Synthesis and properties of an oligomeric divinyl-terminated aromatic ether containing resin

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The synthesis of a novel oligomeric divinyl-terminated aromatic ether containing resin and polymerization with silane containing compounds utilizing a hydrosilylation reaction is demonstrated. The transparent, clear polymers exhibit high thermal and oxidative stability while exhibiting elastomeric and plastic properties depending on the curing temperature and curing agent.

Introduction

High-temperature polymers are an important class of materials that offers a variety of opportunities for new technological applications especially in the modern aerospace, marine, energy, and electrical industries.[1] Two important requirements of elastomeric materials for these applications in extreme environments are good thermal stability up to several hundred degrees and the materials ability to maintain good structural integrity at elevated temperatures. Polysiloxanes have been shown to be good candidates as high-temperature elastomers because of their flexible and heat-resistant backbone.[1] However, it is sometimes difficult to obtain tough materials based solely on the siloxane backbone.

The development of durable high-temperature materials requires the incorporation of thermally stable aromatic or heteroaromatic structural units within the backbone of a polymeric system.[2–6] By designing a polymeric system with these highly stable structural units and with flexible linkages, the desired thermo-oxidative stability and structural properties can be achieved. A simple way to form such systems is by utilizing a modified Ullmann synthesis for the preparation of aryl containing ethers, developed in our laboratory and extensively studied for thermosetting systems.[7–10] This method allows for the formation of difunctional hydroxyl-terminated aryl ether oligomers of variable length and composition. We have endcapped the hydroxyl-terminated oligomers with a vinyl silane group to obtain liquid monomers. The divinyl-terminated monomers are then converted to a linear or crosslinked polymer using hydrosilylation chemistry in the presence of a transition metal catalyst and a multiple Si–H containing compound.

By exploiting this methodology, the liquid divinyl-terminated resin systems can be easily processed into shaped composite components or thin elastomeric films utilizing a cost effective technique such as resin transfer molding or by spray coating at ambient temperatures. In essence, by employing hydrosilylation chemistry, the clear resins are converted to a linear or network system under ambient conditions.

In this paper, we will discuss the synthesis, polymerization, and thermal stability of an oligomeric divinyl-terminated aromatic ether containing resin system and show the conversion of this resin to a transparent polymer *via* a room temperature hydrosilylation reaction.

Experimental

General information

All starting materials were of reagent grade and used without further purification. Differential scanning calorimetric (DSC) analysis was performed on a TA Instruments DSC 2920 modulated thermal analyzer at a heating rate of 10 °C min^{-1} and a nitrogen purge of 50 $\mathrm{cm}^3\ \mathrm{min}^{-1}$. The glass transition temperature (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 Q50 at a heating rate of 10 °C min^{-1} under a nitrogen or air purge of 50 $\mathrm{cm}^3\ \mathrm{min}^{-1}$. Infrared (IR) spectra were recorded as films on NaCl disks using a Nicolet Magna FTIR 750 spectrometer. ^{1}H-NMR was performed on a Brüker ADVANCE 300 spectrometer.

Synthesis of the hydroxyl-terminated oligomeric aromatic ether 4

To a 250 mL three-necked flask fitted with a thermometer, a Dean–Stark trap with condenser, and an argon inlet were added bisphenol A **2** (30.2 g, 132 mmol), 4,4′-difluorobenzophenone **3** (14.4 g, 66.0 mmol), toluene (20 mL) and *N*,*N*-dimethylformamide (200 mL). The resulting mixture was degassed thoroughly with argon for 10 min and K_2CO_3 (27.3 g, 198 mmol) was added in one portion. The reaction mixture was then refluxed at 135–145 °C for 12 h. The water formed in the reaction was removed by azeotropic distillation. The toluene was then removed by distillation and the mixture was cooled to ambient temperature. Water (300 mL) was then added to the reaction mixture. At this point, the product mixture was slightly basic and 2 M HCl (300 mL) was added. The mixture was then extracted twice with ether (100 mL) and the combined ether layers were washed with 2 M HCl (100 mL) and water (100 mL) until neutral. Carbon black (2 g) was added and the ether extract was filtered through a short plug of silica gel to remove the insoluble components. The solvent was removed at reduced

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pressure yielding a yellow glassy solid, which was vacuum dried to afford the hydroxyl-terminated oligomer **4** ($n \cong 1$, 16.1 g, 97%). ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.77 (d, aromatic-H), 7.71 (dd, aromatic-H), 7.32 (dd, aromatic-H), 7.28–7.21 (m, aromatic-H), 7.05–6.94 (m, aromatic-H), 1.75–1.68 (m, CH_3). IR [cm^{-1}]: λ 3040 (C=CH), 2970 (CH_3), 2232 (CN), 1650 (C=O), 1592 (C=C), 1498 (aromatic), 1308 (aromatic), 1279 (C–O), 1246 (CH_3), 1160 (C–O), 928 (C–O), 837 (aromatic).

Synthesis of the divinyl-terminated oligomeric aromatic ether resin 1

To a 100 mL three-necked flask fitted with a thermometer, a Dean–Stark trap with condenser, and a nitrogen inlet were added the hydroxyl-terminated oligomer **4** (10.0 g, 15.7 mmol), triethylamine (4.72 ml, 33.9 mmol) and anhydrous tetrahydrofuran (100 mL). The reaction mixture was cooled by means of an ice bath and vinyl(chlorodimethyl)silane **5** (4.68 ml, 33.1 mmol) was added dropwise. The resulting mixture was stirred under ambient conditions for 1 h. The product mixture was then poured into water and extracted with diethyl ether. After removing the solvent at reduced pressure, the resulting oil was dissolved in 1 : 1 CH_2Cl_2–hexane, dried over anhydrous Na_2SO_4, and filtered through a silica plug. The solvent was removed *in vacuo* and the clear oil was subjected to a full vacuum to yield **1** (12.0 g, 95%). ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.78 (d, aromatic-H), 7.73 (dd, aromatic-H), 7.32 (dd, aromatic-H), 7.27–7.23 (m, aromatic-H), 7.06–6.95 (m, aromatic-H), 6.27 (dd, alkene-H), 6.05 (dd, alkene-H), 5.75 (dd, alkene-H), 1.77–1.68 (m, CH_3). IR [cm^{-1}]: λ 3052 (C=CH), 2967 (CH_3), 1654 (C=O), 1593 (C=C), 1500 (aromatic), 1242 (C–O), 1171 (C–O), 834 (aromatic).

Polymerization of divinyl-terminated oligomeric aromatic ether resin 1 with tetrakis(dimethylsiloxy)silane (2 : 1 ratio) with a Pt catalyst

Divinyl-terminated resin **1** (0.29 g, 0.361 mmol) and tetrakis-(dimethylsiloxy)silane (0.07 mL, 0.059 g, 0.180 mmol) were mixed in toluene (1 mL). The reaction mixture was heated to 70 °C to ensure dissolution of the monomer and crosslinker silane compound. The resulting solution was cooled to about 0 °C, and 0.1 µl of a platinum cyclovinylmethylsiloxane complex in xylene was added with adequate stirring followed by immediate transfer to a silicone mold. Gelation occurred under ambient temperature conditions within 60 s and the transparent polymer **6b** was subsequently post-cured at 100 °C for 4 h and at 300 °C for 1 h.

Polymerization of divinyl-terminated oligomeric aromatic ether resin 1 with 1,1,3,3-tetramethyldisiloxane (1 : 1 ratio) with a Pt catalyst

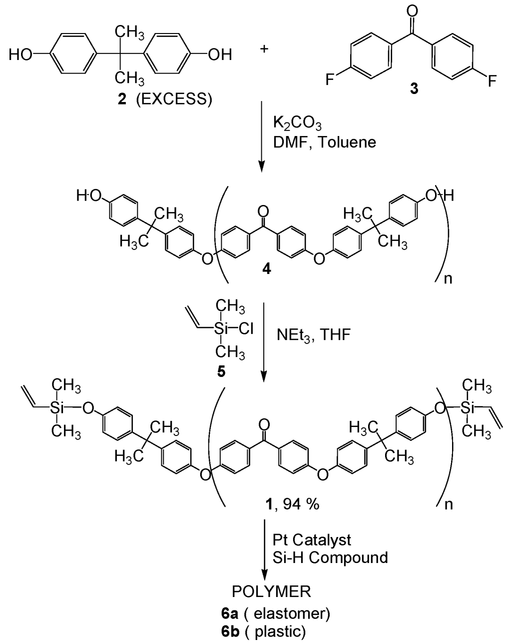
Divinyl-terminated resin **1** (0.54 g, 0.672 mmol) and 1,1,3,3-tetramethyldisiloxane (0.12 mL, 0.09 g, 0.672 mmol) were mixed in toluene (1 mL). The mixture was heated to 70 °C to ensure dissolution of the monomer and 1,1,3,3-tetramethyldisiloxane. The resulting solution was cooled to about 0 °C and 0.1 µl of a platinum cyclovinylmethylsiloxane complex in xylene was added with adequate stirring followed by immediate transfer to a silicone mold. Gelation occurred under ambient temperature conditions within 60 s and the transparent polymer **6a** was subsequently post-cured at 100 °C for 4 h and at 300 °C for 1 h.

Results and discussion

The hydroxyl-terminated oligomer **4** was prepared by reacting bisphenol A **2**, 4,4′-difluorobenzophenone **3**, and K_2CO_3 in the presence of *N*,*N*-dimethylformamide (DMF) and toluene (Scheme 1). Oligomer **4** was isolated as a yellow glassy solid in 97% yield. During the reaction, water that formed as a by-product was removed by azeotropic distillation at 135–145 °C. Oligomer **4** was further reacted with chlorodimethylvinylsilane **5** and triethylamine in dry tetrahydrofuran (THF) to afford **1** as a clear oil in 95% yield. The length of the aromatic spacer between the terminal vinyl silane groups can be varied by changing the ratio between **2** (excess) and **3**. The reactions producing **4** and **1** were monitored by infrared spectroscopy and ^{1}H-NMR.

Oligomer **1** is readily soluble in most organic solvents due to the existence of aliphatic groups in the system. 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 typical hydrosilylation chemistry.[11] In this case, either 1,1,3,3-tetramethyldisiloxane or tetrakis(dimethylsiloxy)silane was reacted with **1** in combination with a platinum cyclovinylmethylsiloxane complex in xylene to facilitate the formation of transparent polymeric material **6** (Fig. 1).

In a typical polymerization reaction, a selected ratio of the divinyl-terminated resin **1** to the silane (Si–H) containing compound was dissolved in a minimal amount of toluene. The mixture was heated to dissolve the monomer **1** and the Si–H containing compound and then cooled to about 0 °C before the addition of the catalyst. Consolidation to an elastomer or plastic was achieved by the addition of 0.1 µl of the Pt catalyst with



Scheme 1 Synthesis of divinyl silane resin **1** and polymer **6**.

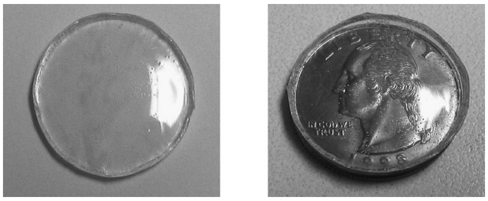


Fig. 1 Photographs of the cured transparent polymer **6b**.

adequate stirring followed by pouring into a mold and allowing the homogenous mixture to react under ambient conditions. The dissolution of **1** and the silane containing compound in toluene proved necessary due to the chemical incompatibility of the monomer with the silane containing compound. After gelation at ambient temperature had occurred, the resulting polymer **6** was post-cured at 100 °C for 4 h and at 300 °C for 1 h. During the post-cure heat treatment, volatilization of the toluene occurred affording a void-free polymer. The transparent elastomeric polymer **6a** prepared from **1** and 1,1,3,3-tetramethyldisiloxane displayed a glass transition temperature (T_g) of approximately −17 °C (Fig. 2, top). A polymeric plastic **6b** (Fig. 2, bottom) prepared from **1** and tetrakis(dimethylsiloxy)silane showed a T_g of around 60 °C. Additionally, DSC analysis of the polymers did not show any visible exothermic transitions and it was assumed that the polymerization reaction was complete.

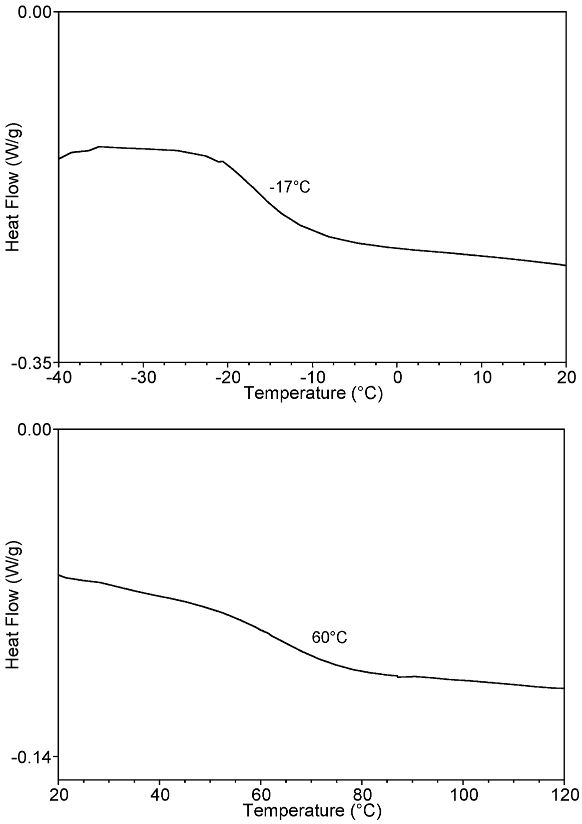


Fig. 2 DSC curves showing the glass transition temperatures of polymers (top plot) **6a** and (bottom plot) **6b**.

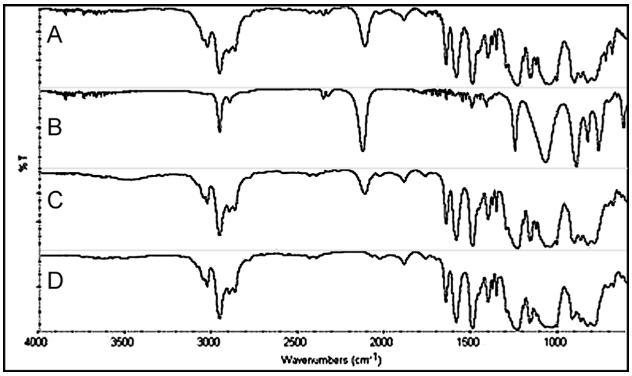


Fig. 3 FTIR spectra of monomer **1** and 1,1,3,3-tetramethyldisiloxane in a 1 : 1 ratio cured in the presence of a Pt catalyst. Initial mixing (A); 1,1,3,3-tetramethyldisiloxane (B); reaction at room temperature for 14 h (C); and reaction at 100 °C for 1 h (D).

IR analysis was used to monitor and to determine the extent of the polymerization reactions forming **6**. Fig. 3 shows the spectra of thin films of **6a** formed from reaction of monomer **1** and 1,1,3,3-tetramethyldisiloxane in a 1 : 1 molar ratio in the presence of a Pt catalyst. Plot A is a spectrum taken immediately after mixing **1**, 1,1,3,3-tetramethyldisiloxane and Pt catalyst. As a comparison, plot B is the spectrum of 1,1,3,3-tetramethyldisiloxane showing the Si–H peak at approximately 2100 cm^{-1}. When the polymerization mixture (plot C) was allowed to sit at room temperature overnight (14 h), the peak attributed to Si–H was considerably diminished. Following heating to 100 °C for 1 h, the Si–H peak was absent (plot D) and the polymerization reaction was assumed to be complete.

The thermal and oxidative stability of **6** was assessed by TGA analyses (Fig. 4). When **1** and tetrakis(dimethylsiloxy)silane were cured in the presence of 0.1 μl of a Pt catalyst at up to a maximum temperature of 300 °C under inert conditions, the resulting networked polymer **6b** showed weight retention of 95% at 430 °C and an overall char yield of 71% upon heating to 1000 °C under a nitrogen atmosphere. A sample of **6b** exhibited a weight retention of 95% at 470 °C and an overall residue of 40% remained upon heating to 1000 °C under a flow of air. Another sample of **6b** that was post-cured to 400 °C for 1 h displayed a weight retention 95% at 495 and 490 °C when heated under nitrogen and air atmospheres, respectively. The post-cured **6b**

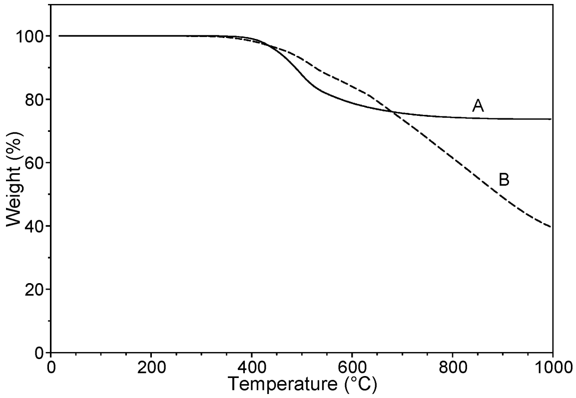


Fig. 4 TGA thermograms of thermoset **6b** post-cured to 300 °C for 1 h: under N_2 (A) and air (B).

exhibited a similar char yield as the 300 °C cured samples, when heated to 1000 °C.

Conclusion

In summary, the liquid properties of monomer **1** along with the prospect of a room temperature polymeric conversion are important features of this new resin. These properties may allow the use of the clear divinyl-terminated aromatic ether containing resin **1** in a wide variety of applications including coatings, adhesives, optics, and potentially as a matrix resin in structural components. Based on the quantity of the reactants **2** and **3** used in the synthesis of **1**, it may be possible to control the flexibility, rigidity, T_g, and other physical properties of the resulting hydrosilylated polymer **6** without severely compromising the thermal and oxidative stability. Additionally, depending on the reactive Si–H sites in the silane containing compound used in the hydrosilylation reaction, either plastic or elastomeric materials can be readily obtained. The procedure to produce oligomer **4** has the potential to be applicable to a variety of bisphenols and dihaloaromatic compounds. In subsequent papers, we will explore the physical and mechanical properties of **6** and other resins produced from different bisphenols.

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