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Synthesis and Characterization of (4-Vinylphenyl)dimethylsilanol Polymer and Copolymers

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ABSTRACT: Poly[(4-vinylphenyl)dimethylsilanol] and its copolymers with styrene were synthesized by an oxygen atom insertion into the Si–H bond via reaction with dimethyldioxirane. Spectroscopic investigations demonstrated that the conversion of silanes to silanols was almost quantitative. The (4-vinylphenyl)-dimethylsilanol polymer and its copolymers with styrene obtained in situ were stable in acetone solution at room temperature. The self-association of silanol groups through hydrogen bonding and the spontaneous condensation of these groups leading to cross-linking and insolubilization were investigated by spectroscopy and differential scanning calorimetry as well as thermogravimetry.

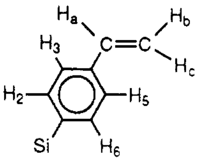
Introduction

The introduction of functional groups which induce strong association between dissimilar chains is one of the most effective ways to enhance polymer miscibility. In this respect, hydrogen bonding between a proton donor and a proton acceptor of the polymers is particularly attractive. Examples of proton donors are poly(4-vinylphenol) and poly[styrene-*co*-(4-vinylphenyl)(hexafluorodimethyl)carbinol], which have been extensively studied in polymer blends.[1,2] In light of the successes achieved in the past, we have expanded our studies to the synthesis of macromolecules with new functional groups. In this paper, we described the synthesis of poly[(4-vinylphenyl)-dimethylsilanol] and its copolymers with styrene by an oxygen atom insertion into the Si–H bond. We have also carried out preliminary investigations of the self-association of the silanol groups and the cross-linking reaction which results from the spontaneous condensation of these groups.

Experimental Section

Materials. 4-Chlorostyrene, magnesium turnings, 1,2-dibromoethane, potassium peroxomonosulfate (Oxone, $2KHSO_5\cdot KHSO_4\cdot K_2SO_4$), sodium hydrogen carbonate, anhydrous tetrahydrofuran (THF), phenyl methyl sulfide (all obtained from Aldrich Co.), and dimethylchlorosilane (Hüls America Co.) were used as received. Benzene, styrene,[3] methylene chloride, and acetone were distilled prior to use. Twice-distilled water was used in the preparation of dimethyldioxirane solutions. 2,2′-Azobis(isobutyronitrile) (AIBN) was recrystallized from methanol.

Preparation of (4-Vinylphenyl)dimethylsilane.[4] Magnesium turnings (4.8 g, 0.2 mol) were mixed with dry THF (20 mL) in a three-neck, round-bottomed flask equipped with a condenser, a nitrogen gas inlet tube, and a pressure-equalized funnel. About 5 mL of the solution of 4-chlorostyrene (13.8 g, 0.1 mol) in dry THF (50 mL) was added with good agitation under nitrogen, followed by the addition of 1,2-dibromoethane (1 mL) in THF (5 mL). After the temperature had risen to about 50 °C, the rest of the 4-chlorostyrene solution in THF was added dropwise. The reaction mixture was refluxed for 30 min and then cooled to room temperature. To the (4-vinylphenyl)magnesium chloride formed in the above solution was added slowly chlorodimethylsilane (9.5 g, 0.1 mol) in THF (25 mL), and the reaction was allowed to proceed for 1 h at room temperature. After decomposition of excess reagents with ice water, the reaction mixture was filtered and extracted with ether, dried with magnesium sulfate overnight, and distilled: bp 46 °C (0.7 mmHg); yield 10.1 g (62%); ^1H NMR ($CDCl_3$) δ 0.31 (d, 6H, $Si(CH_3)_2$, $J = 3.9$ Hz), 4.46 (p, 1H, Si–H, $J = 3.6$ Hz), 5.21 (d, 1H, H_b of the vinyl, $J = 10.8$ Hz), 5.74 (d, 1H, H_c of the vinyl, $J = 17.4$ Hz), 6.66 (q, 1H, H_a of the vinyl, $J_1 = 10.8$ Hz, $J_2 = 17.7$ Hz), 7.34 (d, 2H, H_3 and H_5, $J = 7.8$ Hz), 7.47 (d, 2H, H_2 and H_6, $J = 7.8$ Hz); IR 2118 (Si–H), 1629 ($=CH_2$), 1599 (phenyl), 1389 and 1108 (Si–Ph), 1250 and 881 cm^{-1} ($Si–CH_3$).



Homopolymerization of (4-Vinylphenyl)dimethylsilane. A total of 4.02 g of (4-vinylphenyl)dimethylsilane in benzene (5 mL) was introduced into an ampule of 20-mL capacity in the presence of 2,2′-azobis(isobutyronitrile) (AIBN; 8.4 mg, 0.2 mol %). The polymerization ampule was thoroughly degassed by three freeze–thaw cycles, sealed in an argon atmosphere, and then polymerized at 60 °C for 24 h. The polymer was precipitated by pouring the reaction mixture into methanol while stirring. The precipitated white polymer was dried in vacuum at 40 °C for 6 h. The yield was 74%. The polymer was then redissolved in methylene chloride and reprecipitated in methanol and dried in vacuum at 40 °C for 24 h: ^1H NMR ($CDCl_3$) δ 7.4–6.1 (aromatic hydrogen), 4.6–4.2 (1H, Si–H), 1.9–1.0 (3H, $-CH_2CH-$), 0.4–0.1 (6H, $Si(CH_3)_2$); IR 2117 (Si–H), 1599 (phenyl), 1400 and 1115 (Si–Ph), 1250 and 877 cm^{-1} ($Si–CH_3$).

Copolymerization of (4-Vinylphenyl)dimethylsilane with Styrene. About 20 g of a mixture of (4-vinylphenyl)dimethylsilane (M_1) and styrene (M_2) was introduced into an ampule of 25-mL capacity in the presence of AIBN (0.2 mol %). The polymerization procedure was the same as that used for homopolymerization. The conversion was limited to about 10% (after 4 h). The polymer was isolated by precipitation of the polymerization mixture into methanol and dried in vacuum at 40 °C for 6 h. Purification of the polymer was also performed by precipitation of polymer solution in methylene chloride into methanol, followed by drying in vacuum at 40 °C for 24 h.

Preparation of Dimethyldioxirane in Acetone.[5] A 500-mL, three-neck, round-bottomed flask, containing a mixture of twice-distilled water (50 mL), acetone (40 mL), and sodium hydrogen carbonate (24 g) and a magnetic stirring bar, was equipped with a solid addition funnel containing potassium peroxomonosulfate (50 g), a gas inlet tube extending into the reaction mixture, and an air condenser loosely packed with glass wool. The exit of the air condenser was connected to a condenser filled with dry ice–isopropyl alcohol. The bottom of the dry ice condenser was attached in succession to a receiving flask (50 mL) and two cold traps, all being kept in dry ice–acetone baths. Argon gas was gently passed through the reaction vessel. While applying a slight vacuum (180–220 Torr), the solid potassium peroxomonosulfate was added quickly in one portion with

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vigorous stirring at room temperature. The slightly yellow solution (ca. 30 mL) of dimethyldioxirane in acetone was collected in a receiving flask. A small amount of dimethyldioxirane in acetone was also found in the two cold traps.

Assay for Dimethyldioxirane Concentration. Solutions of dimethyldioxirane in acetone were assayed for dioxirane content by reacting with phenyl methyl sulfide. A solution of dioxirane in acetone (1.5 mL) was mixed with an acetone solution of phenyl methyl sulfide (0.5 mL, 0.51 M) and reacted at room temperature for about 10 min. The ^{1}H NMR spectrum of the reaction mixture was then taken. The ratio of the signal integration of the sulfoxide phenyl protons (δ 7.6–7.9) to that of the unreacted sulfide phenyl protons (δ 7.1–7.3) was measured. The concentrations of the dimethyldioxirane solutions in acetone were calculated to be in the range of 0.06–0.08 M.

Preparation of Poly[(4-vinylphenyl)dimethylsilanol] and Its Copolymer with Styrene. To a solution of poly[(4-vinylphenyl)dimethylsilane] or poly[styrene-*co*-(4-vinylphenyl)-dimethylsilane] in dry methylene chloride was quickly added a cold solution (ca. −10 °C) of dimethyldioxirane in acetone, and the resulting mixture was reacted for 30 min at 0 °C. The mole ratio of dioxirane to polymer was ca. 1.2–1.3. The solvents were removed with a rotary evaporator at 5–10 °C under reduced pressure. A thin white polymer film was formed in the flask. The polymer product was further dried under vacuum for 1 h.

Characterization. ^{1}H NMR spectra were obtained with the use of Varian EM-390 90-MHz or GN 300-MHz NMR instruments. The mole fraction (S) of (4-vinylphenyl)dimethylsilane units in the styrene copolymer was determined by using the following equation:

$$S = \frac{5B}{B + 6A} \qquad (1)$$

where A and B are integrations of signal A (phenyl, δ 7.4–6.1) and B (two methyl, δ 0.4–0.1), respectively.

The intrinsic viscosities were measured in THF at 25 ± 0.01 °C with an Ubbelohde viscometer.

The infrared spectra were obtained with a Digilab FTS-60 FT-IR spectrometer, and 32–64 scans with a resolution of 2 cm^{-1} were used. For poly[(4-vinylphenyl)dimethylsilane], poly[(4-vinylphenyl)dimethylsilanol], and their copolymers with styrene, films were cast from chloroform and acetone, respectively. After slow evaporation of the solvents, the films were dried in a vacuum oven at room temperature for 2 h. Vacuum drying at room temperature is crucial because it minimizes the self-condensation reaction of silanol groups. The silanol-containing homopolymer and copolymers became cross-linked upon heating, e.g., during DSC experiments. The cross-linked polymers were ground into powders, and KBr tablets were prepared for infrared measurements. The spectrum of poly[(4-vinylphenyl)dimethylsilanol] in acetone was measured in a KBr liquid cell 0.035 mm in thickness.

Differential scanning calorimetry (DSC) measurements were performed on a Perkin-Elmer DSC-7 instrument. The temperature scale and the measure of energy input/output were calibrated with indium standards. All the data were processed by means of the Perkin-Elmer TADS system. Sample weights of 5–10 mg and a heating rate of 10 °C/min were used. For poly[(4-vinylphenyl)dimethylsilane] and its copolymers with styrene, the samples were heated to 200 °C, held for 5 min at that temperature, and then quenched in dry ice. For (4-vinylphenyl)-dimethylsilanol homopolymer and its copolymers, the sample was held at 175 °C for 5 min after the first scan from −10 to +175 °C and then quenched in dry ice. The glass transition temperature of the polymer is defined as the midpoint of the specific heat increment in the second run.

Results and Discussion

The compositions of styrene-*co*-(4-vinylphenyl)dimethylsilane copolymers determined from ^{1}H NMR measurements are in agreement with the results calculated from the reported reactivity ratios[4] of $r_1 = 0.56$ and $r_2 = 1.00$. The results are listed in Table I.

Table I. Polymerization of (4-Vinylphenyl)dimethylsilane and Its Copolymerization with Styrene[a]

no.	feed (g) M_1[c]	feed (g) M_2[d]	yield (wt %)	composition (mol %)[e] of M_1	$[\eta]$[f] (dL/g)
1	0.32	19.66	10.5	1.9	0.54
2	0.98	19.18	9.9	4.1	0.58
3	1.81	18.17	11.4	8.7	0.64
4	2.67	17.38	10.6	11.4	0.59
5	4.32	15.69	11.4	18.2	0.67
6	8.03	11.98	13.2	33.9	0.70
7	14.14	5.99	13.8	60.0	0.76
8	17.24	2.81	14.8	80.6	0.66
9[b]	4.02		74.0	100	0.55

[a] Polymerized with ~0.2 mol % AIBN at 60 °C for about 4 h. [b] Polymerized at 60 °C for 24 h. [c] (4-Vinylphenyl)dimethylsilane. [d] Styrene. [e] Calculated from ^{1}H NMR spectra. [f] In THF at 25 ± 0.01 °C.

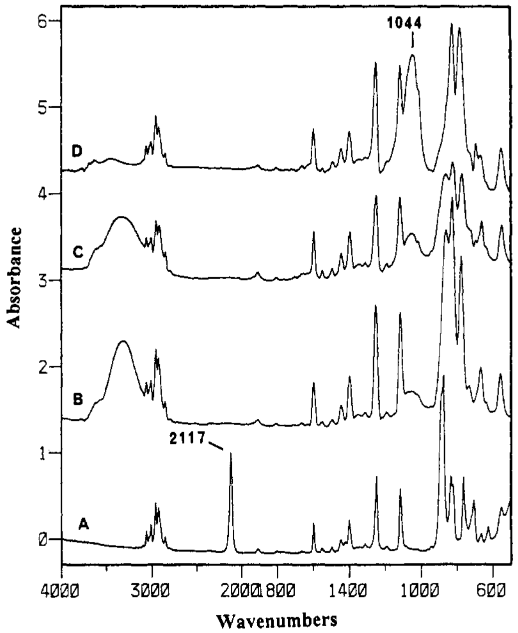
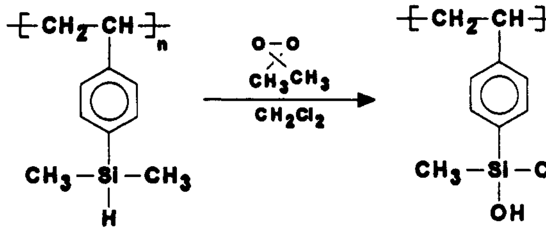


Figure 1. FT-IR spectra of (A) poly[(4-vinylphenyl)dimethylsilane], (B) freshly made poly[(4-vinylphenyl)dimethylsilanol], (C) poly[(4-vinylphenyl)dimethylsilanol] heated at 175 °C for 5 min, and (D) poly[(4-vinylphenyl)dimethylsilanol] heated at 300 °C for 5 min.

Scheme I



Spectroscopy

The direct conversion of silane into silanol by means of an oxygen atom insertion into the Si–H bond by dioxirane was reported by Adam et al.[6] The oxyfunctionalization of silane is so efficient that the conversion of dimethylsilane into dimethylsilanol is almost quantitative even when the silane groups are attached to a polymer chain (Scheme I). The absorption band at 2117 cm^{-1} (Figure 1A), due to the stretching vibration of Si–H groups in the infrared spectra, totally disappeared after the reaction (Figure 1B), while two new bands appeared in the hydroxyl absorption region (Figure 2). The absorption band at 3622 cm^{-1} can be assigned to the free silanol groups and another broad band with a maximum ranging from 3435 to 3319 cm^{-1} to the

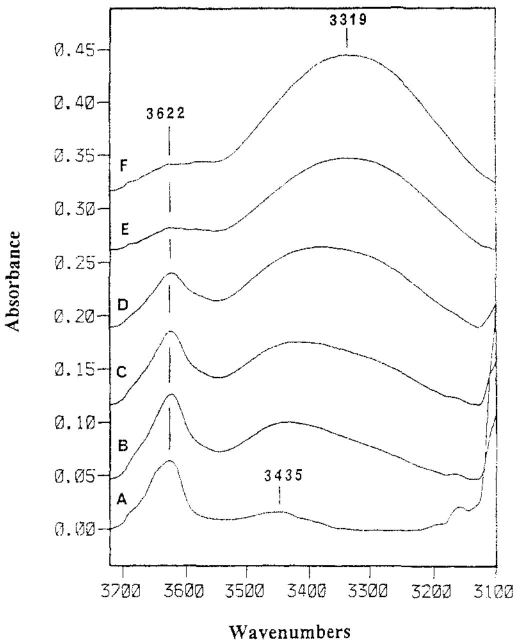


Figure 2. FT-IR spectra in the hydroxyl absorption region for poly[styrene-*co*-(4-vinylphenyl)dimethylsilanol] containing (A) 1.9, (B) 8.7, (C) 11.4, (D) 18.2, (E) 60.0, and (F) 100 mol % VPDMS.

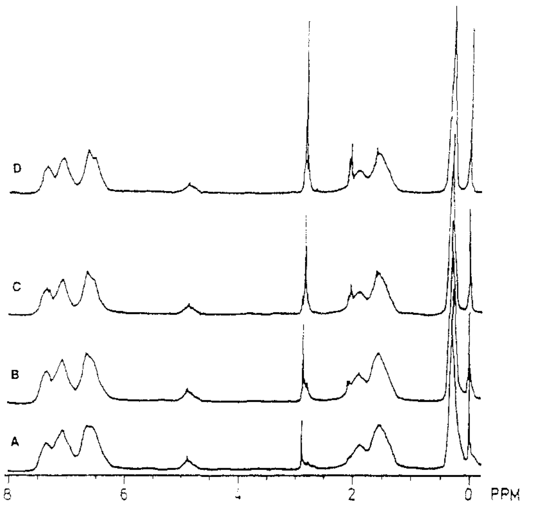


Figure 3. ^{1}H NMR spectra of poly[styrene-*co*-(4-vinylphenyl)-dimethylsilanol] containing 45.0 mol % of VPDMS in acetone-*d*: (A) 6.6, (B) 1.7, (C) 0.4, and (D) 0.1 wt %. (To fit the four curves in one figure, different intensity scales were used so that the four peaks at δ 4.6–5.0 have comparable intensities.)

self-associated silanol groups[7,8] (Figure 2). In addition, a strong absorption band at 829 cm^{-1} due to the stretching vibration of the Si–O band appeared (Figure 1). In the ^{1}H NMR spectra, the resonance peak of Si–H groups at δ 4.6–4.2 was absent, and two resonance peaks of the hydroxyl groups, corresponding respectively to acetone-*d* solvated hydroxyl groups at δ 2.9–2.6 and self-associated hydroxyl groups at δ 5.0–4.6, were present (Figure 3).

The infrared absorption band of the self-associated silanol groups is characterized by a substantial width and a large integral intensity relative to the absorption of the free silanol groups. The frequency shift ($\Delta\nu$) causes by self-association is 180–300 cm^{-1} and depends on the amount of (4-vinylphenyl)dimethylsilanol (VPDMS) in the copolymer (Figure 4). The relatively weak self-association at low (4-vinylphenyl)dimethylsilanol contents is caused by the dilution effect of the styrene groups which isolate and reduce the probability of inter- and intramolecular interactions of the silanols. The magnitude of the frequency shift and hence the strength of the self-association

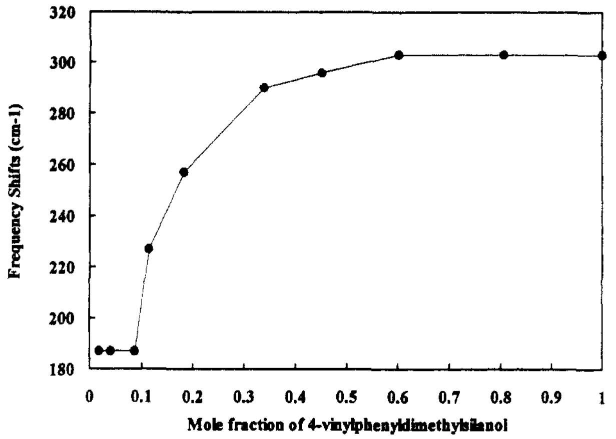


Figure 4. Frequency shifts (cm^{-1}) due to self-association of silanol groups as a function of VPDMS contents in the polymers.

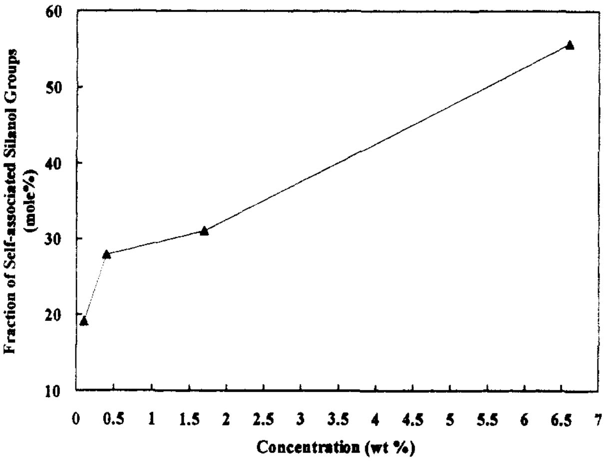


Figure 5. Fraction of self-associated silanol groups in acetone-*d* solution versus concentration of the copolymer containing 45.0 mol % VPDMS.

increase dramatically when the amount of (4-vinylphenyl)-dimethylsilanol in the copolymer is in excess of 10 mol %. The shift is substantially larger than that observed for poly(styrene-*co*-(4-vinylphenyl)(hexafluorodimethyl)-carbinol) and is comparable to the results of poly(styrene-*co*-vinylphenol).[1,2,9] The strong tendency for self-association was also manifested in the ^{1}H NMR spectra of the copolymer in deuterated acetone as shown in Figure 3. At relatively high solution concentrations, the resonance peak at δ 4.6–5.0, corresponding to the self-associated silanol groups, is larger than the peak at δ 2.6–2.9 which is related to acetone-*d* solvated silanol groups. The solvated silanol peak increases with decreasing copolymer concentration in acetone-*d* solution at the expense of the self-associated silanol peak for the copolymer containing 45 mol % VPDMS. The dependence of self-association on polymer concentration is shown quantitatively in Figure 5.

The infrared spectra of poly[(4-vinylphenyl)dimethylsilanol] in acetone, presented in Figure 6, provided additional evidence of silanol hydrogen bonding with acetone. In the silanol absorption region, the free silanol absorption band at 3622 cm^{-1} has disappeared and a broad bond at 3575 cm^{-1} arises, which can be assigned to silanol groups which engage in hydrogen bonding with the carbonyl groups of acetone. The absorption band of the self-associated silanol groups was observed as a shoulder at 3319 cm^{-1} with relatively weak intensity. Meanwhile the carbonyl stretching vibration absorption band of acetone at 1714.5 cm^{-1} shifts to 1712.3 cm^{-1}.

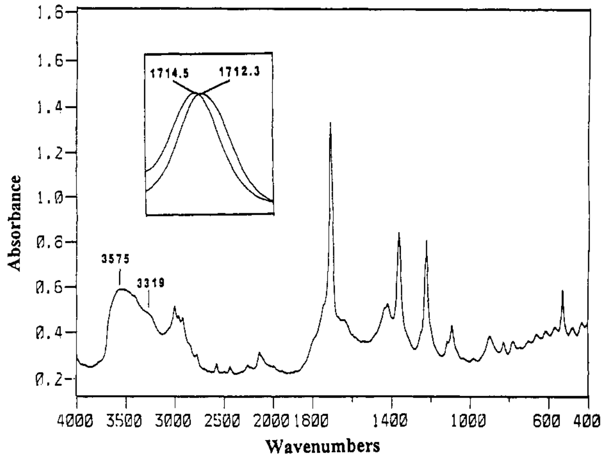


Figure 6. FT-IR spectra of poly[(4-vinylphenyl)dimethylsilanol] in acetone.

Condensation of Silanol Groups

It is well-known that organic silanol molecules have a strong tendency to undergo spontaneous condensation to transform into siloxanes Si–O–Si.[10] The silanol groups in the homopolymer or copolymers are stable in an acetone solution at room temperature. Polymers which contain more than 18.2 mol % VPDMS monomer units become insoluble after drying under reduced pressures at room temperature. The stability of poly[(4-vinylphenyl)dimethylsilanol] and its copolymers in acetone at room temperature can be attributed to both the dilution effect and hydrogen-bond formation between the silanol groups of the polymer and the carbonyl groups of acetone which prevents the spontaneous condensation of silanol groups. However, a large number of small gel particles precipitated from solution when the polymer solution was heated to above 40 °C while stirring. Gelation can also be easily achieved by the addition of small amounts of acids to the polymer solution. A broad peak present at 1044 cm^{-1} in the infrared spectra (Figure 1) indicates the formation of siloxanes via the condensation of silanol groups. We noted that only a weak absorption band at 1044 cm^{-1} was observed for the freshly made silanol polymer (Figure 1B), a moderate band when the polymer was heated at 175 °C for 5 min (Figure 1C), and a strong band when the polymer was heated up to 300 °C for 5 min (Figure 1D).

Thermal Analysis

The dependence of the glass transition temperatures of the copolymers of (4-vinylphenyl)dimethylsilane on composition was investigated by differential scanning calorimetry (DSC) (Figure 7). However, the condensation reaction of the silanol groups in the VPDMS copolymers which occurs even in the freshly made samples complicates the T_g measurements of the silanol-containing polymers. The condition (5–10 °C for 1 h) used in the sample preparation was intended to minimize the condensation reaction. However, the procedure failed to remove solvent completely. The presence of a small amount of residue solvent is seen in the DSC scan (Figure 8) as a shallow endotherm in the temperature range 20–90 °C. There seems to be a step increase in the specific heat of the specimen at about 140 °C which may be considered as the glass transition. However, the assignment is tentative because the step increase is followed shortly by a broad exotherm, i.e., the condensation reaction. In support of the DSC results, thermogravimetric analysis (TGA) was performed as shown in Figure 9. The polymer gradually loses weight upon heating. Extensive weight loss occurs at about 280 °C. In order to avoid extensive condensation of the dimethylsilanol groups at high temperature but at the same time achieve complete removal of solvent, the polymer samples were first heated to 175 °C and maintained for 5 min. When the quenched sample was reheated, the endothermic event was eliminated and the glass transition moved to a slightly higher temperature. The T_g values reported in Figure 10 were determined from the second scan. These values, however, may not represent the true T_g values of the virgin polymers.

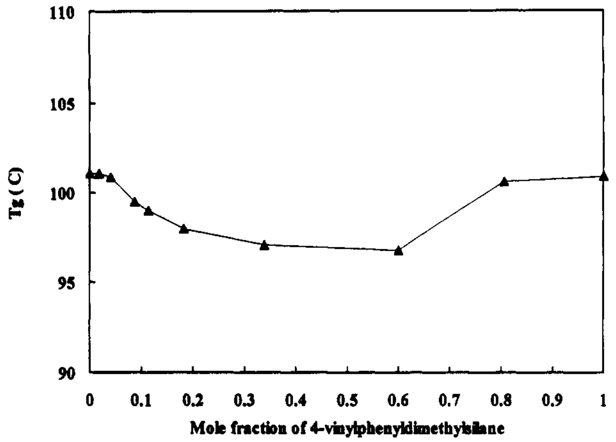


Figure 7. Dependence of the glass transition temperature of the silane copolymers on (4-vinylphenyl)dimethylsilane content.

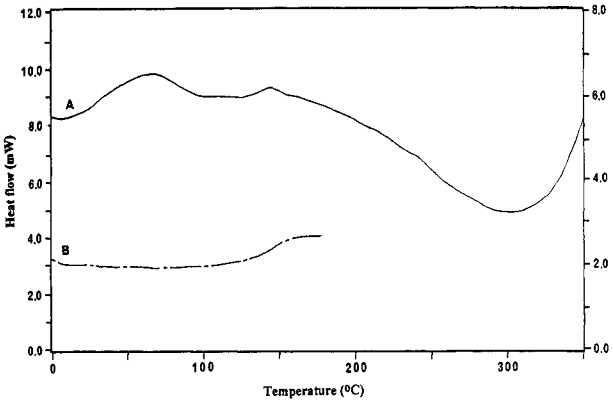


Figure 8. DSC traces of poly[(4-vinylphenyl)dimethylsilanol] at a heating rate of 10 °C/min: (A) the first scan and (B) the second scan.

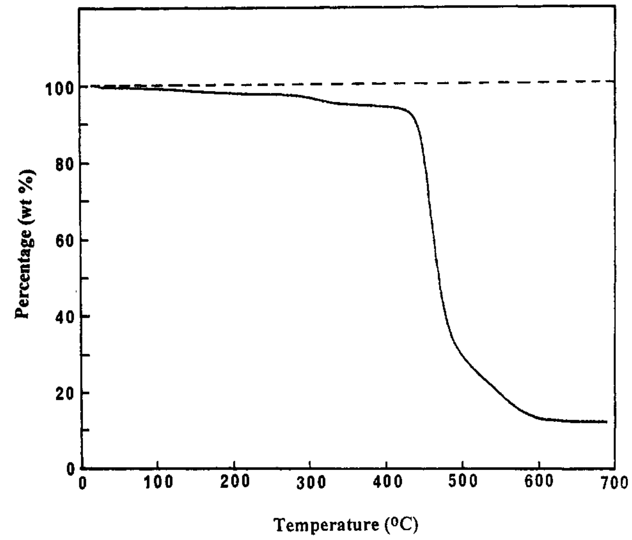


Figure 9. TGA curve of poly[(4-vinylphenyl)dimethylsilanol] at a heating rate of 10 °C/min under a nitrogen atmosphere.

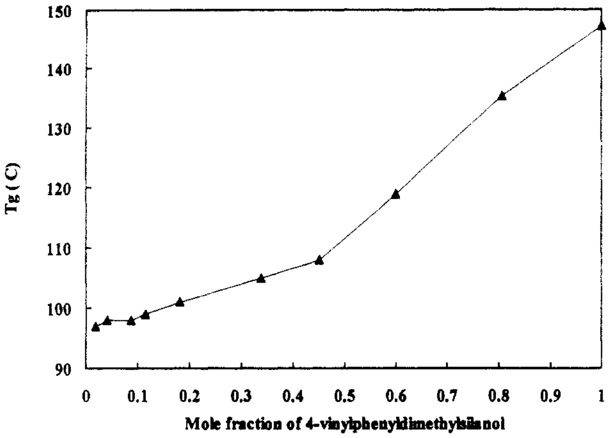


Figure 10. Dependence of the glass transition temperature of the silanol copolymers on the VPDMS content.

It is important to point out that only a small fraction of the silanol groups in the copolymers was transformed into siloxane cross-links at a temperature below 175 °C. The abundance of the remaining silanol groups is indicated by a strong absorption band in the 3461–3352-cm^{-1} region in the infrared spectra after DSC measurements (Figure 1C).

In summary, we have synthesized a new polymer and its styrene copolymers containing dimethylsilanol groups. The experimental results indicate that the dimethylsilanol group has a strong tendency to undergo spontaneous condensation to transform into siloxanes. Styrene copolymers containing less than 10 mol % silanol groups are relatively stable because the active groups are present at low concentrations. From the point of view of molecular structure, the tendency of the silanol groups to undergo spontaneous condensation depends on the steric effect and the electronegativity of the substituting groups. Stable silanol-containing polymers could be obtained by replacing the methyl group bound to the Si atom with bulky substituting groups. This work will be reported in future publications.

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