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Preparation of Titanium-silphenylene-siloxane Hybrid Polymers with High Refractive Index, Transmittance, and Thermal Stability

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Abstract Vinyl-containing titanium-silphenylene-siloxane oligomers (**O1**, **O2**, **O3**, and **O4**) with different molar ratios of titanium to silicon were successfully synthesized in high yields by nonhydrolytic sol-gel reaction, and the obtained four oligomers were further crosslinked with methylphenyl hydro-silicone oil (**4**) to form corresponding polymers (**P1**, **P2**, **P3**, and **P4**) by hydrosilylation reaction. Their structures were characterized with spectroscopic characterization techniques including FTIR, ¹H-NMR, and Raman spectroscopy. The effect of titanium element on crosslinking behavior, thermal resistance, refractive index, transparency, thermal aging stability, glass transition temperature, and surface properties of the polymers were studied. Compared with titanium-free polymer **P1**, the thermal resistance, refractive index, and thermal aging stability of titanium-silphenylene-siloxane polymers (**P2**, **P3**, and **P4**) were significantly improved. The titanium-silphenylene-siloxane polymers achieved a high refractive index ($n = 1.580\text{--}1.584$) and thermostability ($T_{\text{sd}} > 500\text{ }^{\circ}\text{C}$). In thermal aging, the polymers exhibited superior performances with high optical transparency ($\sim 90\%$ at 450 nm) and exhibited high thermal stability ($\sim 84\%$ at 450 nm after thermal aging at 150 $^{\circ}\text{C}$ for 120 h). These data indicate that the polymers have potential application in optical materials such as LED encapsulants.

Keywords Titanium-silphenylene-siloxane hybrid polymers; High refractive index and transmittance; Thermal stability

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INTRODUCTION

Light emitting diodes (LEDs) have gradually substituted the incandescent bulbs and fluorescent lamps owing to their low power consumption, high luminous efficiency, and long service life. The encapsulation materials play increasingly important part in LED chips package as these materials can protect LED chips against humidity, oxygen, and external damage while increasing light extraction efficiency of LED.^[1,2] Therefore, the encapsulation with high transparency, thermostability, long-term thermal aging stability, and high refractive index (n) is essential. In recent years, the high refractive index polymers (HRIPs) have been mainly classified into two types, intrinsic and nanocomposite HRIPs. Nanocomposite HRIPs are inorganic-organic hybrid materials which combine the optical polymer matrix with nanoparticles, such as ZrO_2 ,^[3–6] TiO_2 ,^[7–11] Al_2O_3 ,^[12] and ZnS .^[13,14] The introduction of these nanoparticles greatly improves the refractive index ($n > 1.8$) of polymers whereas sometimes causes poor mechanical properties and processing performance because the nanoparticles are easy to aggregate in polymer matrix due to their high surface energies and low compatibilities with the polymers.^[15] In contrast, intrinsic HRIPs improve their refractive index ($n < 1.8$) by introducing various

substituents with high molar refraction and low molar volume such as sulfur, aromatic, halogen, and others. Although the refractive index properties of intrinsic HRIPs cannot and will not exceed those of the nanocomposites, intrinsic HRIPs have significant advantages in terms of adjustability, stability, and processability.

Among these intrinsic HRIPs, thermosetting epoxy resins and silicone-based materials are commonly used. Epoxy resin has been popular LED encapsulant for its good insulation to moisture, strong adhesion to metal, and mechanical robustness.^[16] However, with the increase of LED device power, the epoxy resin is unable to meet the requirement of LED encapsulants owing to nonnegligible shortcomings such as low thermostability and anti-yellowing. To address this issue, silicone resins are used as LED encapsulants due to their high transmittance and excellent thermostability. Unfortunately, the refractive index of polydimethylsiloxane (PDMS) resin which is the most common product from silicone manufactured is too low ($n \sim 1.41$) compared to that of epoxy resin ($n \sim 1.53$). In general, introducing aromatic groups into the polymer chains is a good strategy to improve the refractive index of organic polymers. Therefore, some polymers containing phenyl,^[17–20] binaphthyl,^[21] thianthrene,^[22] carbazole,^[23] or fluorene groups^[24] were well investigated and exhibited high refractive index.

In this study, considering the above-described shortcom-

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ings of silicones and the design idea of HRIPs for LED encapsulants, silphenylene was selected and introduced into the polymer's backbone through nonhydrolytic sol-gel reaction, which can increase the rigidity of structures so as to enhance thermal stability. Besides, incorporating heterometallic phase to the polymer chains can also improve the refractive index.^[18,19] Thus, a series of novel titanium-silphenylene-siloxane hybrid polymers (**P2**, **P3**, and **P4**, see Chart 1) with high refractive index ($n = 1.580\text{--}1.584$) were prepared, and their transmittance and thermal stability were carefully studied. Due to their easy processability, the obtained polymers were utilized to fabricate free-standing films with good uniformity and smooth surface. Hence, they may have potential applications in optical materials as LED encapsulants.

EXPERIMENTAL

Materials

Titanium(IV) isopropoxide (**1**, 95%) and vinyltrimethoxysilane (**2**, > 97.5%) were obtained from J&K Scientific. 1,4-Phenylene-bis(dimethylsilanol) (**3**, 95%) was received from Macklin. Methylphenyl hydro-silicone oil (**4**, 0.3 wt% of the active hydrogen) was received from Guangzhou Xinhou Chemical Technology Co., Ltd. Barium hydroxide monohydrate (**5**, 95%) was bought from Aladdin. Karstedt's catalyst (**6**, xylene solution of platinum (0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex, 20% Pt) was

obtained from Umicore-Precious Metals Chemistry.

Instrumentation

FTIR spectra were obtained on a Thermofisher Nicolet 6700 spectrometer, and laser confocal micro-Raman spectra were tested on a Renishaw Invia Reflex device. ¹H-NMR spectra were acquired in deuterated chloroform on a Bruker AVANCE III 400 MHz spectrometer. Tetramethylsilane (TMS) was used as an internal standard. Molecular weight (MW) and polydispersity indices (M_w/M_n) were tested with Waters 515 gel permeation chromatography (GPC) system, where tetrahydrofuran (THF) was used as an eluent at 25 °C and a flow rate of 1.0 mL/min. Differential scanning calorimetry (DSC) analysis was conducted under nitrogen using a TA Discover 25 device. Thermogravimetric analysis (TGA) was performed under nitrogen from 50 °C to 1000 °C by a TA Instrument SDT-Q600 apparatus at a heating rate of 20 °C/min. The optical transmittance was measured on a Shimadzu UV-3600 UV-Vis-NIR spectrophotometer. Thermal aging test was conducted by treating the samples at 150 °C for 24, 72, and 120 h, respectively. UV aging test was conducted by treating the samples under UV light (365 nm, 18 W/m²) at 40 °C for 5 and 10 h in a Model SZW-3 ultraviolet irradiation test chamber from Zhengzhou Huisheng Materials Co., Ltd. The refractive index was measured at 25 °C and 589 nm on an Abbe refractometer from Shanghai CSOIF Co., Ltd. X-ray diffraction (XRD) analysis was performed on Rigaku D/max 2500 PC with Cu

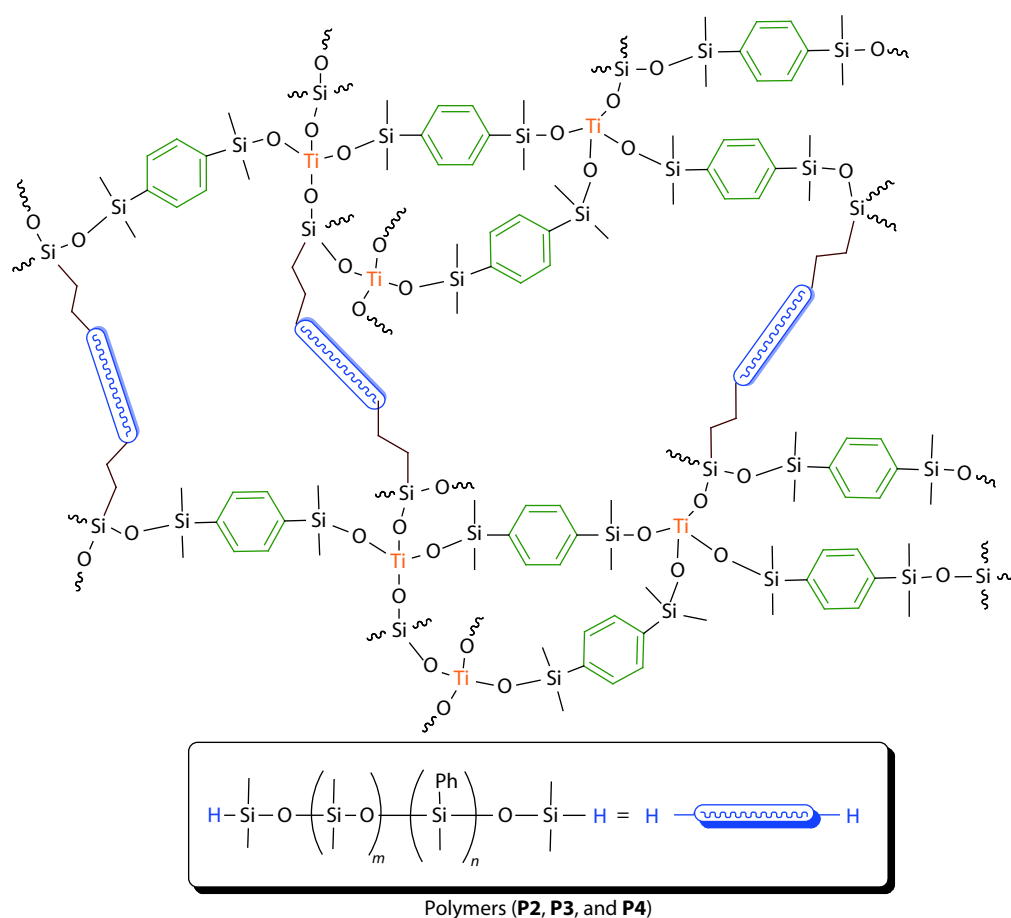


Chart 1 The structure of titanium-silphenylene-siloxane hybrid polymers (**P2**, **P3**, and **P4**).

K α radiation ($\lambda = 1.5406 \text{ \AA}$) at room temperature and the scattering angle ranged from 5° to 80° at $5^\circ/\text{min}$. The contact angle measurement was conducted on SOLON TECH, SL200KS contact angle meter to evaluate the hydrophobicity of the polymer's surface. Atomic force microscopy (AFM) was measured on a Bruker Multimode 8 to probe the surface morphology of polymers.

Synthesis of Vinyl-containing Titanium-silphenylene-siloxane Oligomers (**O1**, **O2**, **O3**, and **O4**)

Vinyl-containing titanium-silphenylene-siloxane oligomers (**O1**, **O2**, **O3**, and **O4**) were synthesized according to the synthetic routes in Scheme 1, and typical experimental procedures for synthesis of **O2** are given below as an example. Into a 100 mL three-neck round-bottom flask equipped with a magnetic stirrer were added vinyltrimethoxysilane (**2**, 3.27 g, 22.1 mmol), 1,4-phenylenebis(dimethylsilanol) (**3**, 5.00 g, 22.1 mmol), and barium hydroxide monohydrate (**5**, 8.30 mg, 0.0438 mmol). The mixture was stirred at 85°C for 3 h. Then titanium(IV) isopropoxide (**1**, 0.19 g, 1 mol% of total Si) was added dropwise into the flask. After the addition of titanium compound, the mixture was further stirred at 85°C for 2 h. The mixture was filtered through $0.45 \mu\text{m}$ Teflon filter to remove the precipitate. The volatiles were removed by vacuum heating (35°C , overnight) to give a clear viscous liquid in a yield of 92.0%. M_n : 1430; M_w/M_n : 1.34 (GPC, polystyrene calibration). FTIR (ν , cm^{-1}): 3051, 2958, 2835, 1925, 1600, 1408, 1381, 1254, 1192, 1137, 1084, 966, 821, 779, 729, 644. $^1\text{H-NMR}$ (400 MHz, CDCl_3 , δ , TMS, ppm): 7.60–7.70 ($-\text{C}_6\text{H}_4-$); 5.88–6.21 ($-\text{CH}=\text{CH}_2$); 3.50–3.64 ($-\text{OCH}_3$); 1.20–1.32 ($-\text{CH}$); 0.35–0.48 ($-\text{CH}_3$).

O3 and **O4** were synthesized by a procedure similar to that used for synthesis of **O2**. The dosage of titanium(IV) isopropoxide (**2**) was 0.57 g (3 mol% of total Si) and 0.95 g (5 mol% of total Si), respectively. **O1** was synthesized without the addition of **2**. The yields of **O1**, **O3**, and **O4** were 88%, 94%, and 90%, respectively.

Characterization data for **O1**: clear viscous liquid; yield 88.0%. M_n : 1260; M_w/M_n : 1.29 (GPC, polystyrene calibration). FTIR (ν , cm^{-1}): 3051, 2958, 2835, 1925, 1600, 1408, 1381, 1254, 1192, 1137, 1084, 966, 821, 779, 729, 644. $^1\text{H-NMR}$ (400 MHz, CDCl_3 , δ , TMS, ppm): 7.60–7.70 ($-\text{C}_6\text{H}_4-$); 5.88–6.21 ($-\text{CH}=\text{CH}_2$); 3.50–3.64 ($-\text{OCH}_3$); 0.35–0.48 ($-\text{CH}_3$).

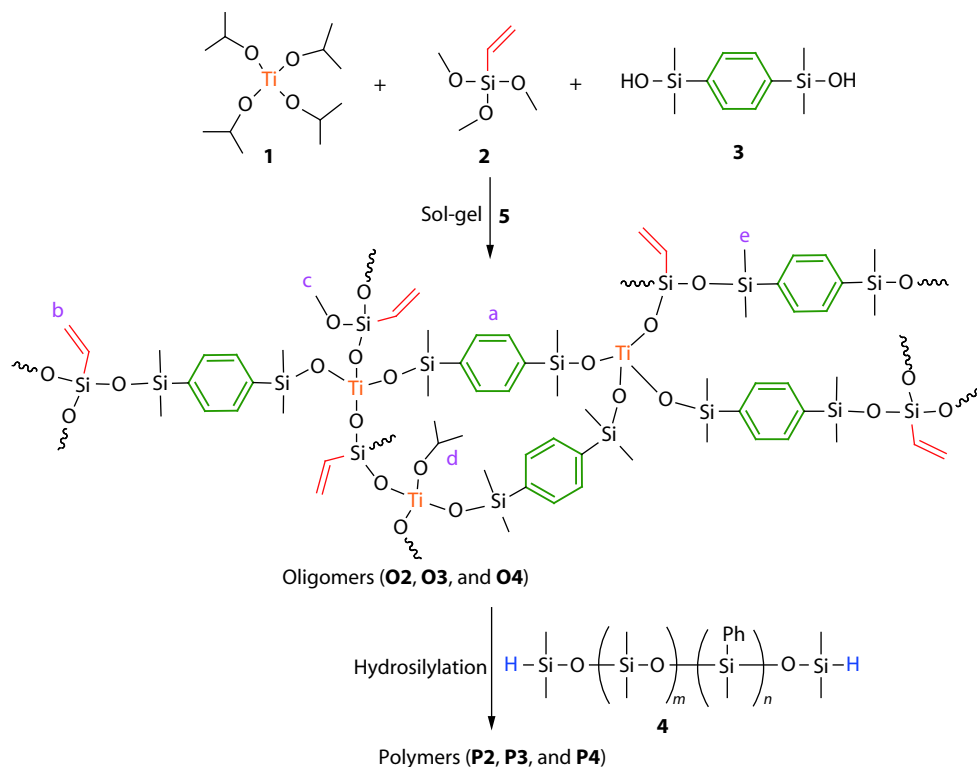
Characterization data for **O3**: clear viscous liquid; yield 94.0%. M_n : 1550; M_w/M_n : 1.37 (GPC, polystyrene calibration). FTIR (ν , cm^{-1}): 3051, 2958, 2835, 1925, 1600, 1408, 1381, 1254, 1192, 1137, 1084, 966, 821, 779, 729, 644. $^1\text{H-NMR}$ (400 MHz, CDCl_3 , δ , TMS, ppm): 7.60–7.70 ($-\text{C}_6\text{H}_4-$); 5.88–6.21 ($-\text{CH}=\text{CH}_2$); 3.50–3.64 ($-\text{OCH}_3$); 1.20–1.32 ($-\text{CH}$); 0.35–0.48 ($-\text{CH}_3$).

Characterization data for **O4**: clear viscous liquid; yield 90.0%. M_n : 1660; M_w/M_n : 1.26 (GPC, polystyrene calibration). FTIR (ν , cm^{-1}): 3051, 2958, 2835, 1925, 1600, 1408, 1381, 1254, 1192, 1137, 1084, 966, 821, 779, 729, 644. $^1\text{H-NMR}$ (400 MHz, CDCl_3 , δ , TMS, ppm): 7.60–7.70 ($-\text{C}_6\text{H}_4-$); 5.88–6.21 ($-\text{CH}=\text{CH}_2$); 3.50–3.64 ($-\text{OCH}_3$); 1.20–1.32 ($-\text{CH}$); 0.35–0.48 ($-\text{CH}_3$).

Characterization data for **O4**: clear viscous liquid; yield 90.0%. M_n : 1660; M_w/M_n : 1.26 (GPC, polystyrene calibration). FTIR (ν , cm^{-1}): 3051, 2958, 2835, 1925, 1600, 1408, 1381, 1254, 1192, 1137, 1084, 966, 821, 779, 729, 644. $^1\text{H-NMR}$ (400 MHz, CDCl_3 , δ , TMS, ppm): 7.60–7.70 ($-\text{C}_6\text{H}_4-$); 5.88–6.21 ($-\text{CH}=\text{CH}_2$); 3.50–3.64 ($-\text{OCH}_3$); 1.20–1.32 ($-\text{CH}$); 0.35–0.48 ($-\text{CH}_3$).

Preparation of Titanium-silphenylene-siloxane Polymers (**P1**, **P2**, **P3**, and **P4**)

Into a 50 mL beaker were added **O1** (1 g, 2.61 mmol of vinyl), methylphenyl hydro-silicone oil (**5**, 0.54 g, 2.61 mmol of SiH), and Karstedt's catalyst (**6**, 10 ppm Pt). The mixture was stirred for 5 min, and then poured into Teflon mold. The mold was kept in oven at 120°C for 4 h. The cured film is designated as **P1**.



Scheme 1 Synthesis of titanium-silphenylene-siloxane oligomers (**O2**, **O3**, and **O4**) and polymers (**P2**, **P3**, and **P4**).

P2, **P3**, and **P4** were prepared from **O2**, **O3**, and **O4** by a procedure similar to that used for preparation of **P1**.

RESULTS AND DISCUSSION

Oligomer Synthesis

Vinyl-containing titanium-silphenylene-siloxane oligomers (**O2**, **O3**, and **O4**) were synthesized *via* nonhydrolytic sol-gel condensation from titanium(IV) isopropoxide (**1**), vinyltrimethoxysilane (**2**), and 1,4-phenylenebis(dimethylsilanol) (**3**) in the presence of barium hydroxide monohydrate (**5**) as catalyst, according to Scheme 1. The feed molar ratio of titanium to silicon was 0.01 (**O2**), 0.03 (**O3**), and 0.05 (**O4**), respectively. Oligomer without titanium (**O1**, Ti/Si = 0) was also prepared by the similar method. Then, the obtained four oligomers were further crosslinked with methylphenyl hydro-silicone oil (**4**) to form titanium-silphenylene-siloxane polymers (**P2**, **P3**, and **P4**) and titanium-free polymer **P1**. The hydrosilylation crosslinking was catalyzed by Karstedt's catalyst (**6**), which will be discussed in detail below.

Multiple spectroscopic methods were utilized to characterize the obtained oligomers (**O1–O4**), and all the analysis data were consistent with the expected molecular structures of the oligomers (see Experimental section for details). FTIR spectra of oligomers (**O1–O4**) are shown in Fig. 1, and it is obvious that the band at 1000–1100 cm^{-1} is corresponded with characteristic absorption of Si—O—Si.^[25] All the oligomers showed absorption bands at 1600 cm^{-1} , which are ascribed to the stretching vibration of vinyl on silicon atom. Besides, the spectra exhibited weak bands at 1137 and 821 cm^{-1} associated with silphenylene structure.^[26–28] Titanium-containing oligomers (**O2**, **O3**, and **O4**) show bands at 966 cm^{-1} , which are the characteristic absorption of Si—O—Ti.^[29] It is interesting that titanium-free oligomer (**O1**) also exhibited absorption band at 966 cm^{-1} owing to the fact that vinyl vibrates at the same position.^[30]

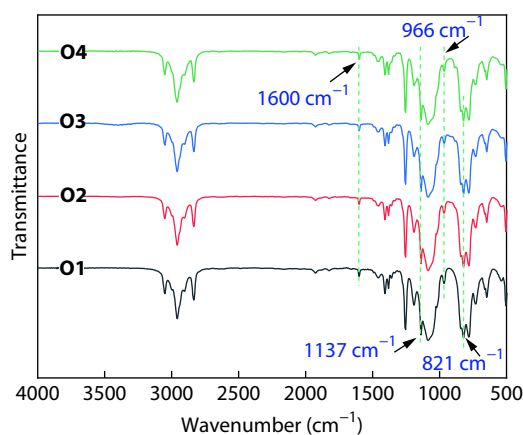


Fig. 1 FTIR spectra of titanium-silphenylene-siloxane oligomers (**O1–O4**).

NMR spectroscopy is an effective method for further characterizing the oligomers. ^1H -NMR spectra of **O1–O4** are shown in Fig. 2. All oligomers showed signals at $\delta \sim 7.60$ – 7.70 , which are associated with silphenylene proton. The weak signals at $\delta \sim 5.88$ – 6.21 are assigned to vinyl pro-

ton, while the signals at $\delta \sim 3.50$ – 3.64 are ascribed to methoxy proton. Besides, as for titanium-containing oligomers (**O2**, **O3**, and **O4**), the signals at $\delta \sim 1.20$ – 1.32 are corresponded with methenyl proton on residual titanate structure, indicating incomplete condensation of isopropoxy. It is reasonable that this signal is absent in the spectrum of titanium-free oligomer **O1**. The signals appear at $\delta \sim 0.35$ – 0.48 , which are assigned to methyl proton of the oligomers.

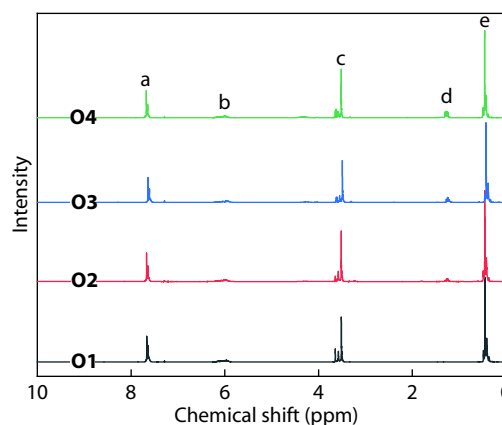


Fig. 2 ^1H -NMR spectra of titanium-silphenylene-siloxane oligomers (**O1–O4**).

Raman spectroscopy was also employed to further confirm the structure of oligomers. It is seen from Fig. 3 that absorption bands at 1407 and 3054 cm^{-1} are identified to C—H bond on vinyl. The silphenylene owns characteristic bands at 633, 1085, and 1200 cm^{-1} . Besides, the ring deformation of silphenylene is located at 1578 cm^{-1} , while bands at 2800–3000 cm^{-1} are related with symmetric and antisymmetric stretching of C—H bond on methyl.

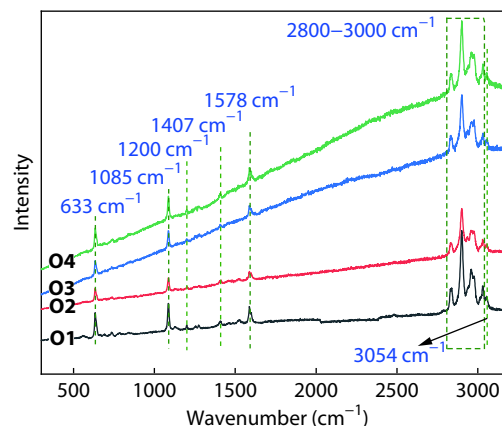


Fig. 3 Raman spectra of titanium-silphenylene-siloxane oligomers (**O1–O4**).

The obtained four polymers (**P1–P4**) were characterized by FTIR spectroscopy. Methylphenyl hydro-silicone oil (**4**) was adopted as crosslinking agent, and was also examined for comparison. As shown in Fig. 4, the absorption bands at 1600 cm^{-1} derived from vinyl disappear after hydrosilylation, indicating complete consumption of vinyl on oligomers. New

bands at 1593 cm^{-1} appear associated with $\text{Si}-\text{C}_6\text{H}_5$ structure since methylphenyl hydro-silicone oil (**4**) was incorporated into the crosslinked structure of polymers. All polymers and methylphenyl hydro-silicone oil (**4**) showed absorption at 3054 , 2958 , and 2900 cm^{-1} , which are ascribed to aromatic C—H stretch vibrations, methyl asymmetric stretch, and methyl symmetrical stretch, respectively. Besides, titanium-containing polymers (**P2**, **P3**, and **P4**) showed absorption bands at 2137 cm^{-1} , indicating residual Si—H existed in these polymers. This phenomenon can be ascribed to the transition metal such as titanium complexes catalyzing vinyl polymerization, which enabled Si—H and vinyl to react incompletely.

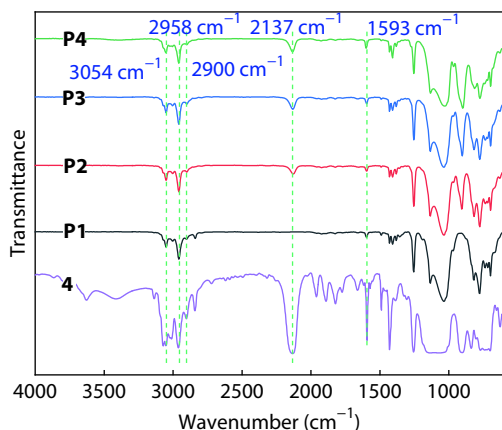


Fig. 4 FTIR spectra of titanium-free polymer (**P1**), titanium-silphenylene-siloxane polymers (**P2–P4**), and methylphenyl hydro-silicone oil (**4**).

Crosslinking Behavior and Thermal Stability

Titanium-silphenylene-siloxane polymers (**P2**, **P3**, and **P4**) and titanium-free **P1** were prepared from oligomers by platinum-catalyzed hydrosilylation crosslinking. Considering hydrosilylation is exothermic, differential scanning calorimetry (DSC) was utilized to study the crosslinking behavior of oligomers, and the result is shown in Fig. 5. It is seen that oligomer **O1** showed prominent exotherm above 140°C , and the maximum exothermic temperature (DSC peak temperature) was 151°C . However, DSC peak temperatures of titanium-containing oligomers (**O2**, **O3**, and **O4**) were 131 , 129 , and 122°C , respectively, much lower than that of their titanium-free counterpart. Thus, titanium-containing oligomers exhibited much higher reactivity, which suggests that the existence of titanium in oligomers promotes the hydrosilylation. In other words, titanium-containing heterometallic phase played an additional catalytic effect. It is well known that the hydrosilylation reaction is catalyzed not only by late-transition metals like platinum,^[31–33] iron,^[34,35] cobalt,^[36–38] and nickel complexes,^[39,40] but also by some early-transition metals such as zirconium and titanium derivatives.^[41] According to common sense in polymer chemistry, the additional catalytic effect is beneficial to the improvement of oligomers' crosslink density, which further contributes to their thermal stability and glass transition temperature.

It is generally known that the outgassing problem of LED encapsulant is often caused by the heat released from LED chip. Therefore, the thermal stability of polymers is one of the

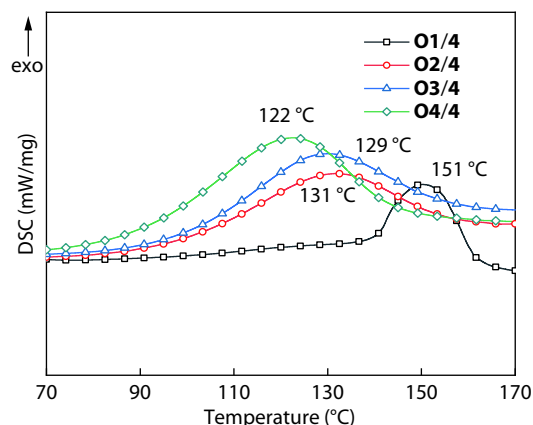


Fig. 5 DSC profiles of oligomers (**O1–O4**) crosslinking.

important factors and thermal gravimetric analysis (TGA) was adopted to evaluate the thermal stability of titanium-silphenylene-siloxane polymers (**P2**, **P3**, and **P4**) and titanium-free polymer **P1**. It can be seen from Fig. 6 that all the polymers showed extraordinarily high initial decomposition temperature (T_{5d} , above 500°C) and residual weight (above 75% at 1000°C) owing to the existence of silphenylene in the main chain.^[42] Specifically, the initial decomposition temperature of **P1** was 506°C , while the T_{5d} values of **P2**, **P3**, and **P4** were 531 , 558 , and 560°C , respectively. Additionally, titanium-silphenylene-siloxane polymers showed much higher residual weight at 1000°C (82.7%, 82.7%, and 83.2% for **P2**, **P3**, and **P4**, respectively) than their titanium-free counterpart (76.1%). It is concluded that the incorporation of titanium improved the thermal stability of polymers effectively. As is well known, the thermal stability of the crosslinked polymer mainly depends on the main chain structure and crosslink density. In this study, both factors were adjusted by the introduction of titanium. On the one hand, titanium exerted an additional catalytic effect on the crosslinking behavior, which increased the crosslink density. On the other hand, Si—O—Ti linkage owns higher bond energy (662.0 kJ/mol)^[43] than Si—O—Si (443.7 kJ/mol)^[44] and thus the obtained organic-inorganic hybrid polymers exhibited higher T_{5d} values and residual weight. The hybrid polymers can be transformed to amorph-

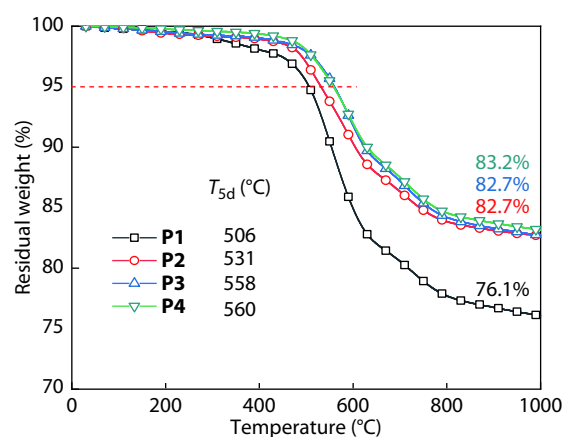


Fig. 6 TGA thermograms of titanium-silphenylene-siloxane polymers (**P2**, **P3**, and **P4**) and titanium-free polymer **P1**.

ous silica and titanium dioxide at elevated temperature.

Optical Properties

High refractive index (n) is generally required for LED encapsulants since higher refractive index leads to higher luminous efficiency of LED.^[45] Thus, the refractive indices of all polymers (**P1**, **P2**, **P3**, and **P4**) were measured and are shown in Fig. 7. All the samples exhibited refractive index above 1.580. Specifically, the refractive index of titanium-free polymer **P1** was 1.580, while those of titanium-silphenylene-siloxane polymers (**P2**, **P3**, and **P4**) were 1.582, 1.583 and 1.584, respectively. Compared to the conventional organic LED encapsulants (epoxy or silicone, $n \sim 1.500$), the refractive index of polymers increased markedly. In general, the Lorentz-Lorenz equation (Eq. 1) can be used to predict the refractive index of polymers.^[46,47]

$$\frac{(n^2 - 1)}{(n^2 + 1)} = \frac{R}{M} \times \frac{M}{V} = \frac{R_m}{V_m} \quad (1)$$

where R is the molecular refraction, M is the molecular weight, and V is the molecular volume of the repeat unit. R/M can also be represented as molar refraction (R_m) and M/V as the reciprocal of molar volume (V_m). Accordingly, the polymer with a high molar refraction and a low molar volume will possess higher refractive index. Consequently, we will adjust the refractive index of polymer by introducing some functional groups with larger molar refraction (R_m), such as phenyl ($R_m = 25.463$), naphthyl ($R_m = 43.000$), halogen ($R_m = 6-14$) except for fluorine, sulfur ($R_m = 7.691$), etc.^[48,49] In other words, introducing aromatic group into polymer backbone will increase the refractive index of the polymers. In addition, nanoparticles such as crystalline silicone ($R_m = 3.497$), TiO_2 (rutile $R_m = 2.571$), and diamond ($R_m = 2.417$) are also beneficial to increasing the refractive index of polymers. In this study, the refractive index of titanium-free polymer **P1** was higher than those of common silicone encapsulants, which can be attributed to the introduction of silphenylene. Besides, the refractive index of titanium-silphenylene-siloxane polymers (**P2**, **P3**, and **P4**) improved with the increase of molar ratio of titanium to silicon owing to the introduction of silphenylene and formation of heterometallic structure. Summarily, the control of refractive index has been achieved by synergic effects of silphenylene and titanium element which were both combined into the polymer backbone.

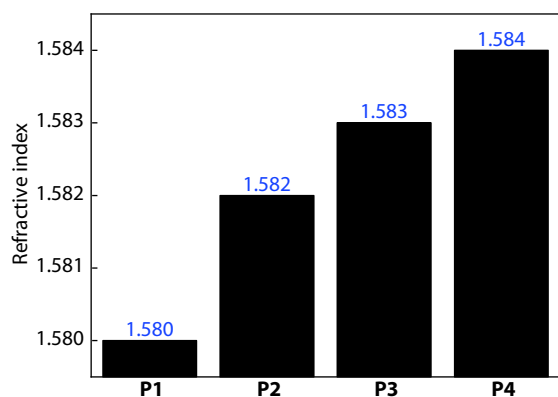


Fig. 7 Refractive index of titanium-silphenylene-siloxane polymers (**P2**, **P3**, and **P4**) and titanium-free polymer **P1**.

On the other hand, optical transparency is also a vital characteristic for LED encapsulants. The optical transmittance spectra of polymers (**P1**, **P2**, **P3**, and **P4**) containing different molar ratios of titanium to silicon were measured. As is shown in Fig. 8, it is obvious that all polymers exhibited good transparency in the visible range. Besides, the titanium-silphenylene-siloxane polymers (**P2**, **P3**, and **P4**) added with titanium elements exhibited better optical transparency than the polymer without it (**P1**). For instance, titanium-free polymer **P1** had the transmittance of 82.5% at 450 nm, whereas titanium-silphenylene-siloxane polymers (**P2**, **P3**, and **P4**) exhibited higher transmittance of 90.1%, 88.2%, and 88.9%, respectively. This can be attributed to the formation of heterometallic structure. Additionally, the transmittance of titanium-silphenylene-siloxane polymers (**P2**, **P3**, and **P4**) had little difference, which can be attributed to slight difference in feed molar ratio of titanium to silicon.

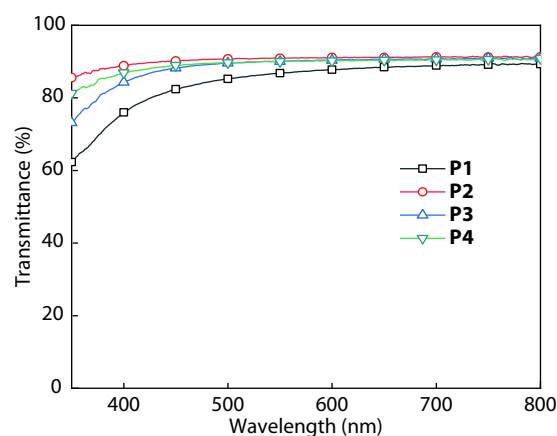


Fig. 8 Initial transmittance of titanium-silphenylene-siloxane polymers (**P2**, **P3**, and **P4**) and titanium-free polymer **P1**.

To evaluate the performance reliability in terms of optical transparency stability, the polymers (**P1**, **P2**, **P3**, and **P4**) were subjected to thermal aging test at 150 °C for 24, 72, and 120 h and the transmittance of the polymers was checked before and after the thermal aging. As is shown in Fig. 9, the transmittance of polymers was above 80% at 450 nm after thermal aging, which indicates all polymers exhibited excellent thermal aging properties. Moreover, the transmittance of titanium-silphenylene-siloxane polymers (**P2**, **P3**, and **P4**) was much higher than that of titanium-free polymer **P1** after thermal aging. For instant, **P4** had the transmittance of 88.9% at 450 nm before aging and 84.6% after aging, while **P1** had the transmittance of 82.5% before aging and 80.6% after aging. Moreover, titanium-free **P1** showed the smallest transmittance drop of 1.9% (from 82.5% to 80.6%), whereas titanium-silphenylene-siloxane polymer **P2** showed a significant transmittance drop of 7.6% (from 90.1% to 82.5%). It is interesting that the existence of titanium atom can adversely affect the optical transparency stability of titanium-silphenylene-siloxane polymers (**P2**, **P3**, and **P4**) during thermal aging, as is clearly shown in Fig. 9. We think the titanium-containing heterometallic phase plays a catalytic role in the thermal aging process, so the titanium-silphenylene-siloxane

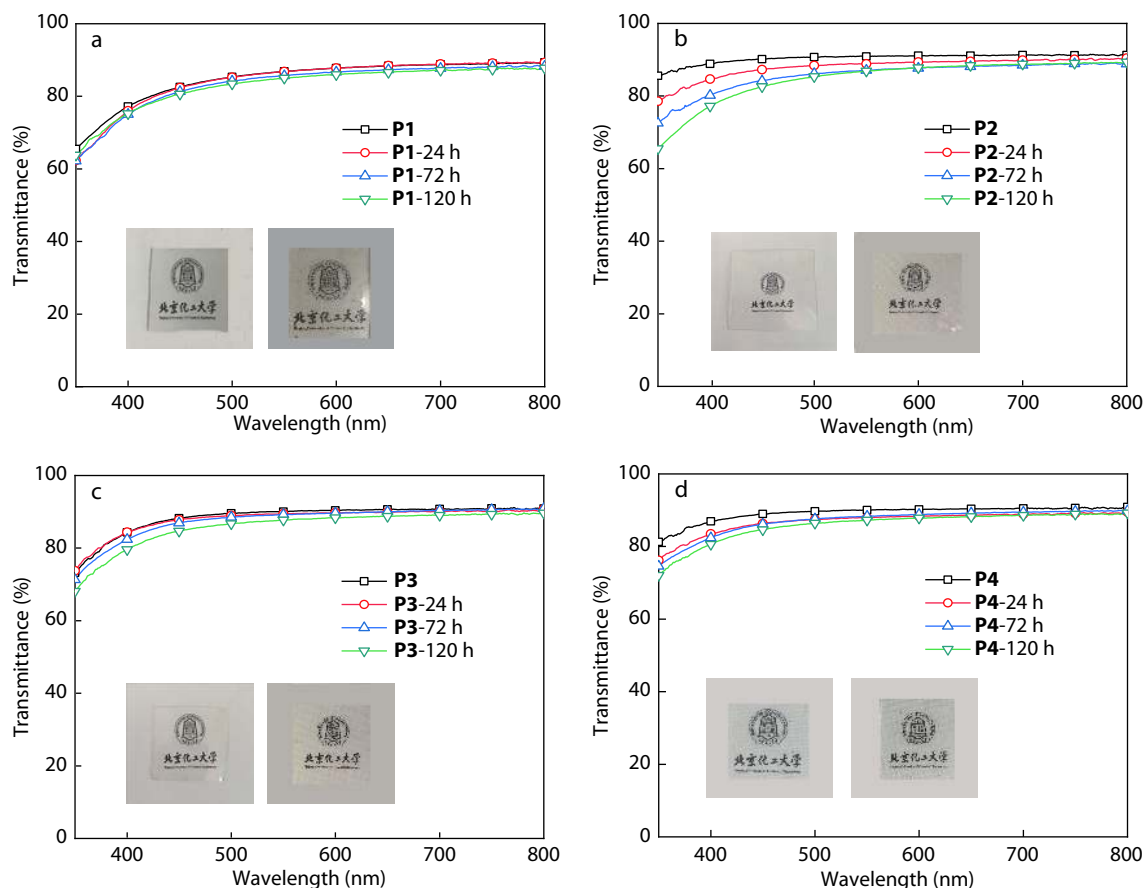


Fig. 9 Transmittance spectra and optical images of polymers (**P1**, **P2**, **P3**, and **P4**) before and after thermal aging at 150 °C for 24, 72, and 120 h.

polymers showed lower optical transparency stability. In any case, titanium-silphenylene-siloxane polymers (**P2**, **P3**, and **P4**) owned better optical transparency than **P1** before and after thermal aging owing to the formation of heterometallic structure containing titanium atoms.

Furthermore, polymer samples were treated under UV light (365 nm, 18 W/m²) at 40 °C for 5 and 10 h, respectively, and their transmittance is shown in Table 1. It is obvious that all the polymers owned excellent optical transparency stability during UV aging.

Table 1 Transmittance of polymers (**P1**, **P2**, **P3**, and **P4**) at 450 nm before and after UV aging.^a

Aging time (h)	Transmittance (%)			
	P1	P2	P3	P4
0	82.5	90.1	88.2	88.9
5	80.9	84.2	84.0	84.1
10	80.4	83.9	83.6	83.3

^a UV aging was conducted by treating the samples under UV light (365 nm, 18 W/m²) at 40 °C for 5 and 10 h, respectively.

Glass Transition Behavior

The glass transition temperature (T_g) is an important parameter which gives information about the structure of crosslinking polymers. It is well known that glass transition temperature is the temperature at which the polymer segments begin to move

and T_g is determined by the degree of freedom for the segmental motion, crosslinking and entanglement constraints, and the packing density of the segments. The DSC traces of polymers (**P1**, **P2**, **P3**, and **P4**) are demonstrated in Fig. 10. It is seen that T_g of polymers **P1**, **P2**, **P3**, and **P4** was −6.2, 1.8, 2.7, and 14.7 °C, respectively. Obviously, the polymers exhibited an increased T_g with the rise of molar ratio of titanium to silicon. This phenomenon can be attributed to the fact that titanium(IV)

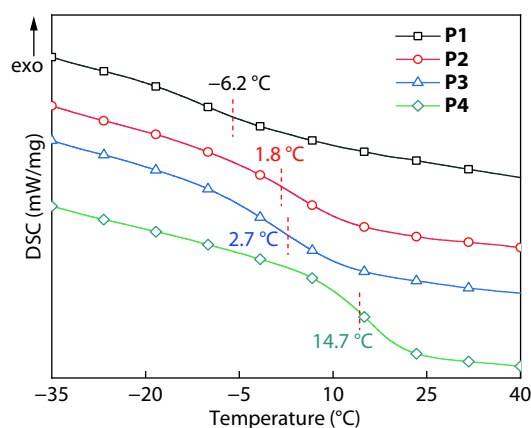


Fig. 10 Glass transition temperature of titanium-silphenylene-siloxane polymers (**P2**, **P3**, and **P4**) and titanium-free polymer **P1**.

isopropoxide (**1**) is a tetra-functional raw material which will promote the formation of crosslinking three-dimensional network. In other words, the achievement of higher degree of curing is owing to additional catalytic effect of titanium element with the rise of molar ratio of titanium to silicon.

Surface Properties

It is well known that surface properties such as surface energy are important in LED encapsulants. As is shown in Fig. 11, the contact angle of polymers **P1**, **P2**, **P3**, and **P4** was 106.26°, 101.61°, 99.91°, and 89.16°, respectively. Obviously, the contact angle decreased with the rise of molar ratio of titanium to silicon. Surprisingly, when molar ratio of titanium to silicon reached 0.05, the titanium-silphenylene-siloxane polymer **P4** was hydrophilic, whereas **P1**, **P2**, and **P3** were hydrophobic, which indicates that the polymer with enough titanium element would turn to hydrophilic. This phenomenon is attributed to the formation of the TiO₂ heterometallic phase.

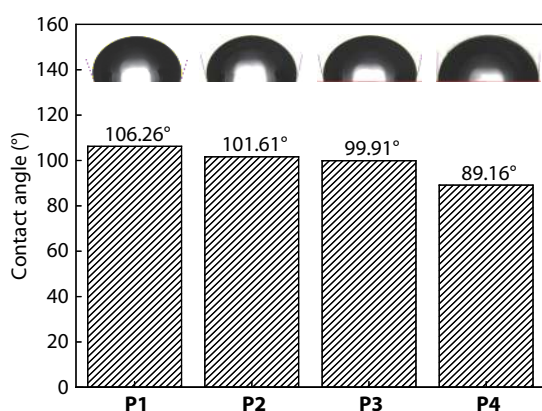


Fig. 11 Contact angle measurement of titanium-silphenylene-siloxane polymers (**P2**, **P3**, and **P4**) and titanium-free polymer **P1**.

As we all know, surface roughness is a vital performance for LED encapsulants and it will influence the luminous efficiency of LED. Therefore, the morphology of titanium-silphenylene-siloxane polymer **P4** was measured by atomic force microscopy (AFM). As illustrated in Fig. 12, **P4** exhibited uniform and planar surface with root-mean-square roughness (R_q) of 3.8 nm and surface roughness (R_a) of 2.8 nm in a 2 $\mu\text{m} \times 2 \mu\text{m}$ area. These data suggest **P4** was smooth enough to satisfy the application as LED encapsulants.

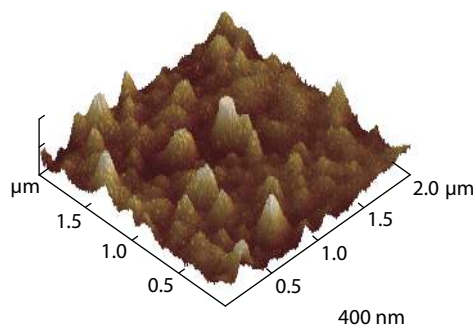


Fig. 12 AFM surface image of titanium-silphenylene-siloxane polymer **P4**.

The organization information of polymers (**P1**, **P2**, **P3**, and **P4**) at a molecular level and long-range order was measured by XRD, and the patterns are recorded in Fig. 13. It can be seen that all polymers had the similarly remarkable broad peaks at the angles about 21.9°, which reveals all polymers were amorphous and without any crystalline regions. Moreover, it is indicated that there is no influence on long-range order to introduce titanium element.

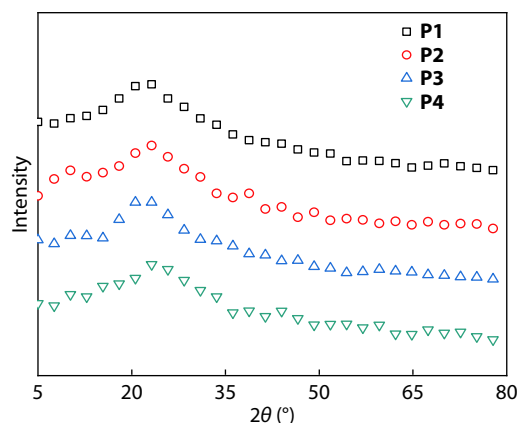


Fig. 13 XRD patterns of titanium-silphenylene-siloxane polymers (**P2**, **P3**, and **P4**) and titanium-free polymer **P1**.

CONCLUSIONS

In summary, a series of vinyl-containing titanium-silphenylene-siloxane oligomers (**O1**, **O2**, **O3**, and **O4**) with different molar ratios of titanium to silicon were successfully synthesized in high yields by nonhydrolytic sol-gel reaction, and the obtained four oligomers were further crosslinked with methylphenyl hydro-silicone oil (**4**) to form corresponding polymers (**P1**, **P2**, **P3**, and **P4**) by hydrosilylation reaction. Their structures have been characterized with spectroscopic characterization techniques including FTIR, ¹H-NMR, and Raman spectroscopy. The cross-linking behavior of titanium-silphenylene-siloxane oligomers was studied by differential scanning calorimetry (DSC), using methylphenyl hydro-silicone oil (**4**) as crosslinking agent and Karstedt's catalyst (**6**) as catalyst. The titanium-containing oligomers exhibited much higher reactivity because titanium-containing heterometallic phase played an additional catalytic effect.

TGA measurements were conducted under nitrogen and results showed that all the polymers (**P1**, **P2**, **P3**, and **P4**) exhibited extraordinarily high initial decomposition temperature (T_{5d} , above 500 °C) and residual weight (above 75% at 1000 °C). Moreover, the refractive index of polymers **P1**, **P2**, **P3**, and **P4** was 1.580, 1.582, 1.583, and 1.584, respectively, which is much higher than that of the conventional silicone ($n \sim 1.5$). These results demonstrated that increment of molar ratio of titanium to silicone can lead to not only the improvement of thermal stability, but also the increased refractive index of polymers. Additionally, all the polymers exhibited good transparency in the visible region and showed excellent thermal aging resistance in 120 h of thermal aging at 150 °C. The glass transition temperature of polymers increased with an increment of molar ratio of titanium to silic-

on due to additional catalytic effect of titanium element. In addition, the surface of polymers was smooth enough for LED encapsulants. Therefore, we believe their excellent overall properties could satisfy the potential application in optical material as LED encapsulant.

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