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Thermally Stable Silphenylene Vinyl Siloxane Elastomers and Their Blends

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ABSTRACT: Vinyl-substituted silphenylene siloxane elastomers (VSPSEs) with variable vinyl content were synthesized using the disilanol−diaminosilane polycondensation method. High molecular weight elastomers were obtained by using carefully purified monomers. The polymers were characterized by gel permeation chromatography, differential scanning calorimetry (DSC), and thermogravimetric analyses (TGA). Analysis by ^{29}Si NMR established that the samples have exactly alternating chemical structures. VSPSEs have low glass transition temperatures (T_g's) ranging from −26 to −63 °C. Substitution of the methyl group on silicon with phenyl increases the T_g as well as the TGA residues in both air and nitrogen. TGA experiments showed that the VSPSEs synthesized in this study have the highest degradation temperatures reported so far. The TGA residues at 900 °C increased to 70% in nitrogen and 57% in air as the vinyl content increased. Furthermore, remarkable isothermal weight losses were shown by the VSPSEs. For example, the elastomer with one vinyl group per repeating unit had a weight loss of 0.7% in nitrogen and 3% in air after 5 h at 400 °C. Blends of VSPSEs with conventional styrene butadiene rubbers (SBR) and also with styrene−butadiene−styrene triblock copolymers (SBS) were prepared using solution blending. DSC studies indicated that these blends were not miscible. Cross-linking the blends broadened the T_gs for the blend constituents indicating a small degree of interfacial phase mixing. Thermal-oxidative stability of the blends is intermediate between that of the VSPSEs and the SBR or SBS.

Introduction

Flame retardant polymers have been developed for many applications including airplanes, cars, textiles, and electrical devices. Traditionally, flame retardant polymers can be prepared by blending polymers with flame retardant additives such as halogenated or phosphorus compounds.[1] However, this approach often generates toxic, corrosive, or halogenated gases during combustion. We report here the study of nonhalogenated flame retardant elastomeric materials based on silphenylene siloxane elastomers containing vinyl substituents on the central silicon atom. Silphenylene siloxane elastomers possess low-temperature flexibility and high-temperature stability.[2] The incorporation of vinyl groups into silphenylene siloxane elastomers (VSPSEs), has been reported to yield high char residues upon pyrolysis. While VSPSEs have been synthesized previously by the chlorosilane or ureidosilane condensation route,[3−6] we found that the silanol−aminosilane condensation[7] produced superior elastomers with narrower molecular weight distributions in short reaction times. The present study involves the preparation and characterization of purified VSPSE. Blends of VSPSEs with styrene butadiene rubber (SBR) or styrene−butadiene−styrene (SBS) thermoplastic elastomers will also be described. The VSPSEs can also be chemically modified and combined with a variety of other polymers via derivatization of the vinyl group, but this will be the subject of another report.

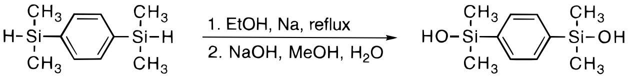
Experimental Section

Reagents. 1,4-Bis(dimethylsilyl)benzene, bis(dimethylamino)dimethylsilane, bis(dimethylamino)methylvinylsilane, and bis(dimethylamino)methylphenylsilane were obtained from United Chemical Technologies. The bis(dimethylamino)silanes were purified by distillation under an argon atmosphere. SBR and SBS were obtained from Scientific Polymer Products. They were purified by dissolution in toluene and reprecipitation with methanol which removed inhibitors and stabilizers. All other reagents used were purified using either recrystallization or distillation.

Characterization Methods. The elemental analyses were carried out by the Microanalysis Laboratory at the University of Massachusetts. Inherent viscosities for polymers were determined at 30 °C in tetrahydrofuran, using a Cannon-Ubbelohde viscometer at a polymer concentration of 0.01 g/mL. ^{1}H NMR spectra were obtained with a Bruker/IBM 200AC NMR spectrometer operating at 200 MHz. ^{13}C NMR spectra were obtained with a Varian XL-300 NMR spectrometer operating at 75 MHz in deuterated solvents. ^{29}Si NMR spectra were recorded on a Varian XL-300 NMR spectrometer operating at 60 MHz. Gel permeation chromatography (GPC) measurements were performed on a Waters Model 6000A with a Waters differential refractometer using THF as mobile phase. Polystyrene standards were used for calibration.

Differential scanning calorimetry (DSC) measurements were conducted with a Perkin-Elmer DSC-7 on samples ranging from 7 to 10 mg. The temperature and power ordinates of the DSC were calibrated with the known melting point and heat of fusion of a high-purity indium standard supplied by Perkin-Elmer. The glass transition temperature (T_g) was defined as the midpoint of the change in the specific heat. Thermogravimetric analysis (TGA) experiments were conducted with a Perkin-Elmer TGA-7 on samples ranging from 10 to 15 mg.

1,4-Bis(hydroxydimethylsilyl)benzene. Into a flame dried 50 mL three-neck round bottom flask equipped with magnetic stirrer and water condenser was added anhydrous ethanol (10 mL) and a small piece of sodium metal under argon. The ethanol was heated to reflux. Then 1,4-bis-



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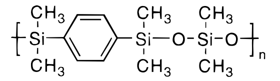
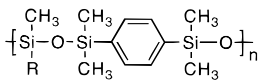
(dimethylsilyl)benzene (8.200 g, 42.3 mmol) was added dropwise to the reaction flask with stirring over 10 min. When hydrogen evolution ceased, the reaction mixture was added with vigorous stirring to a mixture of NaOH (5.7 g), CH_3OH (35 mL) and H_2O (4 mL). After the mixture was allowed to stand for 15 min, another solution of NaOH (5.7 g) in H_2O (38 mL) was added to the mixture. The mixture was allowed to stand for 30 min with occasional shaking and then poured into a vigorously stirred solution of KH_2PO_4 (50 g) in excess ice and H_2O (200 mL). The crude disilanol product was precipitated as a white solid, filtered, dissolved in ethyl ether (50 mL), and washed with an equal volume of water. The ether solution of the product was dried with anhydrous Na_2SO_4 and concentrated to give a white solid. The solid was recrystallized from hot CCl_4 (200 mL) and dried at 70 °C overnight in vacuo to provide the final needle-like white solid product (8.5 g, yield 89%). ^{1}H NMR (d_6-DMSO, 200 MHz) δ 7.48 (s, $-C_6H_4-$ aromatic protons), 5.85 (s, $-OH$), 0.19 (s, $-CH_3$). ^{13}C NMR (d_6-DMSO, 75 MHz) δ 141.2, 132.0, 0.5. Anal. Calcd for $C_{10}H_{18}Si_2O_2$: C, 53.05; H, 8.01. Found: C, 52.71; H, 8.02. Melting point (T_m): 137 °C.

Poly(1,4-phenylenehexamethyltrisiloxanyl), VSPSE 1.



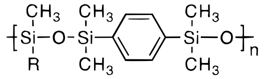
Into a flame-dried 50 mL three-neck round bottom flask equipped with magnetic stirrer and water condenser was added under argon 1,4-bis (hydroxydimethylsilyl)benzene (4.00 g, 17.67 mmol). Then dry toluene (6 mL) was transferred into the flask by syringe. With stirring, bis(dimethylamino)-dimethylsilane (2.512 g, 17.17 mmol) was transferred by syringe into the reaction flask. The flask was heated to 105−110 °C within 20 min, and the evolution of dimethylamine was noted. After 1 h of reaction, an additional amount of bis-(dimethylamino)dimethylsilane (20 μL each time) was added at a time interval of 15 min until there was no significant gas evolution (total 100 μL) and the reaction mixture gelled. Then the reaction mixture was precipitated into methanol (40 mL). A transparent gumlike elastomer (4.5 g, yield 90%) was obtained after drying in a vacuum oven at 70 °C for 8 h. ^{29}Si NMR ($CDCl_3$, 60 MHz) δ −2.62, −19.6. Anal. Calcd for $C_{12}H_{22}Si_3O_2$: C, 51.01; H, 7.85. Found: C, 51.20; H, 7.67.

Poly(1,4-phenylenehexamethyltrisiloxanyl)-*co*-(1,4-phenylene-1,1,3,5,5-pentamethyl-3-vinyltrisiloxanyl), VSPSE 2 (Vinyl Content, 10 mol %). Into a flame-dried 50 mL three-neck round bottom flask equipped with magnetic stirrer and water condenser was added under argon 1,4-bis (hydroxydimethylsilyl)benzene (4.00 g, 17.67 mmol). Then dry toluene (3 mL) was transferred into the flask by syringe. With stirring, a solution of bis(dimethylamino)dimethylsilane (2.268 g) and bis(dimethylamino)methylvinylsilane (279.7 mg) in toluene (3 mL) was transferred by syringe into the reaction flask. The flask was heated to 105−110 °C within 20 min and the evolution of dimethylamine was noted. After 1 h reaction, an additional amount of bis(dimethylamino)dimethylsilane (20 μL each time) was added at a time interval of 15 min until there was no significant gas evolution and the reaction mixture gelled. Then the reaction mixture was precipitated into methanol (40 mL). A transparent gumlike material (4.5 g, yield 90%) was obtained after drying in a vacuum oven at 70 °C for 8 h.



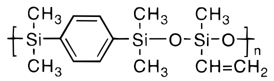
R = $-CH_3$ (90 mol%) and $CH_2{=}CH-$ (10 mol%)

Poly(1,4-phenylenehexamethyltrisiloxanyl)-*co*-(1,4-phenylene-1,1,3,5,5-pentamethyl-3-vinyltrisiloxanyl), VSPSE 3 (Vinyl Content, 20 mol %). The synthesis of VSPSE 3 was similar to that for VSPSE 2. A transparent gum like material (4.6 g, yield 92%) was obtained after drying in a vacuum oven at 70 °C for 8 h.

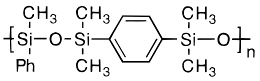


R = $-CH_3$ (80 mol%) and $CH_2{=}CH-$ (20 mol%)

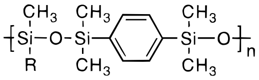
Poly(1,4-phenylene-1,1,3,5,5-pentamethyl-3-vinyltrisiloxanyl), VSPSE 4. The synthesis of VSPSE 4 was similar to that for VSPSE 1. Bis(dimethylamino)methylvinylsilane was used instead of bis(dimethylamino)dimethylsilane. A transparent gum like material (4.8 g, yield 92%) was obtained after drying in a vacuum oven at 70 °C for 8 h.



Poly(1,4-phenylene-1,1,3,5,5-pentamethyl-3-phenyltrisiloxanyl), VSPSE 5. The synthesis of VSPSE 5 was similar to that for VSPSE 1. Bis(dimethylamino)methylphenylsilane was used instead of bis(dimethylamino)dimethylsilane. A transparent gumlike material (5.7 g, yield 93%) was obtained after drying in a vacuum oven at 70 °C for 8 h. ^{29}Si NMR ($CDCl_3$, 60 MHz) δ −1.32, −32.96.



Poly(1,4-phenylene-hexamethyltrisiloxanyl)-co-(1,4-phenylene-1,1,3,5,5-pentamethyl-3-vinyltrisiloxanyl)-co-(1,4-phenylene-1,1,3,5,5-pentamethyl-3-phenyltrisiloxanyl), VSPSE 6. Into a flame-dried 50 mL three-neck round bottom flask equipped with magnetic stirrer and water condenser was added under argon 1, 4-bis(hydroxydimethylsilyl)-benzene (4.00 g, 17.67 mmol). Then dry toluene (3 mL) was transferred into the flask by syringe. With stirring, a solution of bis(dimethylamino)dimethylsilane (1.163 g), bis(dimethylamino)methylphenylsilane (1.654 g) and bis(dimethylamino)-methylvinylsilane (279.7 mg) in toluene (3 mL) was transferred by syringe into the reaction flask. The flask was heated to 105−110 °C within 20 min and the evolution of dimethylamine was noticed. After 1 h of reaction, an additional amount of bis(dimethylamino)dimethylsilane (20 μL each time) was added at a time interval of 15 min until there was no significant gas evolution and the reaction mixture gelled. The reaction mixture was precipitated into methanol (40 mL). A transparent gum like material (4.8 g, yield 88%) was obtained after drying in a vacuum oven at 70 °C for 8 h.



R = Ph (45 mol%), $-CH_3$ (45 mol%) and $CH_2{=}CH-$ (10 mol%)

Preparation of Un-Cross-Linked Polymer Blends. A typical procedure for the preparation of an un-cross-linked polymer blend is described below and in Scheme 2.

Two elastomers to be blended are dissolved together in toluene. The concentration of the blend is less than 5% by weight. Then, it is precipitated by the addition of methanol under vigorous stirring. After the liquid is decanted, a wet blend is obtained. Finally, it is washed with methanol and dried in a vacuum oven at 60 °C for 8 h and recovered quantitatively.

Preparation of Cross-Linked Polymer Blends. A typical procedure for the preparation of a cross-linked polymer blend is described below:

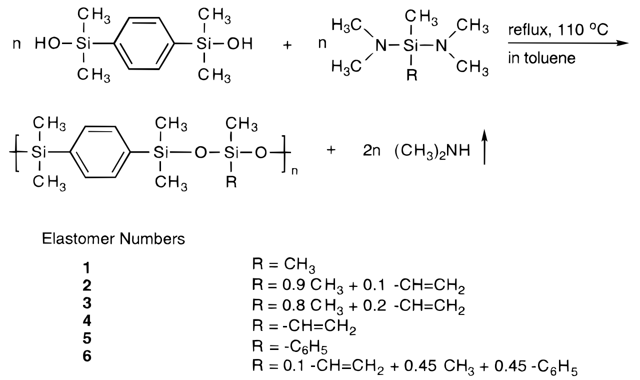
Two polymers to be blended are dissolved first in tetrahydrofuran at a concentration of less than 5% by weight. Then, benzoyl peroxide (BPO, 1% by weight of the blend) is added with stirring into the solution. The blend is obtained by evaporating the THF solvent and drying in a vacuum oven at

Table 1. VSPSE

VSPSE no.	R	yield, %	molecular weight[a]		PDI	T_g,[b] °C
			$M_w \times 10^{-3}$	$M_n \times 10^{-3}$		
1	Me	90	149	64.4	2.3	−59
2	0.9 Me + 0.1 Vi	90	221	66.3	3.3	−59
3	0.8 Me + 0.2 Vi	92	798	168	4.8	−59
4	Vi	92	477	109	4.4	−63
5	Ph	93	96	42.5	2.3	−26
6	0.1Vi + 0.45 Me + 0.45 Ph	88	425	88.7	4.8	−43

[a] Polystyrene samples were used as standards and chloroform as solvent. [b] Obtained by DSC measurement.

Scheme 1



30 °C for 8 h. The blend containing 1% BPO was pressure molded at 130 °C for 40 min. Then, the cross-linked blend was transferred into a vacuum oven at 30 °C for another 3 h.

Results and Discussion

Synthesis and Characterization of VSPSEs. VSPSEs have been synthesized previously using the chlorosilane or the ureidosilane routes.[3−6] The chlorosilane−silanol condensation reaction will generate HCl which can catalyze the self-condensation of the silanol monomer, thus preventing the formation of exactly alternating polymer structures. Although the ureidosilane approach can produce alternating VSPSEs, the reaction times are very long and broad molecular weight distributions are common. We believe that the presence of ureido end groups would cause lower thermal stability in the VSPSEs. For these reasons, we selected the disilanol−diaminosilane polycondensation route in which the byproduct amine is generated as a gas providing a clean reaction.[7] The reaction was carried out in toluene at 110 °C under argon atmosphere as shown in Scheme 1. By careful purification of the starting monomers, either by distillation or recrystallization, all VSPSEs were obtained as transparent, high molecular weight, gumlike materials with high yields ranging from 88 to 93%. With the use of unpurified monomers, low molecular weight oil-like polymers were obtained with yellow color. From VSPSE 1 to VSPSE 4 in Scheme 1, the R substituent on the central silicon atom may be either methyl or vinyl, or a combination of both with a vinyl content from 10 to 20 mol %. VSPSE 5 has a phenyl group only for the R substituent. For VSPSE 6, the R substituent has a combination of vinyl (10%), methyl (45%), and phenyl groups (45%). The presence of vinyl groups in these elastomers provides a covulcanization potential when blended with other unsaturated hydrocarbon rubbers. The phenyl group in VSPSE 6 also may promote some compatibility with SBR type elastomers.

GPC and DSC techniques were used to characterize the VSPSEs. Table 1 summarizes the characterization results. In general, they had relatively high molecular weights ranging from a M_w of 96000−798000. The molecular weight distribution indexes ranged from 2.3 to 4.8, which is much lower than those attained by the ureido route, which were typically around 10. They exhibited low T_gs, ranging from −26 to −63 °C. Substituting the central methyl group with vinyl did not affect the T_g significantly. Substituting the central methyl with phenyl increased T_g by about 40 °C. VSPSE 5 had the highest T_g of −26 °C. ^{29}Si solution NMR analyses were also carried out for all VSPSEs. In the case of VSPSE 1 and 5, only two peaks were observed, which is consistent with the presence of an alternating chemical structure, exhibiting one peak for the silicon atom adjacent to the phenylene ring and a second peak for the central silicon atom. VSPSE 2, 3, and 6 showed additional peaks due to their more complex compositions since they are copolymers.

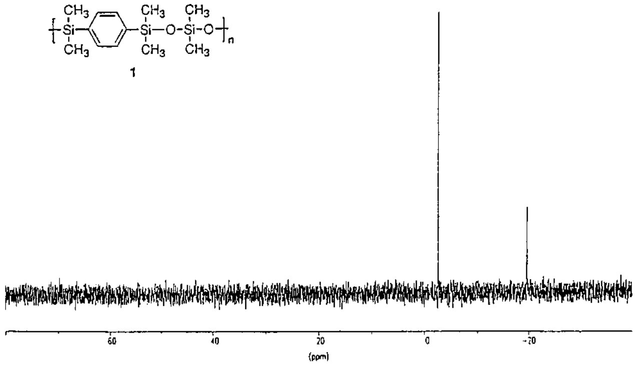


Figure 1. 60 MHz ^{29}Si Solution NMR of VSPSE 1.

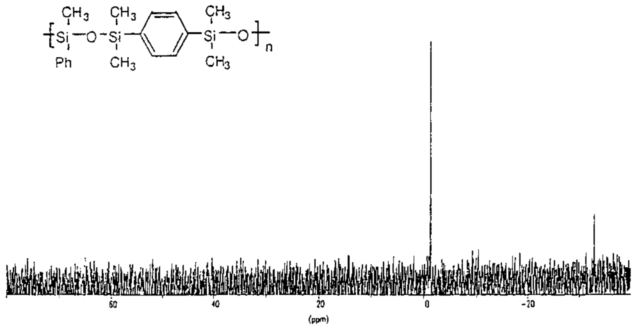


Figure 2. 60 MHz ^{29}Si Solution NMR of VSPSE 5.

^{29}Si NMR spectra for VSPSE 1 and 5 are shown in Figures 1 and 2, respectively. Table 1 presents a summary of the six elastomers that were prepared by Scheme 1 and includes yields, molecular weights, and glass transition temperatures.

Thermal stability and decomposition of VSPSE. Figure 3 gives the TGA curves for each VSPSE 1 to 6 under nitrogen atmosphere at a heating rate of 15 °C/min. A summary of the TGA results in nitrogen is given in Table 2. The VSPSEs have high onset degradation temperatures ranging from 395 to 547 °C in nitrogen atmosphere, which is from 60 °C to more than 100 °C higher than decomposition values reported before.[5,6] The temperatures for 50% weight loss are well above 600 °C, and the end of the major degradation ranges from 671 to 688 °C. From VSPSE 1 to VSPSE 4, the final residue increases from 20% up to 70% as the vinyl content is increased, which is a trend that has been observed before.[5,6] Comparing VSPSE 2 and 6, substitution of 50% of the methyl groups with phenyl increases the onset degradation temperature by 42 °C and the residue by 14%. In nitrogen, all VSPSEs exhibit a single major break in their decomposition curves before their major weight losses level off at about 670 °C. This behavior is indicative of a single mechanism of

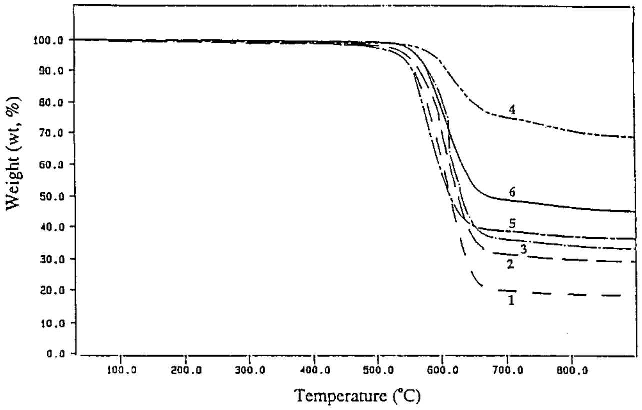


Figure 3. TGA of VSPSEs (in N_2, 15 °C/min). Curves 1, 2, 3, 4, 5, and 6 correspond to VSPSE 1, 2, 3, 4, 5, and 6, respectively.

Table 2. TGA Data of VSPSE 1–6 in Nitrogen (15 °C/min)

VSPSE no.	onset of degradation T_d (°C)[a]	temp for 50% wt loss (°C)	end of major degradation (°C)	% residue at 900 °C
1	462	614	676	20
2	491	626	686	31
3	517	633	674	33
4	547	—[b]	675	70
5	395	614	671	39
6	523	668	688	45

[a] The temperature at which the major degradation starts. [b] Since E4 loses only 30% weight at 900 °C, the 50% weight loss temperature is clearly considerably above 900 °C.

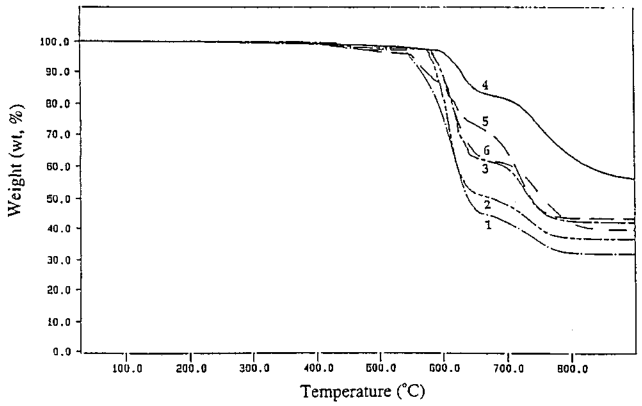


Figure 4. TGA of VSPSEs (in air, 15 °C/min). Curves 1, 2, 3, 4, 5, and 6 Correspond to VSPSE 1, 2, 3, 4, 5, and 6, respectively.

decomposition which is similar for all the VSPSEs. However, the larger residues for higher vinyl-containing compositions also indicate thermally induced vinyl polymerization or aromatization via cyclization reactions.

Figure 4 presents the TGA curves of VSPSE 1 to 6 in air at a heating rate of 15 °C/min, and these results are summarized in Table 3. Similar to their decomposition in nitrogen, they exhibit high onset degradation temperatures ranging from 374 to 462 °C. As expected, the stability in air is generally less than the corresponding stability in nitrogen, except for VSPSE 5, which is about the same. The temperatures for 50% weight loss are above 600 °C and the end of the major degradation temperature ranges from 781 to 883 °C. From VSPSE 1 to 4, the final residue at 900 °C is increased from 32% to 57% as the vinyl content is increased. VSPSE 5 and 6, again, have higher residues and onset degradation temperatures than those of VSPSE 2. The most outstanding thermal and oxidative stability behavior is shown by VSPSE 4, with one vinyl group per repeating unit. This actually corresponds to one vinyl group out of six aliphatic substituents or a 16.7 mol % vinyl content. It will be interesting to examine the thermooxidative behavior of VSPSE with even higher vinyl content.

Table 3. TGA Data of VSPSE 1–6 in Air (15 °C/min)

VSPSE no.	onset of degradation T_d (°C)[a]	temp for 50% wt loss (°C)	end of major degradation (°C)	% residue at 900 °C
1	374	639	787	32
2	419	672	781	37
3	387	736	795	43
4	431	—[b]	883	57
5	396	738	783	44
6	462	756	838	40

[a] The temperature at which the major degradation starts. [b] Since E4 loses only 43% weight at 900 °C, the 50% weight loss temperature is above 900 °C.

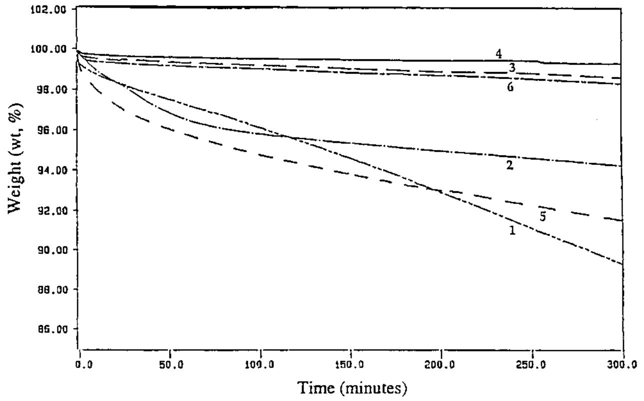


Figure 5. Isothermal studies of VSPSEs (400 °C, in N_2). Curves 1, 2, 3, 4, 5, and 6 correspond to VSPSE 1, 2, 3, 4, 5, and 6, respectively.

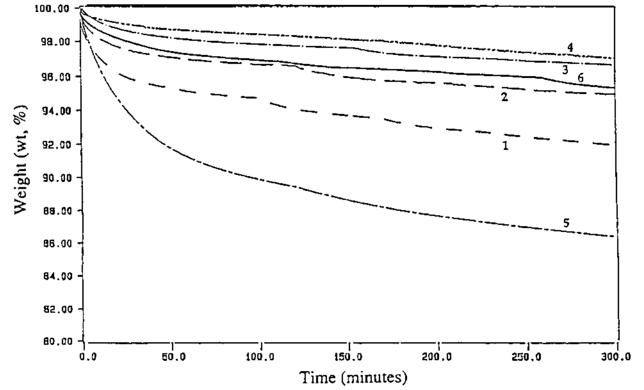


Figure 6. Isothermal studies of VSPSE (400 °C, in air). Curves 1, 2, 3, 4, 5, and 6 correspond to VSPSE 1, 2, 3, 4, 5, and 6, respectively.

One of the most interesting features of the air decomposition curves is the apparent two-step break in the weight loss curves compared to the single step break in nitrogen. This behavior suggests two distinct and separate decomposition pathways in air, with the second one of these occurring at higher temperatures. At this time, it is not possible to present detailed degradation mechanisms for the decomposition of the VSPSE.

Figures 5 and 6 show the isothermal decomposition curves for VSPSE 1 to 6 in nitrogen and air, respectively. All of them are remarkably stable under such conditions. The mass losses summarized in Table 4 range from 0.7% to 10.7% in nitrogen and from 3.0% to 13% in air after 5 h at 400 °C.

These results are unusually low and represent the most thermally stable elastomers reported to date. Previous studies show that 20% mass loss for such elastomers is common.[5,6] We also observed that the isothermal stability for the VSPSE increases from VSPSE 1 to 4 when the vinyl content is

Table 4. Isothermal Weight Loss for VSPSE in Air and Nitrogen Atmosphere After 5 h at 400 °C

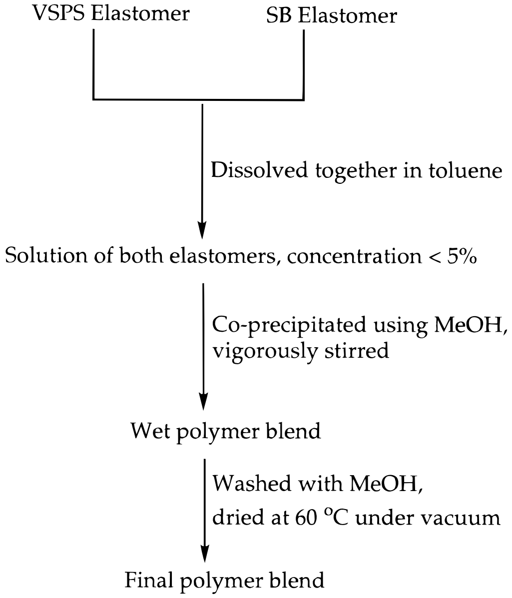
	VSPSE 1	VSPSE 2	VSPSE 3	VSPSE 4	VSPSE 5	VSPSE 6
in nitrogen, %	10.7	5.9	1.5	0.7	8.0	1.8
in air, %	7.9	5.0	3.5	3.0	13	4.6

Table 5. Characterization of Commercial SB Elastomers

SB no.	T_g (°C)	M_w ($\times 10^{-3}$)[a]	styrene content, wt %	1, 2 addition content, wt %
SBR-199	−75	838	5	12
SBR-200	−58	545	23	9
SBR-201	−30	348	45	6
SBS-057	−94	131	30	6
SBS-451	−92	90	28	4

[a] Polystyrene samples were used as standards and chloroform as solvent for GPC measurements.

Scheme 2. Typical Procedure for Polymer Blend Preparation



increased. Some VSPSEs such as 6, 3, and 4 have weight losses even less than 2% in nitrogen and VSPSE 2, 6, 3, and 4 have weight losses less than 5% in air. The most remarkable stability was shown by VSPSE 4, with R = 100% vinyl, which had a weight loss of only 0.7% after 5 h at 400 °C in nitrogen and 3.0% after 5 h at 400 °C in air. When all the dynamic and isothermal TGA studies were compared, VSPSE 4 was consistently the most thermally stable.

Polymer Blends from VSPSE and SBR or SBS. Commercially available SBR and SBS were purified to remove stabilizers and other additives and impurities. These styrene−butadiene rubbers have low glass transition temperatures ranging from −94 to −30 °C and high molecular weights as shown in Table 5.

The weight percentage for 1,2 addition units of poly(1,4-butadiene) was determined using ^{1}H NMR integration of olefinic protons. The 1,2 addition content ranges from 4% to 12% by weight. A modest content of 1,2 addition units is preferred for efficient covulcanization of the blends.

Un-cross-linked polymer blends from VSPSE and SBR or SBS were prepared according to Scheme 2. All the polymer blends listed in Table 6 were prepared. All polymer blends were made either with elastomer 4 or with elastomer 6. A weight ratio of 50 to 50 was used for most polymer blends. In all, a total of ten blend compositions, both un-cross-linked and cross-linked were prepared.

DSC was used to investigate the extent of miscibility for the two constituent polymers in un-cross-linked and cross-linked blends. Table 6 shows the T_g results for un-cross-linked blends and for un-cross-linked individual constituents in these blends. In all cases, two individual unshifted T_gs were observed for VSPSE 4 and 6 blends indicating their lack of miscibility, which is expected for siloxane and hydrocarbon elastomers. Figure 7 shows the DSC results for the un-cross-linked VSPSE4/SBR199 (50/50) blend, which are typical for all un-cross-linked blends.

Table 6. Glass Transition Temperatures of Blends

elastomers and blends	blend composition	T_g, °C[a] un-cross-linked	T_g, °C[a] cross-linked[b]
VSPSE 4		−63	−60
VSPSE 6		−43	−42
SBS 057		−94	−92
SBS 451		−92	−91
SBR 199		−75	−74
SBR 200		−58	−54
SBR 201		−31	−30
VSPSE4/SBS057	50/50	−63, −94	−57, −92
VSPSE4/SBS451	50/50	−63, −92	−57, −91
VSPSE4/SBR199	50/50	−63, −76	−58, −75
VSPSE4/SBR200	50/50	−63, −55	−57
VSPSE4/SBR201	50/50	−65, −28	−59, −26
VSPSE6/SBS057	50/50	−43, −96	−41, −93
VSPSE6/SBS451	50/50	−43, −94	−42, −91
VSPSE6/SBR199	50/50	−43, −76	−41, −74
VSPSE6/SBR200	75/25	−44, −57	−41, −52
VSPSE6/SBR201	50/50	−44, −27	−41, −24

[a] For the blend, the first number in the column corresponds to the T_g of the VSPSE and the second number is the T_g of the hydrocarbon elastomer. [b] Cross-linked with benzoyl peroxide, 1% by weight of the blend.

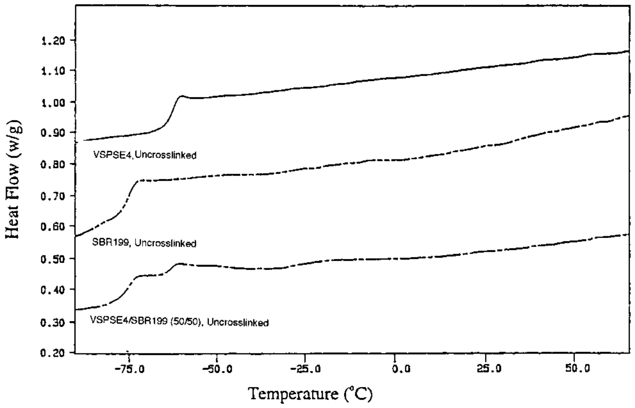


Figure 7. DSC curves for un-cross-linked VSPSE 4, SBR199, and VSPSE4/SBR199 (50/50) blend.

The DSC results for the cross-linked blends are also given in Table 6, which also includes the glass transition temperatures of the individual cross-linked blend constituents. It was observed that cross-linking raised the T_gs of the individual polymers in these blends to some degree but did not enhance substantially the miscibility of the blend. The principal effect of cross-linking on the T_g was the broadening of the T_gs of the individual constituents in the blends, which could be due to some degree of phase mixing. This broadening effect is seen in Figure 8. This could be caused by cross-linking some of the chains of the individual components together. The VSPSE4/SBR200 blend shows only one T_g after cross-linking due to the broadening of glass transition peaks. This single T_g was observed because the T_gs of the individual un-cross-linked constituents were very close to each other.

In order to determine if there were any synergistic effect of blending on the thermal-oxidative behavior of the blends, TGA experiments were carried out for un-cross-linked and cross-

Table 7. TGA Data Summary of Un-Cross-Linked Polymer Blends (15 °C/min)

	onset of degradation T_d (°C)[a]		temp for 50% wt loss (°C)		end of major degradation (°C)		% residue (900 °C)	
VSPSE no.	N_2	air	N_2	air	N_2	air	N_2	air
E4/SBR199	370	361	592	485	659	674	32	7
E4/SBR200	363	352	601	505	658	774	34	20
E4/SBR201	365	364	507	535	642	750	20	23
E4/SBS057	365	332	498	492	642	745	9	19
E4/SBS451	376	379	525	525	646	663	26	26
E6/SBR199	359	358	509	510	652	745	9	19
E6/SBR200	384	377	513	624	665	801	12	26
E6/SBR201	371	344	496	552	642	740	10	18
E6/SBS057	386	330	514	510	650	730	11	15
E6/SBS451	384	359	527	571	645	742	14	16

[a] The temperature at which the major degradation starts.

Table 8. TGA Data Summary of Cross-Linked Polymer Blends (15 °C/min)

	onset of degradation T_d (°C)[a]		temp for 50% wt loss (°C)		end of major degradation (°C)		% residue (900 °C)	
VSPSE no.	N_2	air	N_2	air	N_2	air	N_2	air
E4/SBR199	380	340	567	603	651	739	27	25
E4/SBR200	363	314	495	602	643	746	13	24
E4/SBR201	369	301	489	497	640	693	16	15
E4/SBS057	380	276	601	547	656	761	36	25
E4/SBS451	383	299	588	511	661	741	32	21
E6/SBR199	379	347	528	511	655	734	13	13
E6/SBR200	371	334	597	662	661	786	27	30
E6/SBR201	356	319	476	478	634	717	6	13
E6/SBS057	375	313	512	537	648	736	11	16
E6/SBS451	373	315	504	509	641	754	11	17

[a] The temperature at which the major degradation starts.

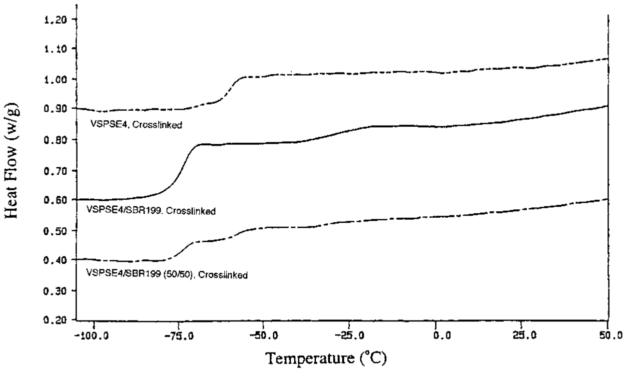


Figure 8. DSC curves for cross-linked VSPSE4, SBR199, and VSPSE4/SBR199 (50/50) blend.

linked blends in both nitrogen and air atmosphere. The results for un-cross-linked blends are summarized in Table 7.

In nitrogen atmosphere, a two-step degradation was generally observed. The first step corresponded to the degradation of the SB elastomer and the second step corresponded to the VSPSE degradation. In the case of decomposition in air, a three-step degradation was observed in which the first step corresponded to SB elastomer degradation and the other two steps corresponded to the decomposition of the VSPSE. Our data indicated that a "rule of mixtures" behavior was observed for all un-cross-linked blends based on TGA experiments.

The cross-linked blends were also characterized by TGA, and these results are listed in Table 8.

The degradation temperatures in air for the cross-linked blends are lower than those of the un-cross-linked blends. It was also noticed that some blends have higher residues while others have lower residues after cross-linking. Significant increases in the residue amount are observed for VSPSE4/SBS057 blends in both air and nitrogen atmosphere after cross-linking. This effect cannot be explained at this time since there does not appear to be a consistent behavior of the thermal degradation of the blends either before or after cross-linking.

Conclusions

VSPSEs were successfully synthesized through the disilanol–diaminosilane polycondensation route by using carefully purified starting materials. They were characterized by GPC, DSC, TGA and ^{29}Si NMR spectroscopy. The results were consistent with the presence of an alternating structure in these polymers. The VSPSEs which were obtained in high yields and with high molecular weights can best be described as stiff gums. They had low T_gs ranging from −26 to −63 °C and exhibited the highest degree of thermal and oxidative stability that has been observed so far for any elastomers. The char yield upon pyrolysis increased when the vinyl content increased. Substitution of a methyl group with a phenyl group also increased the final TGA residues. The isothermal weight loss properties for these VSPSEs are exceptional. The 100% vinyl-containing VSPSEs had a weight loss of only 0.7% after 5 h at 400 °C in nitrogen. Polymer blends were prepared from the VSPEs and SBR or SBS with and without cross-linking. The blends showed no evidence of miscibility. "Rule of mixtures" behavior was observed for the thermal degradation of the blends of VSPSEs and either SBR or SBS.

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