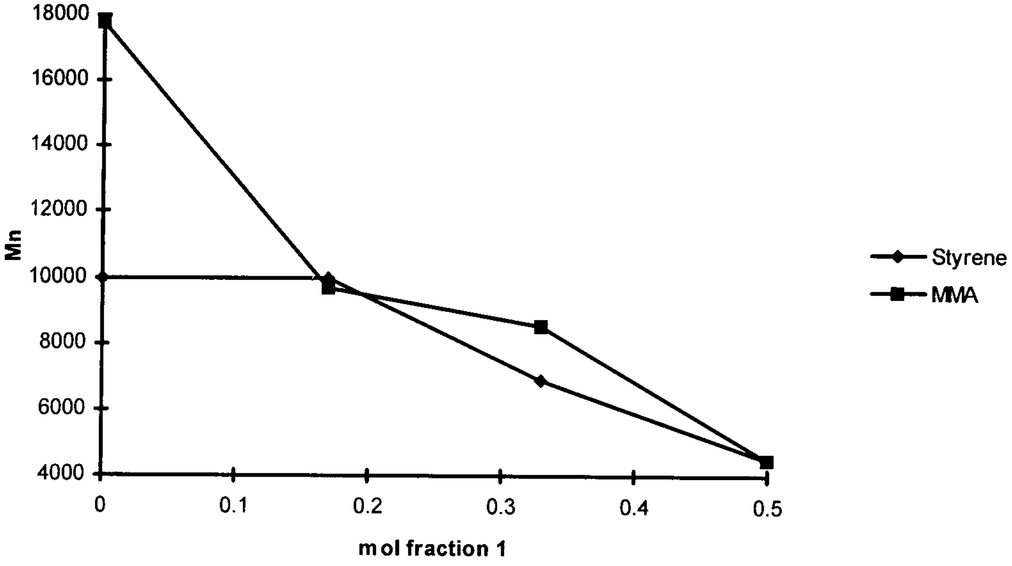


FIGURE 1 Correlation between mole fraction **1** and molecular weight in the copolymerization with styrene and MMA.

TABLE 2 The Relative Reactivity of Si–H and Si-vinyl Groups (of **1**) in the Copolymerizations

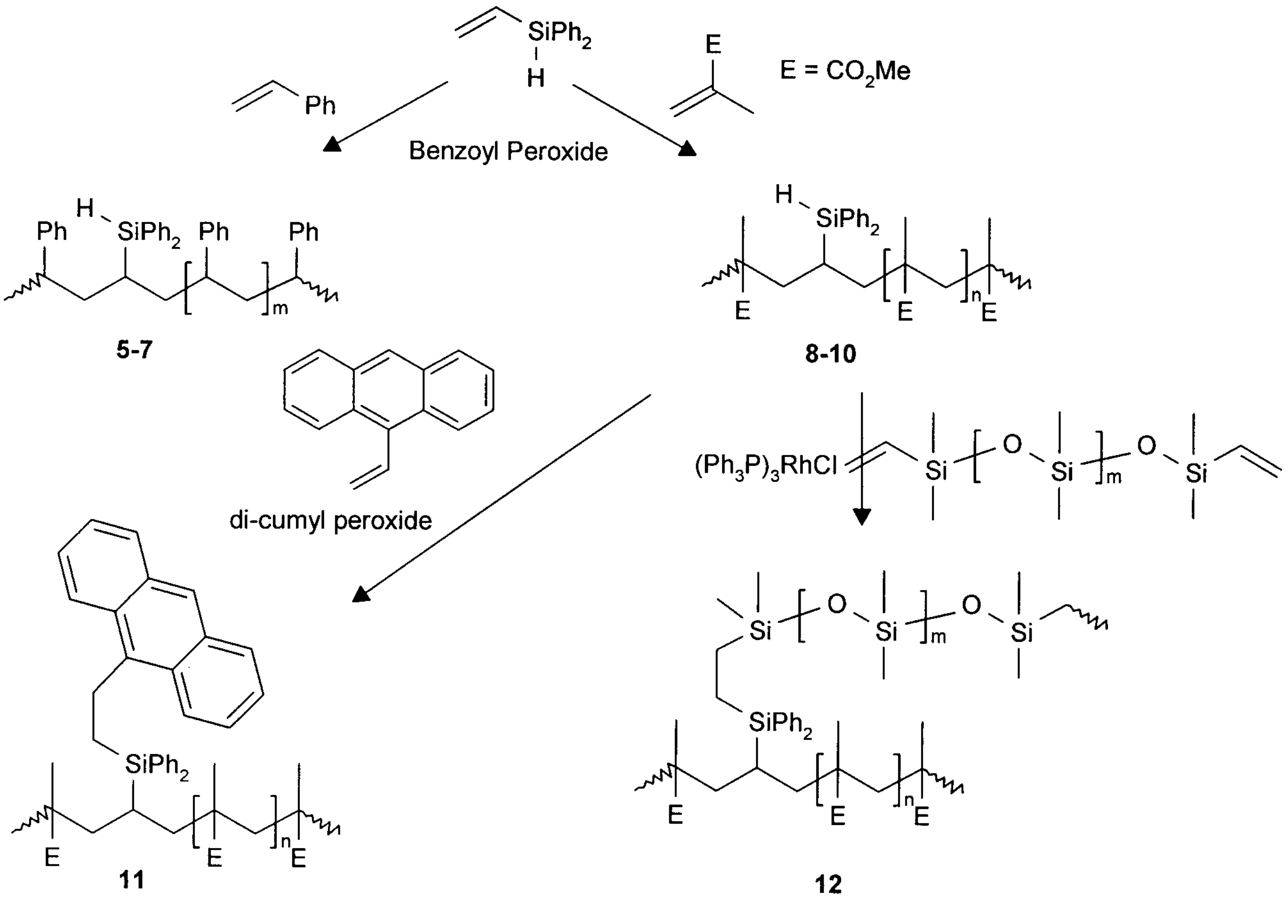
Monomer	*Styrene*	*Styrene*	*Styrene*	*MMA*	*MMA*	*MMA*
Ratio of monomer:**1** in reaction mixture	5:1	2:1	1:1	5:1	2:1	1:1
$\frac{[\text{Si–H}]}{[\text{Monomers } (\mathbf{1} + \text{Styrene or MMA})]}$ in copolymer	0.02	0.01	0.006	0.01	0.01	0.006
$\frac{[\text{Si–H}]}{[\mathbf{1}]}$ in copolymer	ND[a]	ND[a]	ND[a]0.14	0.23	0.22	
$\frac{[\text{Si} - \text{vinyl}]}{[\mathbf{1}]}$ in copolymer	0	0	0	0.12	0.04	0.24
$\frac{k_{\text{Si-CH=CH}_2}}{k_{\text{Si-H}}}$	ND[a]	ND[a]	ND[a]	1.0	5.8	1.0

[a] ND: Because the amount of **1** in the copolymer product could not be determined (Table 1), this value is similarly not calculable.

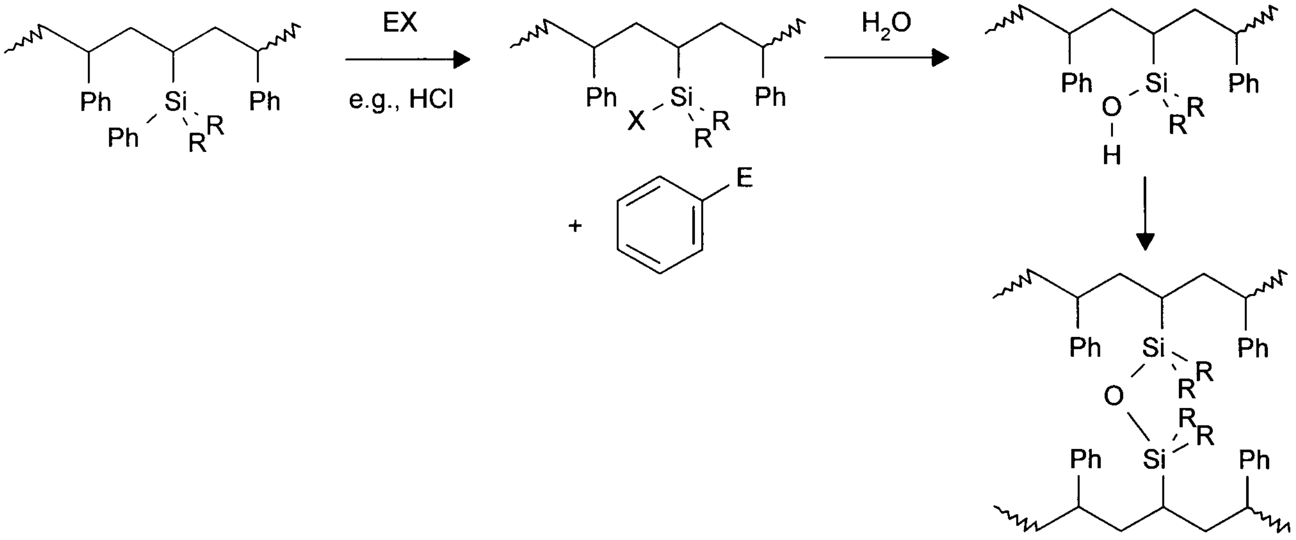
ical methods were attempted with 9 (Scheme 3). The $(PPh_3)_3RhCl$ catalyzed hydrosilation of 9 with a low molecular weight divinyl-terminated silicone was performed in benzene at 50°C and proceeded with complete conversion of Si–H groups to **11**.

9-Vinylanthracene was chosen for the radical grafting reaction onto 9 because of the ease with which the reaction could be monitored using UV light. The reaction was carried out in a sealed ampoule at 140°C in benzene using dicumyl peroxide as the radical catalyst. All the Si–H groups were consumed in the process. Simultaneous monitoring of the GPC by refractive index and UV detectors (at λ 370 nm) showed that the product **12**, unlike **9**, contained anthracene groups. The efficiency of vinylanthracene grafting, as judged by ^1H NMR spectroscopy, was about 60%. The increase in molecular weight (by about 50%) from the starting material suggests that the remaining Si–H groups underwent cross-linking reactions, presumably in analogy to room- or high-temperature vulcanization systems [2]. In this case, of course, the conversion would occur through oxidation of Si–H (2Si–H → 2Si–OH → SiOSi + H_2O).

These copolymers offer a further possibility for cross-linking. Arylsilanes readily undergo cleavage by electrophiles including acids [19]. Aside from the obvious complications of releasing benzene, one could imagine using this process to initiate moisture cure (Scheme 4).



SCHEME 3



SCHEME 4

DISCUSSION

In work described by others, the copolymerization of reactive olefins and vinylsilanes was accompanied by the complete absence of polymerization, or low molecular weights and poor incorporation of the vinylsilane monomer, as noted earlier [7–12]. This suggests that the presence of the vinylsilane facilitates termination processes relative to propagation. Our results follow this pattern.

It is reasonable to consider that the increased stabilization of radicals α- to a silyl group acts to suppress polymer propagation but not termination [20]. That is, for electronic and perhaps steric reasons, the α-silyl radical propagates the polymerization only poorly such that the k_{prop} (for RCH·Si) $\ll$ k_{prop} (for $\text{RCH}^{\bullet}2$). As termination rates will be very large for all the radicals, higher monomer concentrations of **1** should lead to a suppression of polymer chains [21].

With Si–H-containing monomers, there is, in addition, an alternate termination mechanism; hydrosilanes can terminate polymers by chain transfer, a process of radically induced hydrosilation [17,22]. To the degree that chain transfer participates in the radical process, the molecular weights and concentration of residual Si–H groups should be further attenuated.

In the copolymers of styrene or methyl methacrylate and **1**, incorporation of the vinylsilane monomer **1** was relatively low (Table 1). As the initial concentration of **1** was increased, both the yield and molecular weights of polymer products were reduced (Figure 1). The low yields, particularly with the styrene copolymers, speak to the inadequacy of propagation by $\text{RMe}_3\text{SiCH}^{\bullet}$ radicals and the efficiency of the termination and chain transfer processes previously outlined.

The radical homopolymerization of **1** leads to low molecular weight oligomers ($\bar{M}_n \approx 800$) [1]. The rate of consumption of Si-vinyl groups (radical oligomerization) was approximately twice that of the Si–H groups (radical hydrosilation); the oligomers possess both residual Si–H and Si-vinyl groups. In the copolymerizations, the relative rate of consumption of Si-vinyl to Si–H was dependent on the organic monomer. ^{1}H NMR and infrared spectroscopic analyses revealed that **1** underwent copolymerizations with styrene through preferential vinyl consumption: as all vinyl was consumed, a relative rate cannot be calculated (Table 2). With the MMA copolymers, both the Si-vinyl and Si–H groups of **1** were consumed (about 80% of the Si–H or Si-vinyl functional groups were consumed during polymerization based on the incorporation of the **1** in the copolymer, Table 2). From the incorporation of **1** in the copolymers **8–10** and the concentration of residual functional groups (Tables 1 and 2), the overall rate ratio of the two groups $k_{\text{Si–CH=CH}_2}/k_{\text{Si-H}}$ can be seen to be about 1, slightly less than during the homopolymerization of **1** or its copolymerization with styrene. The reactivity of the Si–H groups in these reactions is much higher than that indicated in previous reports [23].

The residual vinyl and Si–H groups can be used for further synthetic elaboration: hydrosilation catalyzed by transition metals or radical initiators can further modify the copolymers under very different processing conditions. Cross-linking can also be effected by radical means. These reactions demonstrate the general utility of the Si–H functionality.

CONCLUSION

Hydrovinylsilanes are useful comonomers in that the copolymers formed from them contain residual Si–H functional groups: They may also contain Si–$\text{CH}=\text{CH}_2$ groups. The relative rate of reaction of the two functional groups is similar under radical conditions but depends on the nature of the comonomer. The functional products may be used for further synthetic elaboration including moisture cure/cross-linking, radical grafting, and transition metal-catalyzed modification via the hydrosilation reaction to tether other small molecules or polymers (Scheme 3). On the other hand, premature termination leading to low molecular weight polymers and unreacted monomer is clearly an inefficient process. To be useful, therefore, a careful balance of the relative concentrations of both starting monomers is required: sufficient hydrovinylsilane must be present to ensure that functional silyl groups are present in the final product, but not so much that yield and molecular weight are significantly attenuated.

EXPERIMENTAL

Apparatus, Materials, and Methods

The continuous wave ^{1}H NMR spectra were recorded on a Varian EM-390 (90 MHz) spectrometer and the Fourier spectra on a Bruker AM-500 (500 MHz) spectrometer, a Bruker AC-300 (300 MHz) spectrometer, or a Bruker AC-200 (200 MHz) spectrometer. ^{13}C NMR and ^{29}Si NMR determinations were performed on a Bruker AC-200 (at 50.3 MHz for carbon) and Bruker AC-300 (at 75.5 MHz for carbon and 59.6 MHz for silicon, respectively). Chemical shifts are reported with respect to tetramethylsilane as standard, set to 0 ppm. Coupling constants (J) are recorded in hertz (Hz). The abbreviations s (singlet), d (doublet), t (triplet), dd (doublet of doublets), ddd (doublet of doublet of doublets), and m (multiplet) are used in reporting the spectra.

Electron impact (EI) and chemical ionization (CI, NH_3) mass spectra were recorded at 70 eV with a source temperature of ca. 200°C on a VG analytical ZAB-E mass spectrometer equipped with a VG 11-250 data system. High-resolution mass spectral (HRMS) data were obtained with the VG-ZAB-E instrument by the EI method. Infrared spectra were run on a Perkin Elmer 283 spectrometer and Fourier spectra on a BIO RAD FTS-40 spectrometer, as a neat film.

The molecular weight distributions of the oligomers were analyzed using a Waters Gel Permeation Chromatograph equipped with a Waters 410 Differential Refractive Index detector. Two Jordi mixed-bed columns in series were utilized with 1,1,1-trichloroethane as solvent flowing at 1.5 mL/min. Narrow molecular weight polystyrene standards from Polymer Laboratories were used for calibration of the chromatographic system.

Sources of Material

Methanol (Caledon, reagent grade), hexanes (Caledon, reagent grade), chloroform (BDH, reagent grade), vinylmagnesium bromide (Aldrich, 1.0 M solution in tetrahydrofuran), 9-vinylanthracene (Aldrich, 97%), benzoyl peroxide (Aldrich), dicumyl peroxide (Aldrich), chlorodiphenylsilane (United Chemicals, 95%), (trimethylsilyl)acetylene (Aldrich, 98%), vinyldimethyl-terminated poly(dimethylsiloxane) (United Chemicals, viscosity = 4–6 centistokes), Karstedt's catalyst $[(Pt)_2(H_2C{=}CHMe_2SiOSiMe_2CH{=}CH_2)_4]$ (United Chemicals), and tris(triphenylphosphine)-rhodium (I) chloride (Aldrich) were used as received. Styrene (Aldrich, 99%) and methyl methacrylate (Aldrich, 99%) were purified by vacuum distillation and stored under a nitrogen atmosphere.

All solvents were thoroughly dried before use. Diethyl ether was distilled over sodium/benzophenone. Benzene was washed with concentrated sulfuric acid, distilled, and then redistilled over sodium. 1,1,1-Trichloroethane (Caledon, reagent grade) was filtered using a type-HA 0.45 μm Millipore filter. *iso*-Octane (Caledon, reagent grade) was refluxed for 2 days and then distilled from calcium hydride (Aldrich).

Due to the tendency of halo groups on silicon to hydrolyze easily, Grignard reactions were carried out in dry apparatus under a nitrogen atmosphere with the use of septa and syringes for the transfer of reagents.

The "conversion" numbers in the Experimental reflect consumption of monomers as determined in the ^{1}H NMR spectra of the crude product mixture.

GENERAL EXPERIMENTAL PROCEDURES FOR GRIGNARD REACTIONS

Diphenylvinylsilane 1

Chlorodiphenylsilane (10 g, 45.9 mmol) was added dropwise to a stirred solution of vinylmagnesium bromide (1.1 equiv., 1.0 M in Et_2O, 50.5 mL, 50.5 mmol) in THF (50 mL). Once addition was complete, the mixture was slowly warmed to room temperature and stirred for an additional 2 hours. The reaction mixture was then slowly poured into an ice water bath, extracted with diethyl ether, and washed with saturated brine. The organic layer was dried over anhydrous sodium sulfate, and the solvent was removed *in vacuo*. Distillation gave the silane as a colorless liquid.

Bp: 108°C/1 mm Hg; yield: **1** 90% (8.7 g, 41.4 mmol); ^{1}H NMR ($CDCl_3$, 200 MHz): δ 5.11 (d, 1H, J = 3.0 Hz), 5.89 (dd, 1H, J = 19.4, 4.4 Hz), 6.24 (dd, 1H, J = 14.5, 4.4 Hz), 6.45 (ddd, 1H, J = 19.4, 14.5, 3.0 Hz), 7.30–7.60, 7.50–7.70 (m, 10H); ^{13}C NMR ($CDCl_3$, 50.3 MHz); δ 128.00, 129.71, 132.62, 133.25, 135.43, 136.99; ^{29}Si NMR ($CDCl_3$, 59.6 MHz): δ −21.60; IR (neat) ν 3051, 3003, 2971, 2124, 1590, 1485, 1428, 1404, 1304, 1115, 1007, 960, 816, 796 cm^{-1}; MS (m/z) 210 (29, M$^+$), 181 (47), 155 (8), 132 (100), 105 (72), 91 (7), 79 (14), 53 (24).

General Procedure for Radical Polymerization

Nitrogen was bubbled through the benzene for 1 hour before beginning the reactions. A benzene solution of the monomer(s) and benzoyl peroxide was heated at 80°C for 12 hours. The solvent was removed in vacuo, and the crude products were purified by radial chromatography using a hexane/ether (99:1) mixed solvent system.

Homopolymerization of **1** *with 10 mol% BPO [1]*

Diphenylvinylsilane (0.6 M, 1 g, 4.8 mmol), benzoyl peroxide (0.1 eq., 115.1 mg, 0.48 mmol), benzene (7 mL), 12 hours, 80°C.

Crude: ^{1}H NMR ($CDCl_3$ 200 MHz, integration based on the 10 aromatic protons of $SiPh_2$): δ 0.2–2.80 (m, 1.47H), 4.63–4.95, 5.14–5.15 (m, 0.77H), 5.64–6.57 (m, 1.78H), 7.00–7.59, 7.50–7.80 (m, 10H). 50% (0.50 g) of diphenylvinylsilane recovered. From ^{1}H NMR of crude material, 43% Si-vinyl reacted and 23% Si–H reacted.

Product after starting material was separated: **4** and related isomers, yield 50% (0.50 g). ^{1}H NMR ($CDCl_3$, 200 MHz): δ 0.1–0.14, 0.1–2.8 (m, 3.52H), 4.42–5.01 (m, 0.27H), 5.68–6.57 (m, 0.21H), 6.60–8.00 (m, 10H); ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ 4.14, 4.67, 6.03, 14.20, 24.64, 29.70, 30.44, 127.81, 128.00, 129.33, 129.53, 129.69, 130.16, 132.64, 133.20, 135.10, 135.22, 135.43, 136.93; ^{29}Si NMR ($CDCl_3$, 59.6 MHz): $\delta -12.87$, -12.04, -11.30, -9.16, -7.98, -3.85; IR (neat): ν 3067, 2910, 2112, 1589, 1483, 1427, 1262, 1110, 806, 728. $\bar{M}_n$ = 770, $\bar{M}_w/\bar{M}_n$ = 1.4.

Fractions isolated from preceding material are as follows. Dimer: **2** yield: 8% (0.08 g). ^{1}H NMR ($CDCl_3$, 200 MHz): δ 1.11–1.42 (m, 4H), 4.83 (t, 1H), 5.74 (dd, 1H, J = 4.0, 20.0 Hz), 6.21 (dd, 1H, J = 4.0, 14.7 Hz), 6.48 (dd, 1H, J = 14.7, 20.0 Hz), 7.19–7.60, 7.40–7.62 (m, 20H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 4.59, 6.00, 126.73, 126.84, 126.93, 128.19, 128.30, 128.39, 128.49, 128.59, 128.84, 128.95, 129.05, 130.41, 130.50, 130.61, 134.10, 136.11, 136.20, 136.29, 136.38, 137.95; IR (KBr): ν 3085, 3067, 3049, 3011, 2914, 2119, 1589, 1486, 1428, 1405, 1112, 1053, 1009, 808, 758, 700 cm^{-1}; MS (m/z): 420 (8, M^+), 393 (10), 342 (20), 314 (18), 259 (40), 238 (10), 209 (74), 183 (100), 131 (9), 105 (43), 53 (8).

Trimer: **3** yield: 4% (0.04 g), ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.14, 0.78–2.33 (m, 7H), 4.55–4.82 (m, 2H), 5.71 (dd, 1H, J = 3.8, 20.2 Hz), 6.20 (dd, 1H, J = 3.8, 14.7 Hz), 6.46 (dd, 1H, J = 14.7, 20.2 Hz), 7.15–7.61, 7.40–7.70 (m, 30H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 4.60, 6.00, 8.20, 22.70, 34.90, 127.74, 127.91, 128.96, 129.08, 129.14, 129.45, 133.73, 134.28, 134.68, 134.85, 135.02, 135.08, 135.19, 135.26, 135.31, 135.38, 135.47, 135.51, 135.66, 135.72; IR (KBr): ν 3067, 2999, 2904, 2848, 2111, 1588, 1485, 1427, 1303, 1262, 1109, 1066, 998, 846, 800, 726 cm^{-1}; MS (m/z): 630 (2, M^+), 553 (4), 447 (4), 393 (8), 369 (4), 341 (4), 259 (46), 209 (9), 183 (100), 159 (12), 105 (34).

General Method for Copolymerization

Nitrogen was bubbled through the benzene for 1 hour before beginning reactions. A benzene solution of styrene or methyl methacrylate (MMA), **1**, and benzoyl peroxide (1 mol% based on styrene or methyl methacrylate) was heated at 80°C for 12 hours. The solvent was removed in vacuo, and the crude product was purified by precipitation. Precipitation involved dissolving the polymer in chloroform, precipitating the polymer with the addition of hexanes, and then decanting the liquid. This process was repeated exhaustively. Since both the aryl groups and backbone CH's originating from **1** fall under the analogous peaks from the polystyrene, it is not possible to establish incorporation of **1** by either ^{1}H NMR or ^{13}C NMR spectroscopy. The amount of residual Si–H is calculated from the integration ratios of the region 4–5 ppm over the aryl region in the ^{1}H NMR spectra. Yield is based upon recovered polymer after repeated dissolution/precipitation cycles.

Styrene:Diphenylvinylsilane (**1**)—*1:1 Preparation of* **5**

Styrene (0.6 M, 2.0 g, 20 mmol), **1** (1 equiv., 4.0 g, 20 mmol), benzoyl peroxide (46.5 mg, 0.20 mmol), benzene (27 mL); yield: 13% (0.2780 g); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.28–1.78, 1.60–2.80 (m, 3H), 4.00–5.00 (m, 0.02H), 6.20–6.90, 6.88–7.64 (m, 5H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 9.92, 17.09, 17.39, 18.80, 40.38, 42.31, 43.46, 44.18, 46.54, 47.31, 125.48, 125.63, 126.40, 126.63, 127.29, 127.41, 127.64, 127.95, 129.03, 129.31, 129.45, 129.71, 130.26, 132.63, 132.75, 133.06, 133.26, 133.50, 134.68, 135.03, 135.08, 135.28, 135.44, 135.53, 145.09, 145.20, 145.30, 145.67, 146.02; ^{29}Si NMR ($CDCl_3$, 59.6 MHz): δ -16.72, -12.63, -7.52, -2.70; IR (KBr) ν 3026, 2922, 2849, 2115, 1601, 1493, 1451, 1111, 908, 806, 757, 734 cm^{-1} $\bar{M}_n$ = 4500, $\bar{M}_w/\bar{M}_n$ = 1.8.

Styrene:Diphenylvinylsilane (**1**)—*2:1 Preparation of* **6**

Styrene (0.6 M, 2.0 g, 20 mmol), **1** (0.5 equiv., 2.0 g, 10 mmol), benzoyl peroxide (0.0465 g, 0.20 mmol), benzene (27.8 mL); yield: 22% (0.4782 g); ^{1}H NMR ($CDCl_3$, 200 MHz): δ 1.20–1.80, 1.60–2.80 (m, 3H), 4.00–5.00 (m, 0.01H), 6.20–7.00, 6.88–7.70 (m, 5H); ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ 16.45, 18.78, 40.38, 42.31, 43.46, 44.18, 46.54, 47.31, 125.63, 127.62, 127.94, 129.00, 129.42, 129.68, 130.22, 132.70, 133.17, 133.50, 135.06, 135.23, 135.51, 145.04, 145.15, 145.25, 145.60, 145.97; ^{29}Si NMR ($CDCl_3$, 59.6 MHz): δ -16.72, -12.63, -7.52, -2.70; IR (KBr) ν 3082, 3060, 3026, 2922, 2849, 2115, 1601, 1493, 1451, 1429, 1272, 1028, 908, 757 cm^{-1}; $\bar{M}_n$ = 8500, $\bar{M}_w/\bar{M}_n$ = 1.8.

Styrene:Diphenylvinylsilane (**1**)—*5:1 Preparation of* **7**

Styrene (0.6 M, 2.0 g, 20 mmol), **1** (0.2 equiv., 0.81 g, 4 mmol), benzoyl peroxide (0.0465 g, 0.20 mmol), benzene (29 mL); yield: 34% (0.7226 g); ^{1}H NMR ($CDCl_3$, 200 MHz): δ 1.05–1.78, 1.60–2.80 (m, 3H), 4.00–4.50 (m, 0.006H), 6.20–6.90, 6.85–7.70 (m, 5H); ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ 16.45, 18.78, 40.36, 42.31, 43.46, 44.18, 46.54, 47.31, 125.60, 127.62, 127.92, 128.99, 129.41, 130.21, 132.71, 135.49, 145.25, 145.61; ^{29}Si NMR ($CDCl_3$, 59.6 MHz): δ −16.72, −12.63, −7.52, −2.70; IR (KBr) v 3082, 3060, 3026, 2923, 2849, 2119, 1601, 1583, 1493, 1451, 1271, 1069, 1028, 908, 757 cm^{-1}; $\bar{M}_n$ = 9700, $\bar{M}_w/\bar{M}_n$ = 1.8.

Poly(styrene) obtained from the same conditions as above but in the absence of diphenylvinylsilane was found to have $\bar{M}_n$ = 10000 and $\bar{M}_w/\bar{M}_n$ of 1.9.

Methyl methacrylate:Diphenylvinylsilane 1

The calculations of incorporation and proton ratios are based upon the integration of the CH–CH_2 backbone protons being 3H. Incorporation of **1** and residual Si–H was based upon crude ^{1}H NMR measurements (comparison of aryl protons, Si–H protons, and Si-vinyl protons to PMMA OMe protons); yield is based upon recovered polymer after repeated dissolution/precipitation cycles.

Methyl Methacrylate:Diphenylvinylsilane (1)—*1:1 Preparation of* 8

Methyl methacrylate (0.6 M, 2.0 g, 20 mmol), **1** (1 equiv., 4.2 g, 20 mmol), benzoyl peroxide (0.0484 g, 0.20 mmol), benzene (27 mL); yield: 54% (1.2947 g); MMA:**1** in product 94:6, [Si–H]/[Si–CH=CH_2] = 0.92; ^{1}H NMR ($CDCl_3$, 200 MHz): δ MMA component 0.84 (broad s, 1.38 H), 1.02 (broad s, 1.04H), 1.82 (bs, 0.76H), 1.90 (bs, 0.63 H), 0.06–1.58 (m, total range 1.18H), 3.44–3.82 (m, 3H); **1** component: 0.06–1.58 (m, 3H), 4.51–5.06 (m, 0.22 H, Si–H), 5.5–6.7 (m, 0.72 H, Si-vinyl), 7.08–7.65 (m, 10H); ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ 16.24, 18.08, 18.85, 20.38, 29.46, 34.99, 37.69, 44.34, 44.70, 51.59, 53.08, 54.62, 127.87, 129.62, 130.00, 134.23, 135.77, 136.54, 176.92, 177.62; ^{29}Si NMR ($CDCl_3$, 59.6 MHz): δ −17.47, −13.60; IR (KBr) v 2996, 2951, 2130, 1731, 1453, 1387, 1241, 1193, 1149, 989, 754 cm^{-1}; $\bar{M}_n$ = 4500, $\bar{M}_w/\bar{M}_n$ = 1.8.

Methyl Methacrylate:Diphenylvinylsilane (1)—*2:1 Preparation of* 9

Methyl methacrylate (0.6 M, 2.0 g, 20 mmol), **1** (0.5 equiv., 2.1 g, 10 mmol), benzoyl peroxide (0.0484 g, 0.20 mmol), benzene (27.8 mL); yield: 65% (1.5859 g); MMA:**1** in product 96:4, [Si–H]/[Si–CH=CH_2] = 5.8; ^{1}H NMR ($CDCl_3$, 200 MHz): δ MMA component 0.84 (broad s, 1.44H), 1.02 (broad s, 1.11H), 1.82 (bs, 0.82H), 1.90 (bs, 0.53H), 0.06–1.58 (m, total range 1.11H), 3.44–3.82 (m, 3H); **1** component: 0.06–1.58 (m, 3H), 4.51–5.06 (m, 0.23H, Si–H), 5.5–6.7 (m, 0.12H, Si-vinyl), 7.08–7.65 (m, 10H); ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ 16.39, 18.69, 44.49, 44.84, 51.71, 53.23, 54.77, 127.99, 129.74, 130.12, 134.35, 134.99, 135.89, 136.66, 177.03, 177.73, 178.57; ^{29}Si NMR ($CDCl_3$, 59.6 MHz): δ −7.23, −16.96; IR (KBr) v 2997, 2951, 2135, 1731, 1484, 1436, 1388, 1242, 1193, 1149, 989, 754 cm^{-1}; $\bar{M}_n$ = 6900, $\bar{M}_w/\bar{M}_n$ = 2.2.

Otherwise identical reaction conditions at a higher concentration (2.0 M, benzene, 8.4 mL) led to very similar spectra. The only differences were the yield [66% (1.5859 g)]; there was more residual Si–H and Si-vinyl [^{1}H NMR 4.51–5.06 (m, 0.27 H, Si–H), 5.5–6.7 (m, 0.04 H, Si-vinyl)], and molecular weight ($\bar{M}_n$ = 6000, $\bar{M}_w/\bar{M}_n$ = 3.0).

Methyl Methacrylate:Diphenylvinylsilane (1)—*5:1 Preparation of* 10

Methyl methacrylate (0.6 M, 2.0 g, 20 mmol), **1** (0.2 equiv., 0.84 g, 4 mmol), benzoyl peroxide (0.0484 g, 0.20 mmol), benzene (29 mL); yield: 75% (1.6698 g); MMA:**1** in product 96:4, [Si–H]/[Si–CH=CH_2] = 1.17; ^{1}H NMR ($CDCl_3$, 200 MHz): δ MMA component 0.84 (broad s, 1.51H), 1.02 (broad s, 1.13H), 1.82 (bs, 0.80H), 1.90 (bs, 0.53H), 0.06–1.58 (m, total range 1.03H), 3.44–3.82 (m, 3H); **1** component: 0.06–1.58 (m, 3H), 4.51–5.06 (m, 0.14 H, Si–H), 5.5–6.7 (m, 0.36H, Si-vinyl), 7.08–7.65 (m, 10H); ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ 16.26, 18.27, 44.38, 44.73, 51.60, 52.97, 54.51, 127.76, 129.50, 129.88, 134.11, 134.75, 135.65, 136.75, 176.81, 177.62, 178.35; ^{29}Si NMR ($CDCl_3$, 59.6 MHz): δ −17.44, −13.57; IR (KBr) v 2996, 2952, 2137, 1722, 1588, 1485, 1388, 1272, 1146, 1146, 989, 842, 753 cm^{-1}; $\bar{M}_n$ 10,000 and $\bar{M}_w/\bar{M}_n$ = 2.3.

Poly(methyl methacrylate) obtained from the same conditions as above but in the absence of diphenylvinylsilane was found to have $\bar{M}_n$ = 21,000 and $\bar{M}_w/\bar{M}_n$ of 3.0.

GRAFTING OF 9

Grafting with Vinylsilicone: Preparation of *11*

Sufficient benzene was added to polymer **9** (0.8 g), vinyldimethyl-terminated poly(dimethylsiloxane 4–6 centistokes, $\bar{M}_n \approx 770$) (2 mL, 1.86 g, 2.4 mmol), and tris(triphenylphosphine)-rhodium (I) chloride (0.05 g, 0.054 mmol) to give a homogenous solution. The reaction mixture was stirred at 50°C for 12 hours. The solvent was removed in vacuo, and the crude product was purified by precipitation as described earlier. In addition, the polymer was washed extensively in hexane in which the silicone but not the modified PMMA is soluble. All Si–H groups were consumed in the reaction. This implies both ends of the silicone graft to the PMMA (i.e., the silicone functions as a cross-linking agent). Yield: 0.4114 g; ratio MMA: OSiMe$_2$ in product 96:4, MMA component; ^{1}H NMR (CDCl$_3$, 200 MHz): δ 0.84 (broad s, 1.34H), 1.02 (broad s, 1.07H), 1.82 (bs, 0.74H), 1.90 (bs, 0.56H), 0.06–1.58 (m, total range 1.28H), 3.44–3.82 (m, 3H); **1** + PDMS component: 0.07 [bs, 6H, (OSiMe$_2$)$_n$], 0.06–1.58 (m, 3H), 5.5–6.7 (m, 0.21 H, vinyl from copolymer or vinyl-terminated PDMS), 7.08–7.65 (m, 10H); ^{13}C NMR (CDCl$_3$, 50.3 MHz): δ -0.71, 0.06, 0.83, 16.24, 18.53, 20.88, 44.33, 44.68, 45.32, 51.55, 52.54, 53.22, 127.59, 129.03, 129.18, 129.36, 129.92, 134.63, 135.10, 135.25, 135.25, 135.75, 136.10; ^{29}Si(CDCl$_3$, 59.6 MHz): δ -21.93, -20.82, -19.52, -16.98, -13.44, -6.19, -5.82, -4.20, -3.84; IR (KBr) ν 2998, 2952, 2843, 1731, 1485, 1450, 1388, 1273, 1243, 1194, 1149, 989, 966, 843, 753 cm^{-1}; $\bar{M}_n$ = 12,000, $\bar{M}_w/\bar{M}_n$ = 1.9.

Grafting with Vinylanthracene: Preparation of **12**

Polymer **9** (0.8 g), 9-vinylanthracene (2.0 g, 1.0 mmol), di-cumyl peroxide (0.2 g, 20.0 mmol), and benzene (10 mL) were introduced into a Pyrex ampoule of 20 mL capacity, degassed three times, and vacuum sealed. The ampoule was then heated in a thermostated oil bath at 140°C for 15 hours. The reaction mixture was purified by precipitation as described earlier. Ratio **1**: anthracene 0.60 MMA component, ^{1}H NMR (CDCl$_3$, 200 MHz): δ 0.84 (broad s, 1.34H), 1.02 (broad s, 1.07H), 1.82 (bs, 0.74H), 1.90 (bs, 0.56 H), 0.06–1.58 (m, total range 1.28H), 3.44–3.82 (m, 3H); **1** + anthracene: 0.06–1.58 (m, 3H), 5.5–6.7 (m, 0.012H, Si-vinyl), 7.08–7.65 [m, 10H (**1**) + 5.4 (anthracene)]; ^{13}C (CDCl$_3$, 50.3 MHz): δ 16.27, 18.57, 20.77, 44.32, 44.67, 45.32, 51.55, 52.55, 54.25, 127.58, 127.82, 129.18, 129.51, 134.81, 135.22, 135.51, 135.75, 176.68, 177.56, 177.85, 178.13; IR (KBr) ν 2998, 2952, 2843, 2135, 1725, 1486, 1435, 1389, 1272, 1144, 989, 914, 843, 753, 702 cm^{-1}; UV-VIS (1,1,1-trichloroethane) λ 392, 371, 353 nm; $\bar{M}_n$ = 10,000, $\bar{M}_w/\bar{M}_n$ = 1.9. The GPC trace with both UV (λ 370) and RI detectors demonstrated that the anthracene groups were uniformly distributed throughout the molecular weight profile (efficiency of the grafting ≈ 60%; the increase in aromatic protons from the starting material **9** arises from the grafted anthracene). The remaining Si–H groups were presumably cleaved with direct oxidation by the peroxide (all Si–H groups disappeared during the process).

ACKNOWLEDGMENT

We gratefully acknowledge the financial support of the Ontario Centre for Materials Research.

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