ARTICLE

# Transparent Room Temperature Cured Elastomers Based on Bisphenol A

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**ABSTRACT**: The synthesis of a divinyl-terminated resin from commercially available bisphenol A and polymerization with silane containing compounds utilizing a room temperature hydrosilylation reaction is demonstrated. The transparent, clear polymers exhibit excellent thermal and oxidative stability while maintaining elastomeric properties and good hardness. These

**INTRODUCTION** Silicone containing polymers exhibit superior flame resistant properties when compared with their hydrocarbon counterparts while still retaining good elastomeric properties over a wide temperature range. Quantum leaps in new technology have outpaced the current materials available in a wide range of applications especially in the modern aerospace, marine, energy, and electrical industries.<sup>1</sup> Two vital requirements of a good elastomeric material for these applications in extreme environments are excellent toughness and wear as well as good thermal properties up to several hundred degrees. Siloxane polymers have shown some promise as coatings, paints and adhesives because of their flexibility, toughness, and heat-resistant properties but they typically exhibit quite low glass transition temperatures  $(T_g)$  and are not suited for long term use over 200 °C.<sup>1</sup>

Efforts have been focused on increasing the toughness and the thermal stability at higher temperatures of elastomeric materials. This can be achieved by the incorporation of aromatic units<sup>2</sup> within the polymer backbone but can significantly add to the cost of the resin limiting it to specialty applications.<sup>3</sup> To circumvent this drawback, modification of the reaction chemistry to produce a liquid divinylsilane terminated resin from a bisphenol using commodity chemicals (e.g., bisphenol A) has been demonstrated.<sup>2</sup> These divinyl terminated monomers are then converted to a linear or crosslinked polymer using hydrosilylation chemistry, Scheme 1, in the presence of a transition metal catalyst<sup>4</sup> and a multiple Si—H containing compound.<sup>5–9</sup> In this reaction, the Pt catalyst facilitates the addition of the Si—H to the vinyl group.

polymers also have the ability to be dyed any color in the spectrum. Published 2013.<sup> $\dagger$ </sup> J. Polym. Sci., Part A: Polym. Chem. **2014**, *52*, 523–526

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Depending on the number of Si—H groups in the curing additive, a linear to highly crosslinked polymer can be formed.

A liquid divinyl terminated resin system with the ability to control the crosslinking density while still being easily processed into transparent shaped composites or thin elastomeric films using a cost effective technique such as resin transfer molding or by spray coating at ambient temperatures would be beneficial. Another added benefit of the polymer's transparent nature is the ability to dye to any color in the spectrum.

In this article, we will discuss the synthesis, polymerization, and physical properties of a liquid divinylsilane-terminated aromatic resin system based on bisphenol A and show the conversion of this resin to a transparent polymer via a room temperature hydrosilylation reaction.

#### **EXPERIMENTAL**

All starting materials were of reagent grade and used without further purification. The divinyl-terminated bisphenol A based resin was prepared using a modified procedure from Bublewitz et al.<sup>3</sup> Differential scanning calorimetric (DSC) analysis was performed on a TA Instruments DSC 2920 modulated thermal analyzer at a heating rate of 10 °C min<sup>-1</sup> and a nitrogen purge of 100 cm<sup>3</sup> min<sup>-1</sup>. The glass  $T_g$  was reported as the temperature centered at the midpoint between the linear baselines of a DSC scan. Thermogravimetric analysis (TGA) was performed on a TA Instruments TGA Q600 at a heating rate of 10 °C min<sup>-1</sup> under a nitrogen or air purge of 100 cm<sup>3</sup> min<sup>-1</sup>. Infrared (IR) spectra were

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**SCHEME 1** General reaction of a divinylsilane compound with a Si–H compound.

recorded as films on NaCl disks using a Nicolet iS50 FTIR spectrometer. NMR was performed on a Brüker ADVANCE 300 spectrometer. The Shore A hardness was measured using a PTC Instruments Model 306L durometer.

Synthesis of the Divinyl-Terminated Bisphenol A Resin 1 To a flame dried 1000 mL, three necked flask fitted with a condenser and a nitrogen inlet were added bisphenol A 2 (40.0 g, 175 mmol), triethylamine (122 mL, 88.6 g, 875 mmol) and anhydrous acetone (300 mL). Vinyl(chlorodimethyl)silane 3 (57.0 mL, 50.4 g, 419 mmol) was added slowly via syringe so as to keep the solution under gentle reflux. During addition of 3 a voluminous white precipitate of NEt<sub>3</sub>H<sup>+</sup>Cl<sup>-</sup> was formed. The resulting mixture was stirred under ambient conditions for 1 h and refluxed at 80 °C for 16 h. The product mixture was cooled to 0 °C and the precipitate was filtered under vacuum and washed with cold hexanes. The solvents were removed by heating at 120 °C for several hours. The mixture was distilled resulting in a pale yellow oil **1** (59.7 g, 86%). B.p: 176 °C at 98 mTorr. <sup>1</sup>H-NMR (300 MHz,  $CDCl_3$ ):  $\delta$  7.05 (d, 4H, aromatic-H), 6.71 (d, 4H, aromatic-H), 6.23 (dd, 2H, alkene-H), 6.04 (dd, 2H, alkene-H), 5.84 (dd, 2H, alkene-H), 1.60 (s, 6H, aliphatic-H), and 0.31 (s, 12H, Si-CH<sub>3</sub>). <sup>13</sup>C-NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  152.7, 143.8, 137.0, 133.7, 127.6, 119.1 (aromatic, alkene), 41.69, 31.06 (alkane), -1.480 (Si-CH<sub>3</sub>). IR [cm<sup>-1</sup>]:  $\lambda$  3051 (C=CH), 2966 (CH=CH<sub>2</sub>, CH<sub>3</sub>), 1606 (C=C), 1508 (C=CH), 1406 (CH=CH<sub>2</sub>), 1260 (Si-CH), 1176 (Si-O-CH<sub>3</sub>), 1011 (aromatic), 920 (Si-CH=CH<sub>2</sub>), 837 (Si-O-CH), 788 (aromatic), 708 (CH=CH<sub>2</sub>).

# Polymerization of Divinyl Terminated Resin 1 with Tetrakis(dimethylsiloxy)silane and p-

## Bis(dimethylsilyl)benzene with a Pt Catalyst

A 50:50 TMSS/DMSB mixture was reacted with 1 by the following procedure: To the divinyl terminated resin 1 (0.502 g, 1.26 mmol) in 0.5 mL of anhydrous toluene was added 10 µL of a platinum-cyclovinylmethylsiloxane complex in xylene with adequate stirring. Tetrakis(dimethylsiloxy)silane (0.12 mL, 0.104 g, 0.316 mmol) and p-bis(dimethylsilyl)benzene (0.14 mL, 0.123 g, 0.633 mmol) were added simultaneously. The reaction mixture was stirred vigorously and transferred to a metal pan treated with a Teflon mold release. The pan was placed onto a metal block to act as a heat sink to allow the reaction not to overheat and to minimize bubble formation. This clear resin can be dyed any color by the incorporation of the appropriate dye in 1 to 10 wt % into the toluene solution before the catalyst is added and transferred to the appropriate mold. After 16 h at room temperature, the polymer 4 was heated at 100 °C for 2 h. Selected samples were postcured to 300 °C for 1 h before their properties were determined.



SCHEME 2 Synthesis of divinyl silane resin 1 and polymer 4.

#### **RESULTS AND DISCUSSION**

Divinylsilane-terminated resin **1** was prepared by reacting bisphenol A 2, chlorodimethylvinylsilane 3 and triethylamine in dry acetone to afford 1 followed by distillation to afford a pale yellow oil in 86% yield (Scheme 2). Resin 1 is readily soluble in most organic solvents due to the presence of aliphatic groups in the system and exists as a nonviscous liquid at ambient temperature. Conversion of 1 to a linear or networked polymer occurs at ambient temperature in the presence of any compound containing at least two Si-H moieties and a Pt catalyst using typihydrosilylation chemistry.<sup>10</sup> In this case, either cal tetrakis(dimethylsiloxy)silane (TMSS) or p-dimethylsilylbenzene (DMSB; Fig. 1) were reacted with 1 in varying ratios in the presence of a platinum-cyclovinylmethylsiloxane complex in xylene to facilitate the formation of transparent polymeric material 4. The overall molar ratio of silicone vinyl groups to Si-H groups is 1:1 so that all vinyl groups were reacted.

A series of samples were prepared with varying ratios of the silane (Si—H) containing compounds TMSS and DMSB. In a typical polymerization reaction, a selected amount of the divinyl terminated resin **1** was placed in a minimal amount of toluene and the Pt catalyst was added with adequate stirring. To this solution were added TDMSS and DMSB in varying



**FIGURE 1** Curing additives tetrakis-(dimethylsiloxy)silane (TMSS) or *p*-dimethyl-silylbenzene (DMSB).



**FIGURE 2** Polymers **4c** (left) and **4c** dyed orange with 10 wt % of 9, 10-bis(phenylethynyl)-anthracene (right). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

concentrations with good stirring. The solutions were transferred to a mold and placed on a metal block to act as a heat sink so the reaction would proceed at a slower rate and minimize bubble formation. After 16 h, the reaction was completed and the transparent, bubble free polymers were removed from the mold and the resulting polymer **4** was postcured at 100 °C for 2 h to finish the cure and remove any remaining toluene and selected samples were post-cured at 300 °C for 1 h. Additionally, **4c** was dyed by addition of 10 wt % of the orange dye 9, 10-bis(phenylethynyl)anthracene (Fig. 2).

Figure 3 shows the <sup>1</sup>H-NMR spectra for **4e** in CDCl<sub>3</sub>, which is the 1:1 molar ratio of **1** to DMSB. What we see in this spectra is the absence of the vinyl peaks from **1**, which appear between 6.2 and 5.8 and the appearance of the  $-CH_2-CH_2-$  peaks from the hydrosilylated product as a multiplet centered at 0.7 ppm. All other peaks from **4e** were present in the spectra.

The transparent elastomeric polymer **4b** prepared from **1** and 75:25 TMSS/DMSB displayed a two-stage glass  $T_{g}$  of approxi-

mately -12 and -1 °C while **4c** displayed  $T_g$ 's of approximately -16 and 17 °C. (Fig. 4) At both extremes, polymers with 100% of the TMSS curing additive, 4a, exhibited an elastomeric constancy but were brittle when attempting to bend the samples while the polymeric elastomers **4e** prepared from 1 and 100% of DMSB showed a very tacky semi-liquid consistency. The  $T_{g}$ 's for all of the polymeric compositions appeared between -14 and 16 °C, Table 1, with the magnitude of the transitions varying based on the ratio of TMSS to DMSB. The nature of the appearance to two distant  $T_{g}$ 's can be explained by a phase separation of the aromatic and silicone parts of the polymer. As more of the DMSB was added (4b-4d) to the samples they appeared more mechanically robust due to the incorporation of the aromatic units. DSC analysis of the polymers did not show any visible exothermic transitions indicating that the polymerization reaction was complete upon heating to 100 °C. Additional postcuring to 200 or 300 °C had no measurable impact on the  $T_{\rm g}$  of the resulting polymer.

Examining the elastic properties of polymer **4**, we subjected the void free flat samples to a Shore A durometer. The results are reported in Table 1. We see that the hardness decreases when more of the DMSB is added relative to the TMSS. These results are expected since the addition of DMSB reduces the crosslinking density of the resulting polymer and thus making it more elastic. We were unable to obtain a reliable hardness measurement for sample **4e** due to the tacky consistency of the polymer. From these Shore A measurements, we can calculate a Young's modulus for **4a–4d**, which vary from around 1–2.7 MPa. These values are similar to those noted for other polymeric materials such as polypropylene.

The thermal and oxidative stability of **4** was assessed by TGA analyses.<sup>11</sup> Figure 5 shows data for **4c** as a representative example of the thermal and oxidative stability. When **1** and



**FIGURE 3** <sup>1</sup>H-NMR of linear polymer **4e**. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



**FIGURE 4** DSC curves showing the glass  $T_g$  of polymers **4b** (Top plot) and (Bottom plot) **4c**.

varying ratios of TMSS and DMSB were cured to a maximum temperature of 100 °C under inert conditions, the resulting networked polymers **4a–e** showed weight retention of 95% between 390 and 420 °C and overall char yields varied from 58 to 15% for **4a–4e**, respectively, upon heating to 1000 °C under a nitrogen atmosphere. Only marginal improvement in the thermal stability (~10 °C) was noted upon postcuring to 300 °C. A sample of **4c** exhibited a weight retention of 95% at 350 °C and an overall residue of 35% remained upon heating to 1000 °C under a flow of air. Similar stability results were noted for **4a–b** and **4d–e** with all samples exhibiting char yields ranging from 40 to 30%, respectively.

The hydrolytic stability of polymer **4** was assessed by soaking polymer **4a** and **4c** in water at 25 and 100 °C. After soaking at 25 °C for 4 days, sample **4a** exhibited little noticeable visible changes and absorbed no detectable water and the Shore A hardness was identical to unsoaked materials. However, **4c** turned opaque and absorbed 3% water and the hardness changed from 60 to 50. At 100 °C overnight, both samples of **4a** and **4c** turned opaque and became very rubbery and exhibited a weight loss of 5 and 9%, respectively, and the hardness dropped significantly. This can be attributed to the hydrolysis of the Si–O bond at high temperatures and high humidity with **4a** being more stable due to the higher crosslinking density which makes the water molecules harder to reach the Si–O bond.

#### TABLE 1 Data for Polymer 4

	TMSS (mol %)	DMSB (mol %)	<i>T</i> g (°C)	Shore A Hardness	Young's Modulus (MPa)
4a	100	0	-14/-2	70	2.7
4b	75	25	-12/-1	60	2.2
4c	50	50	-16/17	60	2.2
4d	25	75	-12/-3	30	1.1
4e	0	100	-12/16	n/a	n/a



FIGURE 5 TGA thermograms of polymer 4c cured to 100  $^\circ\text{C}$  for 2 h: under N\_2 (A) and air (B).

#### CONCLUSIONS

In summary, the liquid properties of monomer **1** along with the ability to cure at room temperature to a transparent polymer with good hardness and excellent thermal and oxidative stability demonstrate the potential of the polymers for a variety of applications. This combination of physical properties may allow the use of polymers produced from **1** in coatings, adhesives, and optics and potentially as a spinnable fiber for textile applications. Additionally, depending on the reactive Si—H sites in the silane containing curing additive used in the hydrosilylation reaction, elastomeric materials with varying degrees of crosslinking density and hydrolytic stability can be readily obtained. The procedure to produce resin **1** has the potential to be applicable to a variety of bisphenols. In subsequent articles, we will explore the physical and mechanical properties of **1** and other silanes with varying structure.

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