

## High Refractive Index Thermally Stable Phenoxyphenyl and Phenylthiophenyl Silicones for Light-Emitting Diode Applications

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**ABSTRACT:** Creating high refractive index (RI) thermally stable polymers for encapsulating high-brightness light-emitting diodes (LEDs) remains a challenge and is an opportunity for improving LED efficiencies. The best previously reported RI for a 200°C heat stable encapsulant for LEDs is 1.56. Here, we report the use of novel phenoxyphenyl and phenylthiophenyl silicone monomers to give fully formulated encapsulants with RIs above 1.60. These liquid dispensed encapsulants are highly heat stable, showing little change in optical properties after heat aging at 200°C in air for seven weeks, and were also little changed after cycling between -10°C to 85°C over 6 months. Phenoxyphenyl(phenyl) dimethoxysilane and phenylthiophenyl(phenyl) dimethoxysilane monomers were prepared via Grignard reactions. The resulting monomers were copolymerized with commercial silicone monomers and incorporated into hydrosilation-based thermosets designed for use as LED encapsulants. RIs for the cured polymers were 1.60 at 633 nm (1.62 at 450 nm) for the phenoxyphenyl ether system and 1.62 at 633 nm (1.65 at 450 nm) for the phenylthiophenyl ether system. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 39824.

**KEYWORDS:** optical and photovoltaic applications; optical properties; packaging; properties and characterization; thermosets

Received 22 May 2013; accepted 7 August 2013

DOI: 10.1002/app.39824

### INTRODUCTION

High brightness light-emitting diodes (HBLED) based on GaN semiconductors are expected to replace traditional incandescent and fluorescent lighting as the technology matures and achieves a lower cost per lumen. To improve the cost per lumen for solid-state HBLEDs, encapsulants with the highest possible refractive index (RI) can enable the extraction of more light from the GaN surface. This is due to the effect of total internal reflection when light crosses from a region of high RI (GaN  $\sim$ 2.5) to a region of low RI (typical encapsulants  $\sim$ 1.44). There are additional losses due to the RI mismatch between the encapsulant and the phosphor materials which are used to produce a white output spectrum. While many chemistries can achieve RIs of 1.5–1.70,<sup>1–6</sup> which might enable 5–10% more light output, no high RI materials have met the combined conditions of high heat stability, high light flux stability, room temperature liquid dispensing, and reasonable cost that manufacturers require for HBLEDs. Methyl phenyl silicone thermosets, with a RI of 1.41–1.53, are the current industry standard and to date are the only systems which can tolerate high heat and high light flux for the anticipated 50,000 h lifetimes of a HBLED. Employing phenyl groups to raise the RI of the silicone polymers to a range of 1.53–1.57 has

been done with silicone encapsulants,<sup>1,7</sup> but has achieved little market success for HBLEDs due to issues of reliability, heat-resistance, and a drop-off in optical properties.

Many of today's LEDs are encapsulated via liquid dispensing followed by a thermal cure cycle of the encapsulant. This requires a solvent-free liquid formulation, which places major constraints on the types of chemistry that can be used, particularly with respect to achieving a high RI. The additional major requirements are optical clarity and extremely robust heat and light stability. A transmittance of greater than 90%, a heat stability at 200°C of several weeks, and a light flux stability at 1 W/mm<sup>2</sup> at 450 nm are typical test parameters. We have developed new silicone polymer thermosets with RIs from 1.60 to 1.65 which can be dispensed as liquids and can meet the stringent optical, heat, and light flux requirements of LED manufacturers. We have found that the use of phenyl ether groups allows for silicones with high RIs while readily maintaining a liquid state in the formulations.

The addition of phenyl groups to silicones has long been used to raise the RI for optical applications. However, pure diphenylsiloxane polymer is a solid which precludes its use as the major component of a LED encapsulant. Diphenylsiloxy and methylphenylsiloxy groups can be used to raise the RI of silicones into

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the range of 1.55–1.57, which would correspond to about 65–85 mol % phenyl substituents versus 15–35 mol % methyl substituents. At higher phenyl loadings it becomes difficult to make liquid silicones. Also, the crystallization of diphenyl side chains (creating scattering centers) becomes an issue in optical applications as phenyl content increases. We sought to counteract the tendency toward crystallization of phenyl side groups in siloxanes while still obtaining a high RI by employing heat-stable phenyl ethers as side groups on a non-symmetric silicone monomer. Phenyl ethers have been used as building blocks for liquid materials before. Several US patents document their use as endstoppers in oligomeric heat transfer fluids.<sup>8,9</sup> Additionally, the Santovac fluids are a commercial use of liquid diphenyl ether based oligomers. In contrast to main-chain and end-group diphenyl ether units, employing a diphenyl ether group as a side chain for D siloxane units was reported to give solid polymers when the monomer was octa(phenoxyphenyl)tetracyclosiloxane.<sup>10</sup> Therefore, we targeted having a single phenoxyphenyl group attached to silicon, rather than two phenoxyphenyl groups, the dissymmetry favoring the liquid state.

In this article, we describe the synthesis of novel 4-(phenoxyphenyl)phenyldimethoxysilane (POP) and 4-(phenylthiophenyl)phenyldimethoxysilane (PSP) monomers, and their incorporation into liquid silicone polymers. Data on the RI, optical transmission, heat stability, and properties of thermosets incorporating POP and PSP monomers are presented.

## EXPERIMENTAL

### Preparation of 4-(Phenoxyphenyl)phenyldimethoxysilane Using a Grignard based Procedure

The procedure was carried out in a glove box. A round-bottom flask was charged with 800 mL of diethylether and 10.0 g (413 mmol) of magnesium (Mg) metal powder and ~0.1 mL of methyl iodide. 4-Bromodiphenylether (100 g, 401.4 mmol) was added to the flask with an addition funnel over the course of 6 h; ether reflux with a cold finger was used to control the reaction temperature. The Grignard reagent was then stirred for an additional hour. Phenyltrimethoxysilane (87.6 g, 441.6 mmol) and 200 mL of anhydrous diethyl ether were separately mixed. The Grignard reagent was added to the phenyltrimethoxysilane solution via an addition funnel over the course of 1 h. After the reaction was complete as judged by gas chromatography analysis, the solids were filtered using a glass frit funnel. The ether phase was dried over MgSO<sub>4</sub>, filtered, and rotovaped to yield 129.1 g of crude product, with a purity of 93.8% POP. The product was purified by short path distillation to a purity of 96–98%. Further purification was achieved by column distillation to >99%. <sup>1</sup>H-NMR: 7.50 (d, 6.4 Hz, 2H), 7.45 (d, 8.0 Hz, 2H), 7.28 (td, 7.5 Hz, 2.8 Hz, 1H), 7.22 (t, 7.2 Hz, 2H), 7.18 (t, 7.9 Hz, 2H), 6.96 (t, 7.6 Hz, 1H), 6.88 (d, 8 Hz, 2H), 6.84 (d, 8.5 Hz, 2H), 3.47 (s, 6H). Mass Spec (M<sup>+</sup>): 336.1335 *me*, 336.1182 (calc). Melting point: 40°C.

### Preparation of 4-(Phenylthiophenyl)phenyldimethoxysilane Using a Barbier-Based Procedure

In a drybox, 1.9 g (76.6 mmol) Mg powder, 10 mL tetrahydrofuran + 6–10 iodine crystals were combined in a flask. This mixture was allowed to stir until the iodine color disappeared,

at which time 0.2 mL (2.0 mmol) MeMgBr (1.0M in Et<sub>2</sub>O) was added while stirring and allowed to react for 15 min. Then 17.8 mL (95.7 mmol) trimethoxyphenyl silane was added with stirring. In the drybox, 25.0 mL (29 mmol) 4-bromodiphenyl sulfide (1.16M in tetrahydrofuran) was placed in a syringe. The flask was removed from the drybox and placed in an ultrasonic bath for 5 min. The 4-bromodiphenyl sulfide (25 mL, 29 mmol) was added to the flask under ultrasonication conditions. An initial charge of 5 mL of bromo-compound was injected, which immediately caused a reaction as noted by bubbling and a color change. The remainder of the sulfide solution was added at a rate of 2.0 mL/min. The flask was allowed to react in the ultrasonic bath for a further 60 min. The reaction was diluted with a 50/50 mix of heptane and diethylether and filtered through celite in air. The rotovaped yield was 19.45 g of a yellow liquid, 89% yield. The product was purified by short path distillation to 96.5% purity; boiling point was 167°C at 60 mtorr. The purified product was clear. <sup>1</sup>H-NMR: 7.54 (d, 7.1 Hz, 2H), 7.44 (d, 8.0 Hz, 2H), 7.31 (1H), 7.30 (2H), 7.25 (t, 7.0 Hz, 2H), 7.19 (d, 7.0 Hz, 2H), 7.15 (3H), 3.50 (s, 6H).

### Preparation of Vinyl A (All Vinyl Oligomers Were Prepared in the Same Way)

A 1-L 3-neck flask was equipped with a thermocouple, overhead stirrer, and short-path distillation head. About 220.38 g of POP monomer, 243.28 g of diphenyldimethoxysilane (DPDMS), and 44.38 g of phenylmethylvinylmethoxysilane were combined with 93.73 g of water and 14.79 g of 40% aqueous tetrabutylammonium hydroxide. The stirring rate was 280 RPM. The reaction was heated with a setpoint of 80°C, above the boiling point of methanol, and the reaction temperature slowly rose to 80°C as methanol evolved. The total distillate was 114.06 g, versus an expected 113.64 g of methanol. The reaction was cooled to 50°C, and 350 mL of toluene was added to the flask. The contents were transferred to a 2-L sep funnel, and the reactor was further washed with 450 mL of toluene which was added to the sep funnel. About 400 mL of distilled water was added to the sep funnel, and the mixture was shaken for 60 s followed by a phase cut. The reaction was then washed 3× with 5% (wt/wt) HCl and 2× of distilled water (800 mL volumes). The toluene phase was filtered through a sintered glass funnel to clarify it and rotovaped to remove toluene. The yield of this reaction was 98.3% of theory, 418.68 g of a water-white highly viscous material. Viscosity of the material is approximately 7,000,000 cP when the toluene level is below 0.1% (wt/wt). <sup>1</sup>H-NMR: 7.5–6.5 (aryl protons, 84H), 6.15–5.4 (vinyl protons, 3H), 0.3 to –0.05 (methyl protons, 3H).

### Preparation of Hydride A

About 293.23 g of DPDMS and 108.0 g of methylhydrocyclosiloxanes were combined with 81.0 g of water and 29.42 g of concentrated sulfuric acid in a 4-neck 1000-mL round-bottom flask equipped with an overhead stirrer, glass-sheathed thermocouple, and a short-path distillation head. Stirring was at a rate of 250–300 rpm. The reaction was heated to 80°C and held there for 4.5 h. The reaction was stopped and cooled to 35°C. The total methanol removed via short-path was 40.55 g. Then 200 mL of toluene and 200 mL of water was added, and the reaction was transferred to a 2 L separatory funnel. An additional 400 mL of

**Table I.** Empirical Constants Used for the Lorentz–Lorenz Equation

	Si	O	Phenyl	Vinyl	S	H
$R_i$ (cm <sup>3</sup> )	6.7	1.66	25	10	8.3	0.73
$V_i$ (cm <sup>3</sup> )	12.1	8	75	39	16.6	12.6

toluene was added, and the initial aqueous phase was separated. The organic phase was then extracted 1× with saturated sodium bicarbonate solution and 4× with distilled water (600 mL per extraction). The organic layer was filtered through 40 micron sintered glass to remove a small amount of precipitate, followed by rotovaping at 15 torr to remove toluene. The yield of product was 337.14 g, for a yield of 97.5%. The viscosity is 841 cP. <sup>1</sup>H-NMR: 7.5–6.9 (aryl protons, 7.6H), 4.9–4.3 (hydride protons, 1H), 3.4–3.2 (unhydrolyzed methoxy, 0.25H), 0.1 to –0.4 (methyl protons, 3.4H).

### Formulation and UV–vis Aging Experiments

All formulations were mixed in the following fashion. Formulation A was prepared by mixing 43.25 g of Vinyl A with 8.8 μL of cyclovinylmethylsiloxanes-carbonyl-platinum complex (Gel-est, diluted with xylenes, concentration 2085 ppm from ICP) and 1.8 μL of 3,5-dimethyl-1-hexyn-3-ol. In order for sufficient flow and mixing of Vinyl A and Pt, the temperature was set at 60–80°C under a heat lamp, and mixing was for 30 min on a roller. Then 16.33 g of Hydride A and 3.62 g of phenylvinylmethylsilane were added and the formulation was continuously mixed on a roller with heating at 50–60°C for 1 h. The formulation was then cooled and could be stored at 4°C for >6 months before curing.

Formulations were cured in ovens or on hot plates in air, using quartz slides or glass microbeakers. For UV–vis experiments, ~0.5 g were placed onto a 1 inch square quartz slide and cured at 130 or 160°C for 2–4 h. Aging of thermosets was conducted in furnace(s) set at 200°C in air. For extended heat aging studies, UV–vis spectra were acquired using an Ocean Optics USB 4000 spectrophotometer with a tungsten light source and an Ocean Optics integrating sphere accessory.

### Calculation of Refractive Index of Silicones

We calculated the RIs  $n$  of various proposed structures prior to synthesizing them, in order to understand the tradeoffs between structure and other properties such as  $T_g$ , viscosity, and brittleness. We used the group additivity approach as described by Van Krevelen and Nijenhuis.<sup>11</sup> The RI is calculated from the Lorentz–Lorenz formula:

$$\frac{n^2 - 1}{n^2 + 2} = \frac{\sum_i R_i}{\sum_i V_i}$$

We found that there were no reliable values of molar refraction  $R_i$  and volumes  $V_i$  for Si atom group contribution. So we analyzed several dozen commercial and synthesized silicone liquid compounds with RIs from 1.41 to 1.67 and developed the values in Table I. Using these values, the RIs of various oligomers under consideration in this article were calculated (included in Table III). A plot of  $n_{\text{exp}} - 1$  and  $n_{\text{calc}} - 1$  is linear ( $R^2 = 0.97$ ) and shows good agreement between experiment and cal-

ulation (Supporting Information). The model works well for known polymers such as polydimethylsiloxane, polyphenylmethylsiloxane, and polydiphenylsiloxane (Table III). Using this predictive model, we identified phenyl ether and phenyl thioether as two potential high RI chemical moieties which were also expected to form liquid and heat stable polymers. The model predicts lower RIs than what are measured for the phenoxyphenyl and phenylthiophenyl oligomers in Table III. This is perhaps due to variability in the effects of the vinyl endgroups—the available data used for building the model did not include many vinyl-capped oligomers.

## RESULTS AND DISCUSSION

### Monomer Synthesis

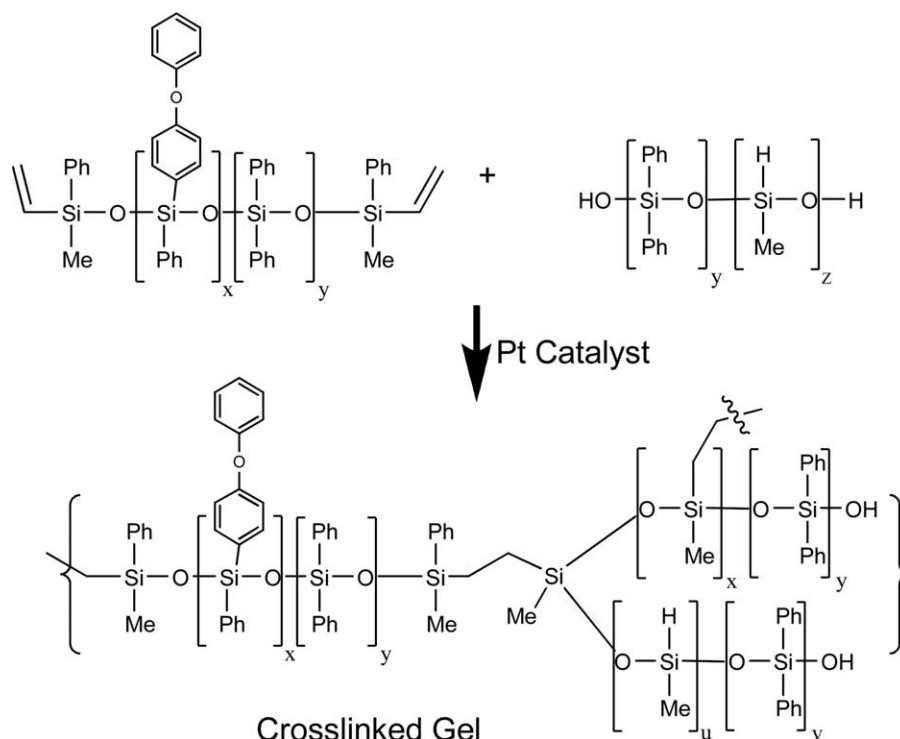
POP and PSP were synthesized by the routes shown in Figure 1. The standard Grignard approach to silane monomer synthesis gave yields of 60–85% for POP after purification by distillation. It was found that the purity of the isolated monomer was critical to achieving polymers which could be heat aged for prolonged periods without yellowing. POP was purified by a combination of short-path and multi-tray distillation processes to greater than 99% purity by gas chromatography analysis. The PSP monomer was synthesized in 89% crude yield by a Barbier-style reaction,<sup>12</sup> which proved to be a simpler and more reliable procedure for both monomers. PSP was purified to 96% purity via short-path distillation.

Platinum hydrosilation chemistry is the most commonly used crosslinking chemistry for electronic-grade silicone encapsulants. It has the advantages of controlled reactivity, no off-gassing, very little volume change upon cure, and reasonable cure rates and temperatures. We sought to incorporate the monomers POP and PSP into polysiloxane systems which could be cured by hydrosilation (Figure 2). Our synthetic approach used condensation polymerization. The resulting low molecular weight oligo- and polysiloxanes are appropriate for crosslinkable optical resins. For monomers like POP and PSP, where a phenyl group is directly attached to the Si atom, polymerization via basic catalysis is preferred due to the electron withdrawing effects of the phenyl ring. When polymerizing silicon hydride moieties, acidic catalysis is preferred to prevent premature hydrolysis of the Si–H bond. Thus, a hydrosilation-based siloxane system using POP or PSP is most easily made as shown in Figure 2, with POP or PSP monomers in the vinyl component only.

### Vinyl Oligomer Synthesis

Using Figure 2 as a basis, we employed a monomer set including POP, PSP, diphenyldimethoxy silane, phenylmethyldimethoxy

**Figure 1.** Grignard synthesis of POP and Barbier synthesis of PSP.



**Figure 2.** Hydrosilylation-based siloxane thermoset system employing phenyl ether monomers.

silane, dimethyldimethoxysilane, methylhydrocyclosiloxanes, phenyltrimethoxysilane, and various M groups such as divinyltetramethyldisiloxane, vinylphenylmethylmethoxysilane, and hexamethyldisiloxane; the goal was to demonstrate liquid thermoset systems with RIs of 1.60 or higher, as well as to explore the chemistry of POP and PSP. When using a base-catalyzed condensation reaction with phenyl-containing monomers, it is expected that cyclic phenylcyclosiloxanes may form, based on both the catalyst type and the monomers involved. In particular, diphenyl D monomers are known to readily form insoluble hexaphenyltricyclosiloxane and octaphenyltetracyclosiloxane when polymerized under basic conditions, due to the thermodynamic stability of the cyclosiloxanes.<sup>13–16</sup> Catalyst screening was done to minimize this known reaction using a model condensation reaction (see Supporting Information). Based on this screening, tetrabutylammonium hydroxide (TBAH) gave the best combination

of polymerization rate, ease of handling, and low cyclic formation.

Initial polymerizations of POP were conducted with TBAH as a catalyst and divinyltetramethyldisiloxane to control molecular weight and provide crosslinking points. The RI of these POP (>90% POP units versus vinyl dimethylsilyl groups) oligomers ranged from 1.605 (vinyl equivalent = 1300 g/mol) to 1.624 (vinyl equivalent = 74,000 g/mol) depending on the amount of vinyl contained in the final condensate. Gel permeation chromatography (GPC)  $M_w$  of the homopolymers ranged from 1300 to 2300 g/mol (polystyrene standards) depending on polymerization conditions. Low cost is important for LED encapsulants, and so the blending of POP or PSP monomers with DPDMS monomers was studied due to the low cost of DPDMS. Reactions of POP with DPDMS show that smaller amounts of

**Table II.** Composition Ladder Varying the Ratio of POP to Diphenyldimethoxysilane (DPDMS) in a Condensation Reaction

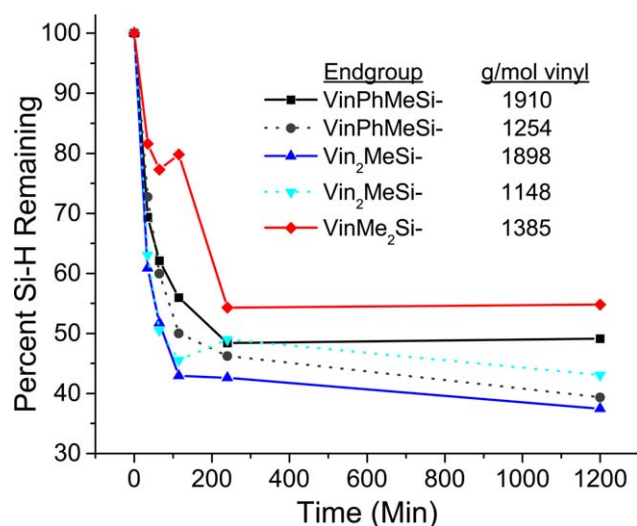
Ratio POP : DPDMS	Clarity	Color	RI	Residual toluene	Vinyl (g/mol)	$T_g$ (DSC), °C	Viscosity 25° (cP)
0.25	Hazy	None	1.5993	0.08%	1236	55.67 and -2.21	507,430
0.43	Slight Haze	None	1.6016	0.09%	1268	-0.01	768,510
0.67	Clear	None	1.6017	0.58%	1285	-1.1	430,870
1.00	Clear	None	1.6004	0.53%	1253	-1.85	316,900
1.50	Clear	None	1.6054	0.23%	1286	4.24	1,756,100
2.33	Clear	None	1.6037	0.14%	1320	4.3	1,067,600

Vinyl loading was due to the incorporation of divinyltetramethyldisiloxane at a typical level of ~7.5 mol %.

**Table III.** Polymer Compositions, Measured and Calculated Refractive Indices, Vinyl/Hydrate Loading, and Typical SEC Results for Polymers Used in This Study

	Composition (mol %)	Exp RI	Calc RI	$M_w^a$	$M_n^a$	$T_g$ (°C)	Functional loading <sup>b</sup> vinyl <sup>c</sup>
Vinyl A	34.5% POP	1.615	1.597	900–1200 <sup>c</sup>	800–1000 <sup>c</sup>	2.5	1600–1900 g/mol vinyl <sup>c</sup>
	52.4% DPDMS						
	13.1% phenylmethylvinylmethoxysilane						
Vinyl B	40% POP	1.604	1.584	2750		–4	2221 g/mol vinyl
	40% DPDMS						
	10% phenylmethylvinylmethoxysilane						
	10% Bis(dimethyl(hydroxysilyl) benzene						
Vinyl C	36.4% POP	1.602	1.579	1384	961	–3.5	2126 g/mol vinyl
	36.3% DPDMS						
	11.3% phenylmethylvinylmethoxysilane						
	8% phenylmethylmethoxysilane						
	8% tetramethyldiethoxydisiloxane						
Vinyl PSP	79% PSP	1.634	1.622				2100 g/mol vinyl
	8% tetramethyldiethoxysilane						
	1.3% phenylmethylvinylmethoxysilane						
Hydrate polymer A	60% methylhydrocyclosiloxanes	1.546	1.561	3500–5000 (70–80%); ~500 (20–30%) <sup>c</sup>	2300–3400 (70–80%); ~480 (20–30%) <sup>c</sup>	–50	200–220 g/mol hydrate <sup>c</sup>
	40% diphenyldimethoxysilane						
PDMS	Poly dimethyl siloxane	1.404	1.405				
PMPS	Poly phenyl methyl siloxane	1.533	1.537				
PDPS	Polydiphenyl siloxane(solid at RT)	1.61	1.60				

<sup>a</sup> SEC values are determined with PS standards.<sup>b</sup> Vinyl and hydrate equivalent weights were determined by proton NMR using an internal toluene standard.<sup>c</sup> Vinyl A and Hydrate A values are given as ranges over many different batches.



**Figure 3.** Curing study of Vinyl A type oligomers with different vinyl endgroups. The vinyl oligomers were crosslinked with two equivalents of Hydride A using 1 ppm of Ossko Pt catalyst. The curing temperature was 130°C for the first 240 min, followed by 16 h at 160°C. Fifty percent of the Si—H bonds are expected to remain after cure if there is no Si—H hydrolysis from water or silanols. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

diphenyl ether side groups can still ensure a liquid product (Table II). Unlike comparable polymerizations involving just DPDMs, the formation of insoluble cyclic diphenylcyclorosiloxanes is not observed, even with loadings approaching 70 mol % diphenylsiloxane (POP : DPDMs ratio of 0.43). The reaction conditions used resulted in oligomers with 3–6 units with  $M_w$  from 1000 to 2000 g/mol. The oligomers are water white with no haze, indicating good miscibility of the two monomers. Viscosities are in the range of 300k–2000k centipoise, and were affected by residual toluene (work-up solvent), making accurate measurements difficult. Finally, the RI ranged from 1.599 to 1.605, an encouraging result. The POP/PSP oligomers are not miscible with silicone hydrides that do not contain at least 20 mol % phenyl side chains.

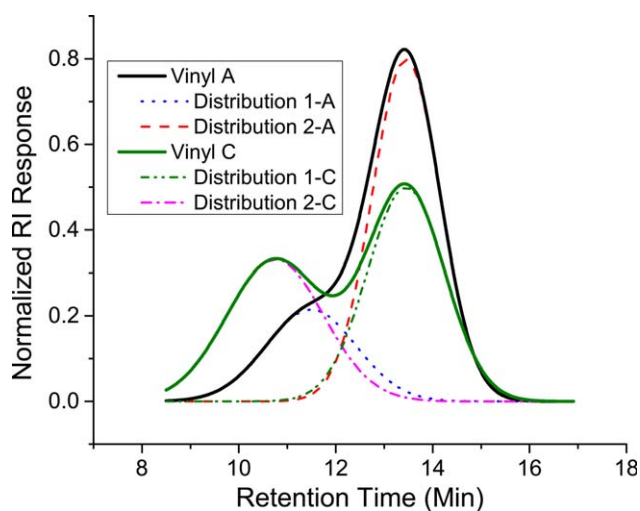
Several approaches were taken to optimize the composition and crosslinking of the POP-containing vinyl oligomers. The hardness,  $T_g$ , crosslinking conditions, RI, and heat stability of the final thermoset are all critical to LED encapsulation applications. Some of the oligomers synthesized are summarized in Table III.

Increasing the oligomer chain length by controlling the amount of vinyl capping groups present could give variations in  $M_w$  from 1000 to ~2500 g/mol. However, once the vinyl equivalent weight became greater than 2000 g/mol crosslinking did not occur. This is because of the presence of cyclic siloxanes and unfunctionalized endgroups. Vinyl group incorporation was examined both in the endgroups and within the chain. Best results for crosslinking involved end group functionalization with vinyl groups. An FTIR study of cure times via hydrosilation for Vinyl A (Table III) with three different endgroups is shown in Figure 3. The reduction in the Si—H stretch at 2128  $\text{cm}^{-1}$  was followed as the formulations cured between salt

plates. Since 2 equivalents of hydride functional groups were present relative to vinyl groups, it is expected that 50% of the Si—H bonds will be consumed when the hydrosilation reaction is complete. The Vinyl A oligomers were initially synthesized using  $\text{Me}_2\text{VinSi-}$  endgroups, as in Table II, and had a cure time with Hydride A of approximately 4 h at 130°C. The use of the M unit— $\text{MeVin}_2\text{Si-}$ —resulted in the fastest cure (1 h) and lowest vinyl loading needed to achieve setting, as expected from the extra functionality. However,  $\text{MeVin}_2\text{Si-}$  did not produce adequate mechanical properties for an encapsulant application—the formulations cracked during thermal cycling. The  $\text{PhMeVinSi-}$  groups were the best compromise of cure speed (2 h), RI, and mechanical properties. Note that Si—H bond consumption does not stop at 50% for all of the formulations. This is expected due to the potential for a two stage cure involving first hydrosilation and then Si—H hydrolysis followed by Si—OH condensation.<sup>17,18</sup> The inconsistencies in Si—H remaining are likely due to variations in film thickness and water diffusion in our method.

The use of small amounts of siloxane monomer units with a greater tendency toward linear polymer formation was investigated to increase molecular weight in the POP containing vinyl oligomers. This approach could successfully raise the  $M_w$  and lower the viscosity of the resulting oligomers, at a small cost to the RI of the resulting oligomer. In particular, phenylmethyl, dimethyl, and silylene D units were useful for lowering the viscosity and  $T_g$ , while raising the  $M_w$  of the oligomers prior to formulation (Table III).

Size exclusion chromatography (SEC)-MALDI, crosslinking, and solvent-extraction studies on the phenoxyphenyl-containing vinyl polymer correlate and show that there is a significant amount of short chain oligomer or cyclic siloxanes present, 3–6 units in length. SEC of Vinyl A and Vinyl C in Figure 4 shows a bimodal distribution. The SEC-RI chromatogram of Vinyl A and Vinyl C can be de-convoluted into two distributions centered at the elution volumes of ~10.5/11.5 mL and ~13.5 mL (illustrated in



**Figure 4.** SEC analysis of Vinyl A and Vinyl C oligomers. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

**Table IV.** Composition of Vinyl A and C Based on SEC-RI and MALDI-MS Analyses

	$M_n$ (g/mole)	Weight %	Major oligomeric species
Vinyl A Distributions	1200	73	Short chain cyclic siloxanes, silanol functionalized oligomers in small amount
	2600	27	Phenylmethylvinylsilyl functionalized polysiloxanes
Vinyl C Distributions	1000	60	Short chain cyclic polysiloxanes, silanol functionalized oligomers in small amount
	2700	40	Phenylmethylvinylsilyl functionalized polysiloxanes

**Table V.** Hydrosilation-Cured Formulations Using POP and PSP Vinyl Oligomers

Formulation	Vinyl	Hydride	Reactive Diluent	Hydride/ Vinyl ratio	Cure Catalyst	RI post-cure (633 nm)
A	Vinyl A	Hydride A	Vinylphenylmethyl-silane (5.7% wt/wt)	2.0	0.25 ppm Pt "Ossko"; 25 ppm 3,5-dimethyl- 1-hexyn-3-ol	1.60
B	Vinyl PSP	Hydride A	1,3-Divinyl-1,3-diphenyl-1,3- dimethyldisiloxane (4% wt/wt)	1.5	0.5 ppm Pt "Ossko"	1.62

dotted lines in Figure 4), respectively. Matrix-assisted laser desorption-ionization mass spectroscopy (MALDI-MS) analysis was used to determine the  $M_n$  and composition of the distributions (Table IV). Note that the amount of higher molecular weight linear polymer is increased in Vinyl C by incorporation of a small amount (by weight) of dimethylsiloxane D units.

Soaking crosslinked formulations of Vinyl A with Hydride A in toluene resulted in the extraction of ~25% by weight of an oligomeric material (Supporting Information). It is clear that a significant portion of the Vinyl A polymer does not participate in crosslinking reactions, either due to incomplete functionalization with vinyl groups or formation of cyclic species. Simple statistical considerations of molecular weight versus vinyl loading indicate that these oligomers are not all end-capped with vinyl groups. We assume that only 25% is extracted from the crosslinked material due to threading and entrapment of cyclic siloxanes within the network.

#### Hydrido-Oligomer Synthesis

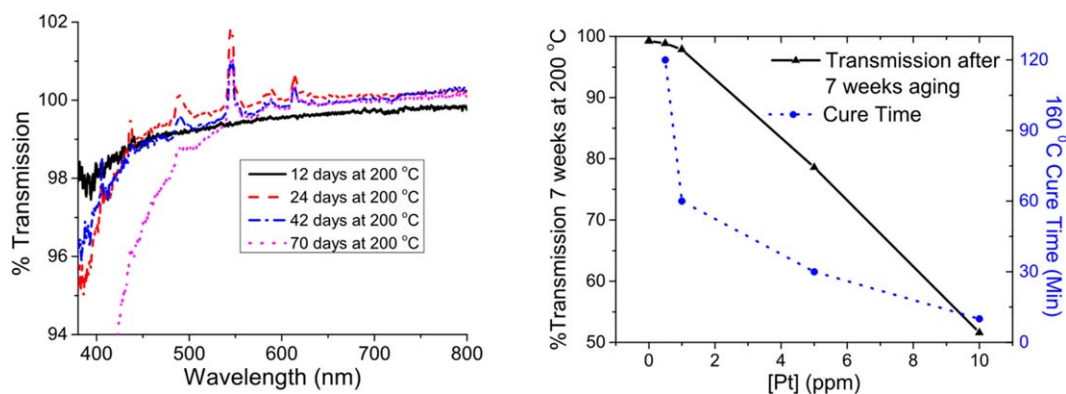
A high RI hydrido-siloxane, Hydride A, to pair with the POP vinyl oligomers was synthesized. It is necessary to incorporate phenyl groups at fairly high levels (>20–25 mol %) to achieve a miscible pre-polymer blend. Polymerizations of Si–H containing monomers are performed under acidic conditions to reduce Si–H hydrolysis reactions, and the need to incorporate phenyl-containing silane monomers necessitates the use of a strong acid catalyst due to the low reactivity of phenyl-substituted silicon atoms in acids. Synthesis under these conditions leads to branching in the resulting polymers due to hydrolysis of Si–H and Si–Ph groups, even if no T siloxane monomers are included in the synthesis. Table III describes the composition of the Hydride A polymer that crosslinked rapidly with the POP vinyl oligomers. It was found that a hydride loading of ~200 g/

mol gave the fastest crosslinking for use as an encapsulant, incorporated into a "linear" polysiloxane\* with a  $M_w$  of 2000–10,000 g/mol.

#### Formulation and Properties

The optimized formulation using a POP vinyl oligomer is summarized in Table V. The phenyl(phenoxyphenyl)silyl-containing vinyl polymer has a very high viscosity. In order to provide a more useful HBLED liquid encapsulant, it is useful to blend down the viscosity, while minimally changing the RI of the final formulation. Encapsulants typically need a viscosity below 10,000 cP at room temperature so that they can adequately flow during dispensing and also make good conformal contact with all optical surfaces before curing. We used two approaches to lower the viscosity of the encapsulant formulation: pre-mixing the lower viscosity hydride polymer with the high viscosity vinyl component; and adding a reactive diluent to reduce viscosity. Pre-mixing the vinyl and hydride components requires the use of a platinum cure inhibitor so that the formulation can be storage stable at room temperature. Alkynyl alcohols have been reported to effectively inhibit Pt hydrosilation catalysts.<sup>19</sup> By using 3,5-dimethyl-1-hexyn-3-ol as the inhibitor it was possible to mix the lower viscosity hydride polymer, the vinyl polymer, and a reactive diluent together with the platinum catalyst to achieve a storage stable liquid prepolymer (>6 months at 4°C). The viscosity of the resulting Formulation A was ~5000 cP over numerous batches. The cure temperature and time for the formulation varied depending on the Pt level, but ranged from 0.5

\*The hydride polymers synthesized have branching as detected by <sup>29</sup>Si-NMR, due to unwanted hydrolysis of side-chain groups during the synthesis. As with the vinyl oligomers, there are also cyclic siloxanes present—the amounts are lesser at ~25% (by GPC).



**Figure 5.** The effects of heat aging on Formulation A containing POP. The graph on the left shows the UV-vis spectra of >1 mm thick cured material aged at 200 °C in air over the course of 2 months. The slight “increase” of transmission for the 24 and 42 day samples is attributed to buckling of the films during aging. Spectra were normalized to 1 mm thickness. The graph on the right shows the effects of increasing Pt loading on both thermoset cure time and %transmission at 400 nm after seven weeks of 200 °C aging. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

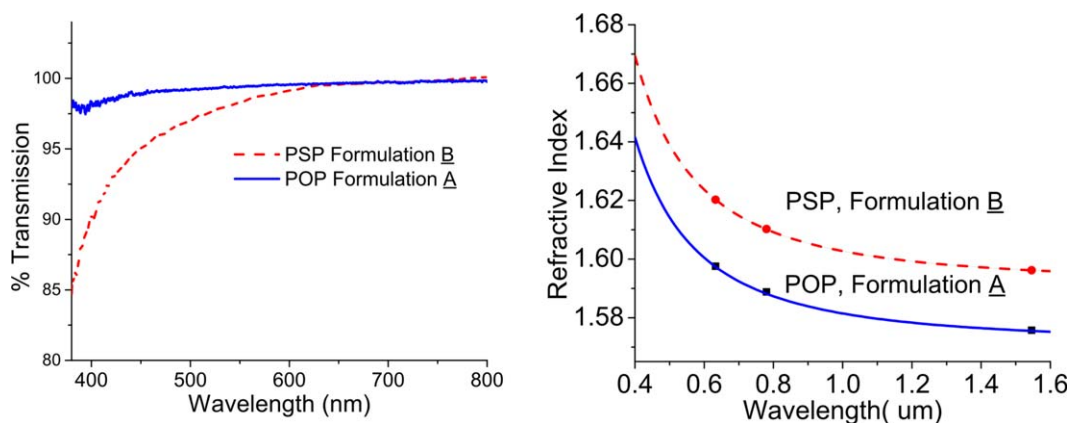
to 2 h at 160 °C (Figure 5). The addition of 3,5-dimethyl-1-hexyn-3-ol as cure inhibitor had no detectable effect on long-term performance. However, other reported alkynyl alcohol inhibitors such as 1-ethynol-1-cyclohexanol performed poorly.

Most important for modern high-brightness LEDs is the ability to maintain a consistent high optical transparency while being exposed to extremely high operating temperatures (potentially up to 180 °C). The amount of platinum catalyst used to cure the thermoset had a dramatic effect on the ability of these polymers to withstand heat aging and retain good transparency (Figure 5). This effect is general for all siloxane polymers, but especially for phenyl-containing siloxane polymers.<sup>20</sup> The degree of yellowing increases with increasing phenyl content. Thus, for formulations containing phenoxyphenylsiloxanes the Pt loading is critical and must be carefully balanced against cure speed and the expected application temperature. Platinum loadings below 2 ppm (wt/wt of metal atoms) were best to achieve good high temperature aging of phenoxyphenylsiloxane polymers (Figure 5). For preventing yellowing it is useful to use an excess of silyl-hydride groups to ensure full reaction of the thermally vulnerable vinyl groups. A ratio of ~2 : 1 hydride to vinyl gave the

best heat aging results. The method of mixing the formulation, the degree of branching, the purity of the platinum catalyst, and the presence of oxygen also affect the degree of yellowing that will be seen.

The mechanism of curing in platinum-based hydrosilation has been the subject of some controversy over the years.<sup>21</sup> It is possible that curing occurs via discrete platinum complexes, but it is also possible that hydrosilation can be catalyzed by platinum nanoparticles after those complexes have degraded.<sup>22</sup> During the course of our work, we found that platinum catalysts that had been partially degraded (either by long storage or excessive heating prior to cure) seemed to result in accelerated polymer degradation during heat aging. There is also a known reaction of the platinum catalysts with silicone hydrides which can lead to degradation of the platinum complex and nanoparticle formation.<sup>23</sup>

The type of platinum hydrosilation catalyst used had minimal impact on the formulation cure time (in the absence of inhibitor). Due to the viscosity of the polymers during initial formulation, it was necessary to heat the system to ~60–80 °C during the initial mixing phase. Commercially available “Karstedt” catalyst,<sup>24</sup> divinyltetramethyldisiloxane-platinum complex, gave



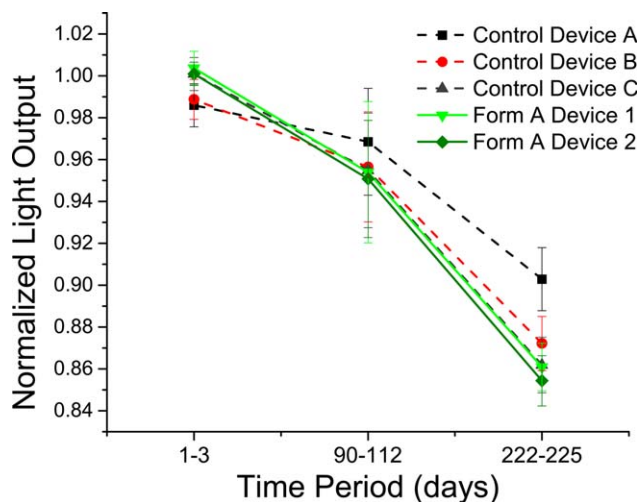
**Figure 6.** Left: Optical transmission of POP and PSP containing thermosets after cure. Right: RI dispersion curves of POP and PSP thermosets fit via the Sellmeier equation. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



poor heat aging results compared to commercial “Ossko” catalyst,<sup>25</sup> cyclovinylmethylsiloxanes-carbonyl-platinum complex. We speculate that the Karstedt catalyst was more easily degraded with mild heat or more easily converted to nanoparticles, and that this created the different heat aging characteristics.

In order to demonstrate the applicability of the phenyl(thio)phenyl monomer PSP, it was polymerized in a similar way to the POP monomer (Table III). The resulting polymer was then used in the place of the phenoxyphenylvinyl polymer in Formulation B. Due to the affinity of sulfur for Pt, it was necessary to cure the material at  $\sim 200^\circ\text{C}$  for 6 h rather than  $160^\circ\text{C}$ . Figure 6 shows the RI dispersion curve and UV-vis of the PSP and POP thermosets. The RI dispersion curve was fit with the Sellmeier equation. Since high-brightness LEDs emit in the range of 450–470 nm, it is interesting to note the RIs at 450 nm, which are  $\sim 1.62$  for POP and  $\sim 1.64$  for PSP compositions. The optical transmission for a POP composition through a 1 mm path-length is 98% or higher throughout the visible light range, whereas the PSP composition drops from 100% down to 90% as the UV region is approached. The PSP monomer had a 96% purity, whereas all POP results used  $>99\%$  purity materials. Since the light transmission of optical polymers is highly sensitive to impurities, it is likely that the optical qualities of a PSP formulation can be further improved. Also due to the impurities present, heat aging of Formulation B does lead to discoloration. However, heat aging experiments using diphenylsulfide indicate that the phenyl-sulfur-phenyl moiety can withstand  $200^\circ\text{C}$  heat aging for  $>1$  week. If the crosslinking chemistry is modified to address the issues of platinum-sulfur interactions, we feel that the PSP monomer can be useful for HBLED or other optical applications.

Dynamic mechanical analysis indicates a  $T_g$  of  $23^\circ\text{C}$  for Formulation A, which could indicate problems with temperature cycling during use in applications. The glassy modulus is  $2 \times 10^8$  Pa, while the rubbery modulus is  $\sim 5 \times 10^4$  Pa. However, Formulation A holds up to humidity and temperature cycling protocols relevant for high-brightness LEDs when used on a functioning LED. One such test is JESD22-A100C, which involves cycling a LED device from 30 to  $65^\circ\text{C}$  at 90–98% relative humidity over a 4–8 h cycle. We built a special LED tester that allowed the thermal cycling of a LED under 1 amp current bias over an extended time period. Luxeon K2 LEDs (Philips Lumileds Lighting company) were modified by removing the lens and silicone, but keeping the phosphor on the LED surface. Then we added Formulation A as an encapsulant and cured it. We were not able to replicate the hemispherical dome lens on the as received K2 devices so the output light after repackaging was  $\sim 50\%$  of the initial devices. However we were interested in measuring the relative change in light output as a function of time and thermal cycling. A track carried an optical detector (Ocean Optics) that moved along and measured the light output in lumens from each LED and recorded it periodically. Temperature inside the box was cycled from  $-10^\circ\text{C}$  to  $85^\circ\text{C}$  every 12 h with relative humidity inside the box kept at 50%. Formulation A and some as received K2 devices were tested for 225 days. The results are shown in Figure 7. Since the decrease in light transmission took so long, the data from the tester was



**Figure 7.** Decrease in light output (lumens) from 1 amp LEDs with commercial encapsulant or encapsulated with Formulation A while temperature cycling from  $-10^\circ\text{C}$  to  $85^\circ\text{C}$ . The light output data was grouped for the beginning, middle, and end of testing. The light output is normalized to 1.0, based on the starting intensity of each repackaged device. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

grouped for the beginning, middle, and end of testing to give better statistics. The two devices repackaged with Formulation A maintained  $\sim 90\%$  of their starting lumens after 5000 h of operation with daily temperature cycling from  $-10$  to  $85^\circ\text{C}$ .

Formulation A also withstands constant humidity aging at  $85^\circ\text{C}$  (JESD22-A101B) as well as temperature cycling from  $-40$  to  $125^\circ\text{C}$  (JESD-A104G) without cracking, discoloring, or shrinking. There are several reasons why Formulation A seems to perform adequately with respect to temperature cycling. Siloxanes are known to be good electronics encapsulants in large part due to their low rubbery modulus and corresponding flexibility. Additionally, the nature of crosslinking in Formulation A, which is driven by the multifunctional hydride polymer component, with a minimally functional vinyl component (with a vinyl loading of less than one vinyl unit per molecule on average), may give some advantage during temperature cycling. It was observed in the formulations using divinylmethylsilyl units (Figure 3) that thermal cycling results were very poor; presumably those formulations were more extensively crosslinked than Formulation A. As mentioned, it is likely that the crosslinked Formulation A material has threaded cyclic siloxanes as well as mobile siloxane oligomers. The result of these factors may allow the crosslinked resin/gel to rearrange or flow just enough to provide good performance under temperature cycling. It is also possible that hydride hydrolysis with water leading to crosslinking between the hydride polymer components contributes to gelation for this system. Further study is needed to understand the mechanical properties of the POP formulations.

## CONCLUSION

We have prepared two new siloxane monomers, POP and PSP. The resulting monomers were copolymerized with commercial silicone monomers and incorporated into hydrosilation-based

thermosets designed for use as LED encapsulants. The molecular structure of the vinyl and hydride components of the thermoset was optimized based on crosslinking, RI, and heat aging properties. RIs at 633 nm for an all liquid prepolymer system were 1.60 for the phenoxyphenyl ether system and 1.62 for the phenylthiophenyl ether system, significantly higher than the best previously reported RI 1.56 for a 200°C heat stable encapsulant.<sup>2</sup> The indices were 1.625 and 1.64, respectively, at the typical emission wavelength (450 nm) of today's high-performing LEDs. The optical properties of the phenoxyphenyl-based systems showed little change after heat aging at 200°C for seven weeks in air or cycling between -10°C and 85°C over >6 months. With further development, these encapsulants might enable improvements in HBLED efficiency of 5–10%, depending on the LED design.

### ACKNOWLEDGMENTS

The authors would like to thank Kevin Calzia, Xiang-Qian Liu, Shailesh Shah, Lester McIntosh, Jay Gregory, Miroslav Janco, Connell Cunningham, Mike Bender, Alan Nakatani, and Kebede Beshah for insights, experiments, and unincorporated work on the chemistry herein. They also thank Ethan Simon and the former Rohm and Haas Electronics organization for supporting the work.

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