CHEMISTRY OF MATERIALS
Article

Chem. Mater. **2010,** *22,* 3549–3555 3549
DOI:10.1021/cm100903b

Thermally Stable Transparent Sol−Gel Based Siloxane Hybrid Material with High Refractive Index for Light Emitting Diode (LED) Encapsulation

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Received March 30, 2010. Revised Manuscript Received May 2, 2010

Nonhydrolytic sol−gel condensation for the synthesis of nanosized inorganic−organic hybrid resin and hydrosilylation reaction under a Pt catalyst for the fabrication of oligosiloxane-based hybrid material (phenyl hybrimer) were used in this research. This combination of two chemical reactions results in material with useful properties for light emitting diode (LED) encapsulation. Until now, no polymers and phenyl polysiloxane materials have been reported with a high refractive index (over 1.52) and high transparency accompanied by resistance to yellowing induced by thermal degradation above 150 °C aging in air. In this article, we focused on the fabrication of a transparent and thermally stable phenyl hybrimer with high refractive index for LED encapsulation through siloxane networking by a hydrosilylation reaction with cross-linker and Pt caltalyst. The phenyl hybrimer has a high refractive index about 1.56. In particular, it has good thermal stability against discoloration to yellow by aging even at 200 °C, which is a key factor for the long lifetime of a LED encapsulant.

Introduction

Optically transparent polymers have been applied to various optical applications such as the fabrication of microlenses, optical coatings, and the encapsulation materials for optical devices.[1−6] With the increasing demands for high performance in these applications, a high refractive index and high thermal stability are especially important for the optical efficiency and lifetime of the devices. Thermal stability in this context requires stable transparency and resistance against discoloration or yellowing, induced by thermal aging, and a high thermal decomposition temperature. Encapsulation materials for optoelectronic devices such as light emitting diodes (LEDs) need to operate at high temperatures for a long time and are especially sensitive to thermal stability and yellowing. Yellowing from thermal decomposition decreases transparency and reduces the light extraction efficiency from these devices. For example, device reliability and lifetime in high-brightness LEDs can be limited by the capability of the encapsulation materials. Also, a high refractive index in the encapsulation material is required for high efficiency light extraction from an LED, significantly improving its illumination performance.[7,8] Thus, the key properties of LED encapsulation materials are excellent transparency, high refractive index, and high resistance to heat, moisture, solvents, and chemical reactions.

Epoxy-based polymers generally used for existing LED encapsulation provide stable light emission at junction temperatures up to 120 °C, but thermal stability past 150 °C is required for satisfactory device reliability and lifetime in some new LED designs, which include higher junction temperatures.[9] Compared to epoxy- or other resin-based encapsulation materials, polysiloxane-based encapsulation, coating, or sealing materials provide excellent thermal stability against discoloration to yellow at high temperatures.[10] Another recent issue involved in the choice of LED encapsulation materials is the requirement of a high refractive index without any yellowing at high junction temperatures. Polydimethylsiloxane (PDMS) resin, which is the most common product from silicone manufacturers, has high thermal stability against yellowing, even up to 200 °C thermal aging, but its refractive index is too low for it to replace the epoxy polymers in these applications. Various types of phenyl polysiloxane resin are being developed with high refractive indices ($n = \sim 1.52$) since the phenyl groups in polymers are highly polarizable. Unfortunately, these materials are not stable against yellowing at high temperatures since the phenyl group in the polymers is also susceptible to heating-induced oxidation when in air for long periods.[11] Until now,

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no polymers and phenyl polysiloxane materials have been reported with a high refractive index (over 1.52) and high transparency accompanied by resistance to yellowing induced by thermal degradation above 150 °C aging in air. Thus, the development of high refractive index, transparent materials which are durable at high temperature is very significant for the advancement of LED encapsulation technology.[12−16]

Inorganic−organic hybrid materials have the potential for use in many optical applications since they provide not only high optical transparency but also combine both inorganic and organic characteristics which could lead to the fabrication of more reliable optical devices. Recently, sol−gel derived organo-oligosiloxane-based hybrid materials (hybrimers) have been studied and used to fabricate many micro-optical devices, taking advantage of their unique characteristics and simple production processes.[17] However, the methacrylate or epoxy-based hybrimers made by radical polymerization have a limited thermal stability against yellowing, even though they show high thermal decomposition temperatures. Thus, these hybrimers are not yet favorable for practical use in LED encapsulation when compared with other candidates. Hybrimers do nevertheless have inherent potential for use in LED encapsulation since they can be created with a high refractive index by adjusting the inorganic components and are easily processed with good encapsulation adhesion.

In this article, we synthesized inorganic−organic hybrid resin through sol−gel condensation and it was cured by a hydrosilylation reaction. The combination of these chemical reactions results in a hybrimer with substantially high thermal stability and refractive index. It keeps its high transparency even at 200 °C for long periods, and the refractive index value is about 1.56 at 633 nm. These parameters are strikingly effective properties for high performance LED encapsulants.

Experimental Section

Inorganic−Organic Hybrid Resin Synthesis by Sol−Gel Condensation. The phenyl-vinyl-oligosiloxane (PVO) resin was synthesized by a sol−gel condensation process between vinyltrimethoxysilane (VTMS, Aldrich, USA) and diphenylsilanediol (DPSD, Gelest, USA) with a precursor molar ratio of 60 mol % DPSD over VTMS. The barium hydroxide monohydrate, $Ba(OH_2)\cdot H_2O$ (BH, Aldrich, USA) was added as a catalyst to promote the direct condensation reaction between the methoxy radical of VTMS and the diol radical of DPSD, which forms siloxane bonds. This synthesis proceeded without the addition of water for hydrolysis, which can reduce the residual silanol contents. The amount of BH was 0.1 mol % of the total silane compound. The condensation process by the BH catalyst of the sol−gel method promotes fast condensation of precursors and results in highly branched structures. VTMS, DPSD, and BH were mixed in a flask, and 20 wt % of *p*-xylene to the total resin was added during the reaction. After adding DPSD to the solution, the 4 h reaction proceeded to complete the condensation. The solution was stirred with a magnetic stirrer during the reaction, which was performed at 80 °C. After the reaction, the byproduct methanol was removed by vacuum heating. Also, BH was removed by a using a 0.45 μm pore-sized Teflon filter.

Phenyl Hybrimer Fabrication by the Hydrosilylation Reaction. The synthesized PVO was thermally cured with a cross-linker, phenyltris(dimethylsiloxy)silane (PTDMSS), through a hydrosilylation reaction under a Pt catalyst, platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex solution (Aldrich, USA). The mixed resin containing PVO and PTDMSS with the Pt catalyst was cast into a glass mold made by two surface-treated glass plates separated by 2 mm (sample size is $2 \times 2 \times 0.2$ cm^3), followed by curing at 180 °C in air atmosphere for 2 h. The glass plates were previously HMDS (hexaphenylcyclotrisiloxane, Aldrich, USA)-coated to allow for easy detachment of the phenyl hybrimer (PH) sample from the glass mold.

Characterization. ^{29}Si nuclear magnetic resonance (NMR) spectra of PVO in 30 vol % of chloroform-*d* were recorded using a FT 600 MHz (Bruker Biospin, DMX600) instrument. Chromium(III) acetylacetonate as a spin relaxation agent of silicon was added at a concentration of 30 mg L^{-1}. Fourier transform−infrared (FT-IR) spectroscopy (JASCO, FT-IR 460 plus) and Fourier transform−Raman (FT-Raman) spectrometry (Bruker, RFS 100/S) were used to examine the structure of PVO. Optical transmittances and yellowness indices were measured by a UV/VIS/NIR spectrophotometer (Shimadzu, UV-3101PC). The calculation of yellowness indices was made using the ASTM method D1925. A prism coupler (Metricon, 2010) was used to measure the refractive index of the PH sample at 633 nm various temperatures from 25 to 100 °C. The shore durometer (Schmidt, HPSD) was used for measuring the shore D hardness. DMA and TMA samples were performed by using the TMA analyzer (SII Nanotechnology Inc., TMA/SS6100) in the temperature range from −150 to 200 °C. The oxygen and water vapor permeability of the PH (sample size is $5 \times 5 \times 0.0312$ cm^3 and $5 \times 5 \times 0.024$ cm^3, respectively) was characterized by permeability analysis (MOCON, OX-TRAN Model 2/21 and PERMATRAN-W MODEL 3/33, respectively).

Results and Discussion

In this research, we fabricated a phenyl-siloxane hybrid material (phenyl hybrimer) with the hydrosilylation reaction of sol−gel synthesized phenyl-vinyl-oligosiloxane (PVO) resin with phenyltris(dimethylsiloxy)silane (PTDMSS) as the cross-linker. This phenyl hybrimer (PH) has high thermal stability against yellowing by heat and a high refractive index (n = ~1.56). The PVO resin was fabricated by sol−gel condensing organo-silanes. The typical sol−gel reaction between silane precursors is carried out with the addition of water for hydrolysis and condensation. However, residual OH groups induced from water in this process cause detrimental effects on optical applications. We used instead the direct sol−gel

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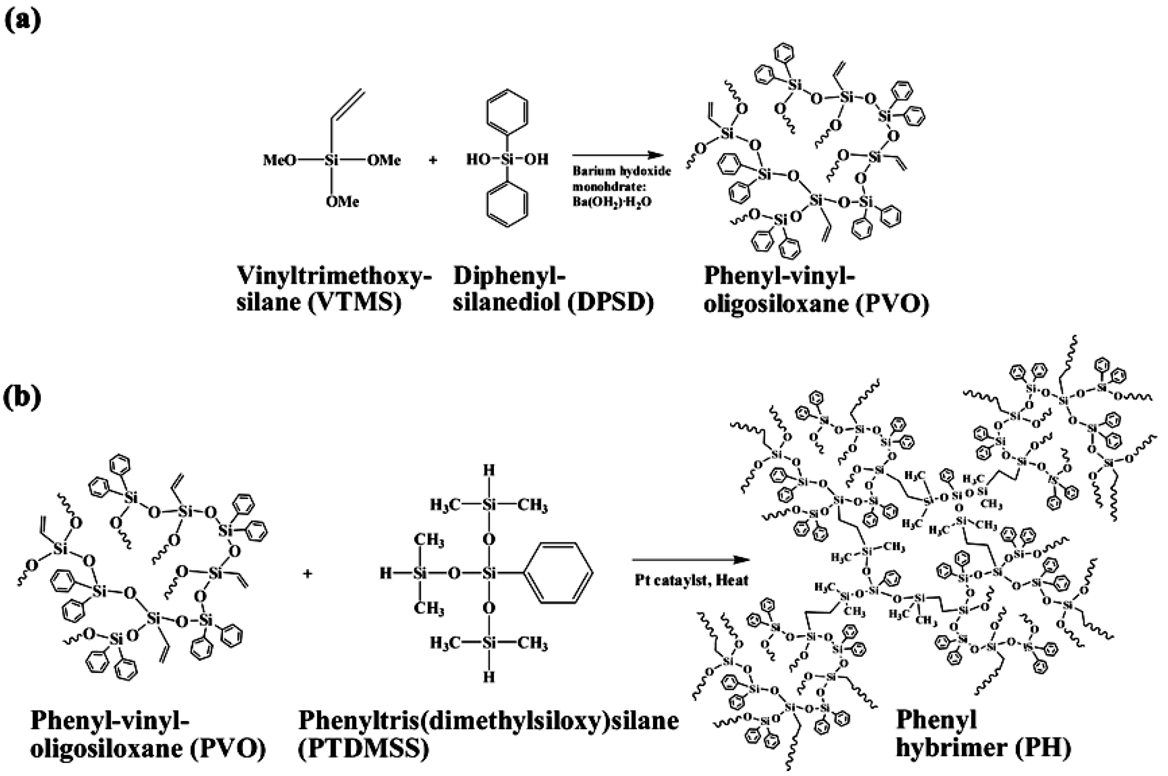
Scheme 1. (a) Synthesis of Phenyl-vinyl-oligosiloxane (PVO) by Sol−Gel Condensation of Vinnyltrimethoxysilane (VTMS) and Diphenylsilanediol (DPSD) and (b) Fabrication of a Phenyl Hybrimer (PH) by a Hydrosilylation Reaction of PVO and Phenyltris(dimethylsiloxy)silane (PTDMSS)



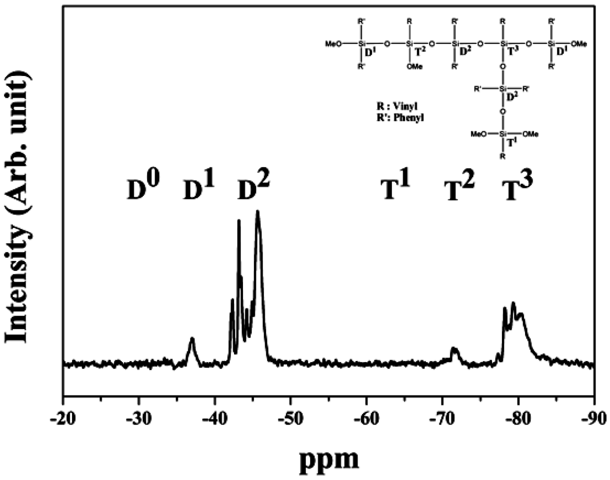


Figure 1. Phenyl-vinyl-oilgosiloxane (PVO) is synthesized through a sol−gel reaction between vinyltrimethoxysilane (VTMS) and diphenylsilanediol (DPSD). Formation of siloxane bonds in PVO is confirmed by ^{29}Si NMR spectroscopy.

Table 1. Characteristics of Phenyl-vinyl-oligosiloxane (PVO)

property	unit	value
degree of condensation (DOC)	%	96.6
density	g mL^{-1}	1.24

condensation reaction between the methoxy group of vinyltrymethoxysilane (VTMS) and the silanol group of diphenylsilanediol (DPSD) to form a siloxane bond, as shown in Scheme 1a. This synthesis reaction without the addition of water can effectively decrease the residual silanol groups and prevent optical loss and moisture penetration. *p*-Xylene is used as a diluent for synthesis of the resin to promote the reaction. Finally, we could successfully synthesize stable PVO resin with a high degree of condensation (DOC), about 96%. The notations of Si atoms in NMR spectroscopy (Figure 1) are D^n and T^n which represent Si atoms from DPSD and VTMS, respectively. The degree of condensation (DOC) of PVO is shown in Table 1. The DOC of PVO was calculated by the following equation from ^{29}Si NMR measurements.

$$\mathrm{DOC} = \frac{D^1 + 2D^2 + T^1 + 2T^2 + 3T^3}{2(D^0 + D^1 + D^2) + 3(T^0 + T^1 + T^2 + T^3)} \times 100 \qquad (1)$$

The peaks at 1020−1120 cm^{-1} in FT-IR spectra (Figure 2) of PVO represent the siloxane network (Si−O−Si). Silanols (peak at 3650 cm^{-1}, Si-OH) from DPSD do not remain after the sol−gel reaction, which means the condensation reaction is fully completed. Further evidence of a completed reaction is that the peaks at 2849 cm^{-1}, methoxy groups on silicon atoms, Si-OCH_3, were no longer present after the reaction, and the peaks at 2940 cm^{-1}, methyl groups on methoxy groups, C-H_3, were also eliminated during the sol−gel reaction. The synthesized PVO possesses a greater density of siloxane branches (1.24 g mL^{-1}) than polydimethylsiloxane (PDMS, 0.96 g mL^{-1}), which contains linear siloxane bonds. The sol−gel condensation of silanes can

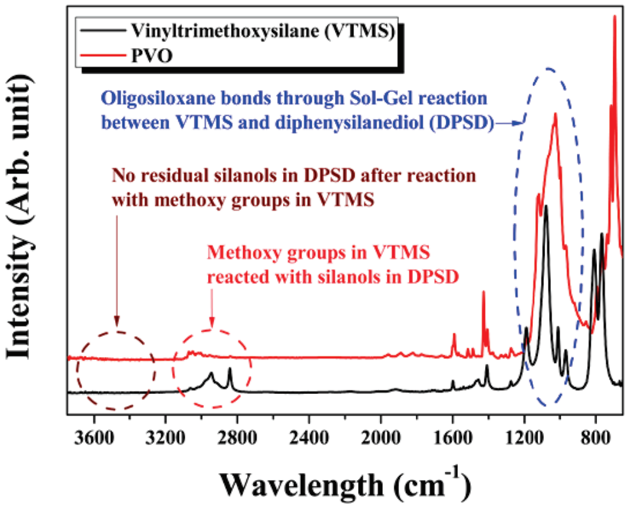


Figure 2. After the sol–gel reaction between VTMS and DPSD, oligosiloxane bonds were formed, and the condensation reaction was completely processed as confirmed by FT-IR spectroscopy.

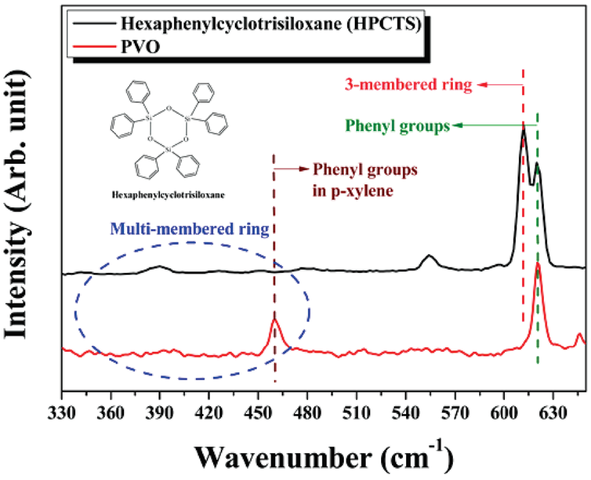


Figure 3. FT-Raman spectra of PVO resin and hexaphenylcyclotrisiloxane (HPCTS) as reference data. The peaks around ~420 cm^{-1} are not detected, which means there are no multimembered cyclic siloxane species present. Even 3-membered ring cyclic siloxanes do not exist in PVO compared to HPCTS, which has 3-membered ring cyclic siloxanes. As confirmed by ^{29}Si NMR and FT-Raman spectrometry, PVO is a branched linear siloxane resin without any cyclic species.

cause oligosiloxane to have branched siloxane bonds. (There is no cyclic species as confirmed by the FT-Raman spectra in Figure 3.) Thus, PVO not only minimizes the content of unnecessary and thermally decomposable organic components but also maximizes the reactivity in the oligosiloxane structure.

Fabrication of the phenyl hybrimer (PH), which is made by the hydrosilylation reaction between the vinyl group (C=C) in PVO and the hydrogen bond (Si–H) in PTDMSS, results in a highly cross-linked network structure as shown in Scheme 1b.[18,19] The molar ratio between the PTDMSS and the PVO was optimized to be 1.25:1, and the hydrosilylation reaction was performed with a Pt catalyst (10 ppm to total weight) at 180 °C in air for 2 h.

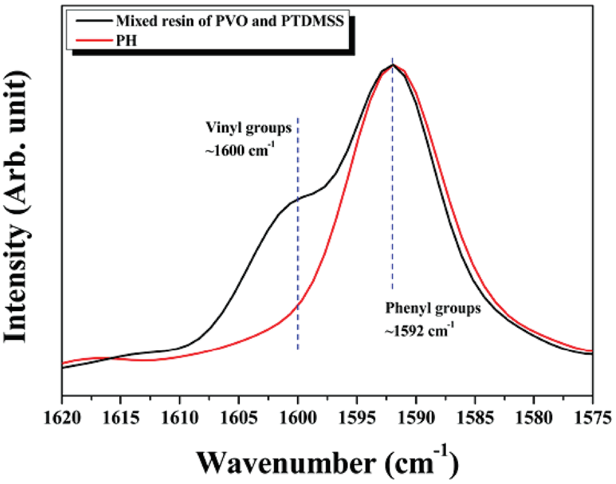


Figure 4. FT-IR spectra of the mixed resin of phenyl-vinly oligosiloxane (PVO) and phenyltris(dimethylsiloxy)silane (PTDMSS) with a Pt catalyst and fabricated phenyl hybrimer (PH) by thermal curing of the resin. Vinyl groups (peak at 1600 cm^{-1}, C=C) in PVO have almost disappeared after the hydrosilylation reaction with PTDMSS.

FT-IR analysis of the vinyl groups (peak at 1600 cm^{-1}, C=C) in the mixed resin of PVO and PTDMSS was performed before and after the hydrosilylation reaction. After the hydrosilylation reaction, the FT-IR signature of the vinyl groups in PVO almost disappeared, as shown in Figure 4.[20]

According to the Chalk–Harrod mechanism of hydrosilylation reactions, C-silylation can be applied for curing PVO in this study, connecting π-bonds in C=C and σ-bonds in Si–H through π–σ-rearrangement, under Pt catalyst and heating.[21–23] O-Silylation, which is another of the Chalk–Harrod mechanisms of hydrosilylation reactions, combines OH groups and Si–H through oxidation addition.[24–27] If nonreacted silanol groups remain, they can also be removed, and molecules can be connected by O-silylation.

The yellowness index (YI) is used for estimating yellowing derived from thermal aging, calculated by the following equation (ASTM, D1925), using the CIE tristimulus values from PH which was measured with a UV/VIS/NIR spectrophotometer.

$$\mathrm{YI(Yellowness\ index)} = \left(\frac{1.28X_{CIE} - 1.06Z_{CIE}}{Y_{CIE}}\right) \times 100 \qquad (2)$$

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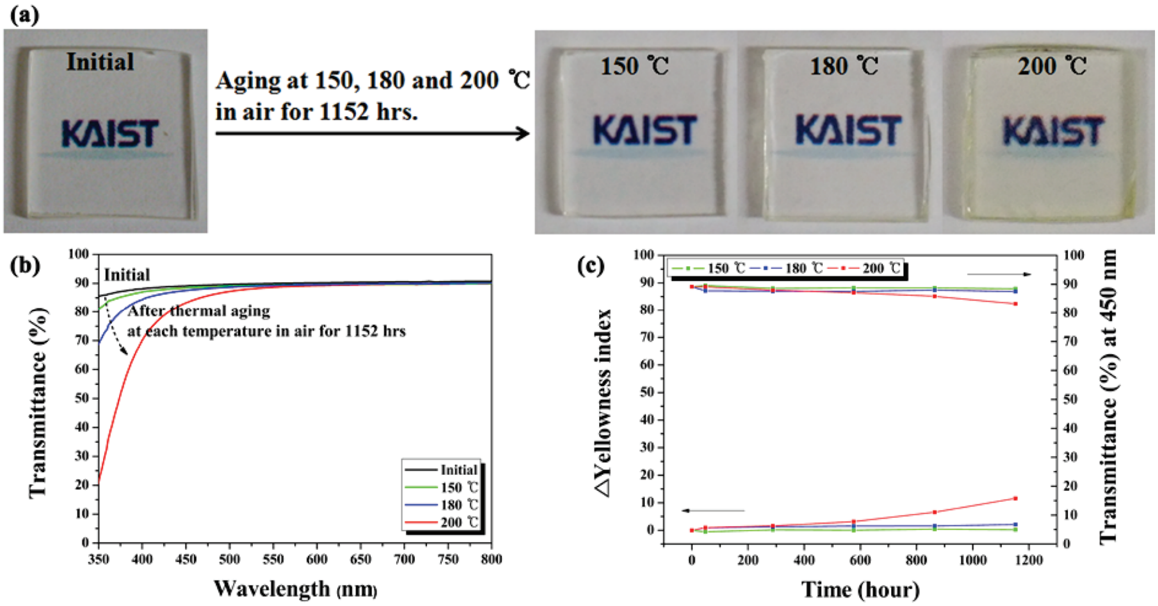

Figure 5. (a) Photographs and (b) optical transmission spectra of the phenyl hybrimer (PH) sample before and after aging at 150, 180, and 200 °C in air for 1152 h. (c) Changes in yellowness index (ΔYI) and transmittance (%) at 450 nm wavelength depending on thermal aging time at each temperature. The sample has a size of $2 \times 2 \times 0.2$ cm^3.

Yellowness index changes (ΔYI) can be described as the difference before and after thermal aging of the samples, as in the following equation.

$$\Delta YI = YI_{\text{After aging}} - YI_{\text{Initial state}} \qquad (3)$$

Figure 5a shows photographs of the samples before and after thermal aging at 150, 180, and 200 °C in air for 1152 h. Discoloration is barely distinguishable by the naked eye for all the samples, even though the aging time was longer than 1000 h. Figure 5 presents optical transmission spectra (Figure 5b) and changes in transmittance (%) at 450 nm wavelength and yellowness index (ΔYI) changes as a function of aging time for the samples aged at 150, 180, and 200 °C (Figure 5c) compared with those of the initial sample before aging. Although UV absorption in the sample increases incrementally with aging time, the transmittance (%) and ΔYI of the samples aged at 150 and 180 °C are almost identical during thermal aging. The samples aged at 200 °C after significant thermal aging show measurable but slight change in transmittance (~6%) and ΔYI (~12). Thus, it can be seen that the PH shows excellent thermal stability against thermal aging. It has never been previously reported that the phenyl polysiloxane materials with high refractive index are thermally stable against yellowing with thermal aging over 150 °C. In general, the phenyl-containing materials are susceptible to yellowing because phenyl radicals are cleaved from backbone chains by thermal aging. However, the PH material is highly rich in phenyl groups as the functional group on oligosiloxane backbones represents a high thermal stability compared to that of other polysiloxanes which have linear structures. This stability is due to strong siloxane network bonds and a branched structure formed by almost complete condensation of organo-silane precursors. This dense and highly condensed oligosiloxane network-based branch structure effectively prevents the generation of cleaved phenyl radicals. In other polysiloxanes with linear structures, the linear siloxane bonds are cut during thermal pyrolysis, forming ring structures.[28] During the pyrolysis process, the phenyl radical is cleaved from the siloxane chain and causes the discoloration to yellow. PVO also has a high density (1.24 g mL^{-1}) due to its branched structure compared to that of the linear structures of polysiloxanes (density of PDMS = 0.96 g mL^{-1}). This contributes to the delay of thermal decomposition and prevents the cleaving of the phenyl radicals from the backbone chain at high temperature.[29]

PVO was synthesized by the sol–gel condensation of silane precursors with short chain functional groups. This reduces unnecessary organic components in the final material which can be thermally decomposed. The byproduct which can negatively affect optical transparency is not generated during thermal curing of PVO since the hydroslylation reaction with cross-linker (under a Pt catalyst) is used for curing.

The PH shows substantial thermal stability against discoloration to yellow, has a high refractive index (n = ~1.56), and can be favorably compared to commercial phenyl polysiloxane resins with phenyl groups for high refractive indices. For example, the highest thermally stable silicone resin which is commercially available for high refractive index use is Shin-Etsu (KER6100/CAT-PH), which provides a yellowing temperature up to 120 °C for 2000 h and a refractive index of ~1.52. Thermal decomposition of the PH was also measured through TGA (thermogravimetric analysis) in N_2 and air. The PH loses 5% of its weight at 442 °C in N_2 and 387 °C in air. Thermal

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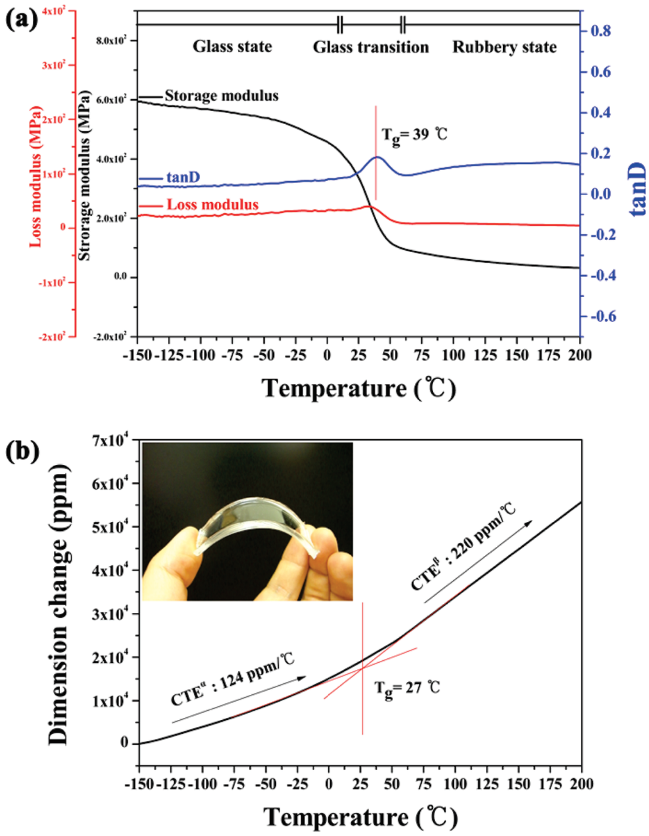

Figure 6. (a) Dynamic mechanical analysis (DMA) and (b) themomechanical analysis (TMA) of the phenyl hybrimer (PH) sample in the temperature range between −150 and 200 °C. Glass transition temperatures measured by DMA and TMA are 39 and 27 °C, respectively. Storage modulus and coefficient of thermal expansion (CTE) of the glass state are about 6.0 × 10^2 MPa and 124 ppm/ °C. Those of the rubbery state are about 20 MPa and 220 ppm/ °C, respectively. The inset shows a photograph of PH sample bending.

oxidation of the PH accelerates the thermal decomposition to the cyclic oligomer, which happens at a lower temperature in air than in N_2.

Dynamic mechanical analysis (DMA) of the PH sample in the temperature range from −150 to 200 °C is represented in Figure 6a. The glass transition temperature (T_g) for maximum tan D is approximately 39 °C, and the storage modulus at the rubbery state above T_g is about 20 MPa. Both values are higher than those for PDMS (−125 °C and 1 MPa) due to its branched linear structure with the siloxane backbone.[30] Figure 6b shows the thermomechanical analysis (TMA) of the PH sample performed from −150 to 200 °C. Dimensional changes show the sample slowly expanding with increased temperature with a broad change in characteristics at around 27 °C, indicating a broad glass transition in the PH. The CTE values represented by the slopes of the dimensional change are 124 ppm °C^{-1} (CTE$^{\alpha}$) below T_g and 220 ppm °C^{-1} (CTE$^{\beta}$) over T_g. CTE$^{\beta}$ of the PH in the rubbery state is less, and the increase in CTE after T_g is smaller than the comparable values for PDMS. This behavior is due to the hybrid characteristics of the highly branched linear structure of the siloxane backbone in the PH material. Because molecules in the PH are cross-linked by branched structures, it is hard for them to become untangled during heating. Even though the PH shows a relatively high storage modulus and CTE$^{\beta}$ as well as T_g compared to the rubbery state PDMS, the PH is actually quite soft, resulting in a bendable sample as shown in Figure 6b, inset. This softness of the PH is desirable for LED encapsulation applications because it protects the delicate wire connections between the PCB and LED, which can be easily broken due to mechanical stress induced by fluctuations at high temperatures. The hardness (shore D) of the PH is approximately 70, which means it can also sufficiently protect encapsulated devices from external shock.

Table 2. Characteristics of the Fabricated Phenyl Hybrimer (PH)

property	unit	value
refractive index[a]	n	1.5597
dn/dT[a]	ppm K^{-1}	−61
hardness	Shore D	70
O_2 permeability	cc mil m^{-2} day^{-1}	1.87 × 10^4
water vapor permeability	gm mil m^{-2} day^{-1}	4.38 × 10^2
T_g (DMA)	°C	39
T_g (TMA)	°C	27
CTE$^{\alpha}$	ppm °C^{-1}	124
CTE$^{\beta}$	ppm °C^{-1}	220
decomposition temp in N_2[b]	°C	442
decomposition temp in air[b]	°C	387

[a] Measured by a prism coupler at 633 nm. [b] Temperature at 5% weight loss by TGA with a heating rate of 5 °C min^{-1}.

We also characterized the refractive index of the PH sample at various temperatures from 25 to 100 °C in order to measure the thermo-optic coefficient (dn/dT). The dn/dT of the PH sample was −61 ppm K^{-1}, which is known to be mainly governed by its thermal expansion behavior according to the Prod'homme theory.[31] The dn/dT value of most organic polymers is generally in the order of 10^2 ppm K^{-1}. Thus, the dn/dT of the PH is lower than that of other polymers, providing another advantage for use in reliable LED encapsulants. In addition, the oxygen and water vapor permeabilities of the PH samples were measured, and the values were 1.87 × 10^4 cc mil m^{-2} day^{-1} and 4.38 × 10^2 gm mil m^{-2} day^{-1}, respectively. These are remarkably lower than those of PDMS (1.6 × 10^{24} cc mil m^{-2} day^{-1} and 3.14 × 10^3 gm mil m^{-2} day^{-1}).[32,33] This improved gas barrier characteristic of the PH could provide an extra benefit for the protection of the LED chips. All of the characteristics of the PH measured in this study are summarized in Table 2. These advanced characteristics for the LED encapsulation application, compared with the polysiloxanes, are caused by the hybrid structural characteristic based on the branched linear siloxane backbone structure of the PH.

Conclusions

In conclusion, the phenyl and vinyl group functionalized oligosiloxane was synthesized by sol−gel condensation of the VTMS and DPSD precursors with barium

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hydroxide monohydrate as a catalyst. The transparent resin can be thermally cured by the hydrosilylation reaction with cross-linker PTDMSS under a Pt catalyst. The fabricated PH showed excellent optical transparency with high refractive index ($n = \sim 1.56$). The transparency in the visible range was maintained even after thermal aging at 200 °C in air for 1152 h. This high thermal stability at high temperature for long periods with high refractive index is a most desirable combination for use in LED encapsulation and would support the long lifetime and high efficiency of light extraction. We confirmed that the PH exhibits a soft mechanical property but has a sufficient shore D hardness to protect the LED from thermal stress during operation and from external forces. Also, the PH has a low oxygen and water vapor permeability and smaller values of $\mathrm{d}n/\mathrm{d}T$ compared to those of existing polysiloxanes. These characteristics could be advantageous if this material were to be used in LED encapsulation.

Acknowledgment. This work was supported by Basic Science Research Program through National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (No. R11-2007-045-03002-0 and No. R01-2007-000-20815-0). We gratefully thank Hak Nam Kim at Korea Basic Science Institute (KBSI) for ^{29}Si NMR spectra measurements.