

**SYNTHESIS AND PROPERTY STUDIES OF METHACRYLATE  
BASED POLY(SILOXANE-SILSESQUIOXANE) RESINS**

**LOH TAT CHUANG**

**UNIVERSITI SAINS MALAYSIA**

**2016**

**SYNTHESIS AND PROPERTY STUDIES OF METHACRYLATE BASED  
POLY(SILOXANE-SILSESQUIOXANE) RESINS**

by

**LOH TAT CHUANG**

Thesis submitted in fulfillment of the requirements

for the degree of

Master of Science

**April 2016**

## **ACKNOWLEDGEMENT**

First of all, I would like to express my gratitude to my supervisor, Assoc. Prof. Dr. Zulkifli Ahmad, co-supervisor, Prof. Hanafi b. Ismail and field supervisor, Assoc. Prof. Dr. Ramamurtikumar for their guidance, valuable advice and support throughout the whole research project. Their advice has led me to explore the methods for solving problems during this project.

I would like to thank the managing director of Penchem Technologies Sdn. Bhd., Dr. Ng Chee Mang for giving me this opportunity and sponsoring me to conduct this research project. In addition, thanks also go to all the laboratory assistants and technicians from School of Materials and Mineral Resources Engineering and Penchem Technologies Sdn. Bhd., especially Encik Shahril Amir b. Saleh, Encik Mohd. Suhaimi b. Sulong, Ms.Sie Hui, and Ms.Khor Seok Fern, for their guidance and technical support in helping me to complete this project.

Besides that, I would like to thank the School of Materials and Mineral Resources Engineering of Universiti Sains Malaysia and Penchem Technologies Sdn. Bhd. for providing me the materials, facilities, equipments and laboratory condition to enable me to complete this project.

Last but not least, I would like to show my appreciation to my parents, and friends for their support and encouragement throughout this research project. Thanks for everything and wishing all things go well in the future for everyone.

Loh Tat Chuang  
School of Materials and Mineral Resources Engineering  
Universiti Sains Malaysia  
Aug 2015

## TABLE OF CONTENTS

Acknowledgement.....	ii
Table of Contents.....	iii
List of Tables.....	viii
List of Figures.....	x
List of Abbreviations.....	xiv
List of Symbols.....	xv
Abstrak.....	xvi
Abstract.....	xviii

### CHAPTER 1 - INTRODUCTION

1.1 Research Background.....	1
1.2 Problem Statement.....	2
1.3 Research Objectives.....	3

### CHAPTER 2 - LITERATURE REVIEWS

2.1 Introduction to Polysiloxanes.....	4
2.1.1 Nomenclature of Polysiloxanes	4
2.1.2 Synthesis of Alkenyl Functional Polysiloxanes Via Sol-Gel Reaction.....	6
2.1.2.1 Hydrolytic Sol-Gel Process.....	7
2.1.2.2 Non-Hydrolytic Sol-Gel Process.....	8
2.1.3 Crosslinking Mechanism of Alkenyl Functional Polysiloxanes	10
2.1.3.1 Hydrosilylation (Addition Polymerization).....	11
2.1.3.2 Free Radical Polymerization.....	13

2.1.4	Properties of Polysiloxanes.....	15
2.2	Silsesquioxanes.....	16
2.2.1	Polyhedral Oligomeric Silsesquioxanes (POSS).....	17
2.2.1.1	Complete and Incomplete Caged POSS.....	20
2.2.2	Polysilsesquioxanes.....	22
2.2.3	POSS Containing Polymer and Copolymer.....	23
2.2.4	Benefits of POSS Technology.....	25
2.3	LED Packaging Technology.....	26
2.3.1	Low Power LED Packaging.....	26
2.3.2	High Power LEDs Packaging.....	27
2.3.3	Requirements of High-Power LED Encapsulant and Lens.....	28
2.3.3.1	Refractive Index of Encapsulant and Lens.....	28
2.3.3.2	Optical Transparency.....	31
2.3.3.3	Stability of Encapsulant and Lens Over Time .....	31
2.3.3.4	Mechanical Properties of Encapsulant and Lens.....	31
2.3.4	Type of LEDs Encapsulant and Lens.....	32
2.3.4.1	Epoxy Resin Encapsulant and Lens.....	32
2.3.4.2	Silicone Encapsulant and Lens.....	32

### CHAPTER 3 - METHODOLOGY

3.1	Introduction to Methacrylate Based Poly(siloxane-silsesquioxane) Hybrid Materials Synthesis.....	35
3.2	Chemicals .....	36
3.2.1	Monomers.....	36
3.2.1.1	Diphenylsilanediol (DPSD).....	36

3.2.1.2	3-methacryloxypropyltrimethoxysilane (MTPS).....	37
3.2.2	Incompletely Condensed Silsesquioxanes.....	37
3.2.2.1	Trisilanol Phenyl POSS .....	37
3.2.3	Condensation Catalyst.....	38
3.2.3.1	Barium Hydroxide, Monohydrated.....	38
3.2.4	Hydrosilylation Catalyst.....	39
3.2.4.1	Ashby-Karstedt Platinum Catalyst.....	39
3.2.5	Crosslinker.....	40
3.2.5.1	Phenyltris(hydrogendimethylsiloxy)silane.....	40
3.2.6	Solvent.....	40
3.2.6.1	Acetone.....	40
3.2.6.2	Toluene.....	41
3.3	Synthesis of Methacrylate Based Poly(siloxane-silsesquioxane) Resins Containing POSS Moieties via Condensation Reaction.....	42
3.4	Crosslink of Methacrylate Based Poly(siloxane-silsesquioxane) Resins Through Hydrosilylation Reaction.....	45
3.5	Characterisation Methods.....	47
3.5.1	PSSQ Resins Characterization.....	47
3.5.1.1	Fourier Transform Infra-Red (FTIR) Spectroscopy...	47
3.5.1.2	<sup>1</sup> H-Nuclear Magnetic Resonance (NMR) Spectroscopy.....	47
3.5.1.3	<sup>29</sup> Si- Nuclear Magnetic Resonance (NMR) Spectroscopy.....	47
3.5.1.4	Gel Permeation Chromatography (GPC).....	48
3.5.2	Crosslinked PSSQ Hybrid Materials Characterization.....	48

3.5.2.1	Differential Scanning Calorimetric (DSC).....	48
3.5.2.2	Refractive Index (RI).....	49
3.5.2.3	Density.....	49
3.5.2.4	Swelling Test.....	50
3.5.2.5	Durometer Hardness Test (Shore A type).....	50
3.5.2.6	Thermal Mechanical Analysis (TMA).....	51
3.5.2.7	Thermal Gravimetric Analysis (TGA).....	51
3.5.2.8	Thermal Aging .....	52

#### CHAPTER 4 - RESULTS AND DISCUSSIONS

4.1	Development of Methacrylate based PSSQ Hybrid Materials.....	53
4.2	Characterization of Methacrylate based PSSQ Resins.....	56
4.2.1	FTIR Analysis.....	56
4.2.2	<sup>1</sup> H-NMR Analysis.....	59
4.2.3	<sup>29</sup> Si-NMR Analysis.....	61
4.2.4	Gel Permeation Chromatography (GPC).....	64
4.3	Characterization of Crosslinked Methacrylate based PSSQ Hybrid Materials.....	66
4.3.1	FTIR Analysis.....	66
4.3.2	Differential Scanning Calorimeter (DSC) Analysis.....	69
4.3.3	Refractive Index.....	71
4.3.4	Hardness.....	75
4.3.5	Swelling Test.....	76
4.3.6	Thermal Mechanical Analysis (TMA).....	78
4.3.7	Thermogravimetric Analysis (TGA).....	81

4.3.8 Thermal Aging.....	85
--------------------------	----

CHAPTER 5 - CONCLUSION

5.1 Conclusion.....	92
---------------------	----

5.2 Recommendation for Future Researches.....	93
---	----

REFERENCES.....	94
-----------------	----

APPENDICES

CONFERENCES

## LIST OF TABLES

		Pages
Table 2.1	M, D, T, and Q silicone backbone nomenclature	5
Table 2.2	Effect of side group substituent in polysiloxane chain.	16
Table 2.3	Example of POSS-containing polymer and copolymer systems	24
Table 2.4	POSS properties in general (Hartmann & Dearmitt, 2011)	25
Table 2.5	Performance comparison of methyl silicones, phenyl silicones and epoxies based LED encapsulant (Schubert, 2006) (Arbebili and Pecht, 2009) (James et al, 2005).	33
Table 3.1	Function of each polymer segments in methacrylate based PSSQ resin	36
Table 3.2	Information of diphenylsilanediol	36
Table 3.3	Information of 3-methacryloxypropyltrimethoxysilane	37
Table 3.4	Information of trisilanol phenyl-POSS	38
Table 3.5	Information of barium hydroxide, monohydrated	38
Table 3.6	Information of platinum-methylvinylcyclosiloxane complex	39
Table 3.7	Information of phenyltris(hydrogendimethylsiloxy)silane	40
Table 3.8	Information of acetone	40
Table 3.9	Information of toluene	41
Table 3.10	Composition of precursors for synthesis of methacrylate based PSSQ resins	42
Table 4.1	IR peak for organosilicon compound	56
Table 4.2	Chemical shifts of silicon according to the bond states, where, R = methacryloxypropyl; R' = phenyl	61
Table 4.3	Average molecular weight (Mw), Number average molecular weight (Mn) and Polydispersity ratio of PSSQ resin	65
Table 4.4	IR peak for organosilicon compound	66

Table 4.5	Enthapy, onset temperature and peak temperature of SQ samples	68
Table 4.6	Refractive index and density of PSSQ hybrid materials	70
Table 4.7	Cured hardness of PSSQ hybrid materials	74
Table 4.8	Percent of swelling by volume for each PSSQ hybrid materials	76
Table 4.9	Tg and CTE ( $\alpha$ -1 and $\alpha$ -1) for PSSQ hybrid materials	77
Table 4.10	5% decomposition temperature ( $T^5_d$ ) and % of decomposition residue yield of PSSQ hybrid materials	81

## LIST OF FIGURES

		Pages
Figure 2.1	General structure for a linear chain polysiloxane	4
Figure 2.2	Sol-gel synthesis route of polysiloxane with organosilanes as starting materials. (Abe & Gunji, 2004).	6
Figure 2.3	Synthesis reactions for silicone resin via hydrolysis and condensation reaction, where the R can be represent an alkyl or aryl groups. (Licari, 2003)	8
Figure 2.4	Synthesis reactions for polyorganosiloxane via non-hydrolytic condensation reaction, where the R might be represent an alkyl or aryl groups. (Bae, 2010).	8
Figure 2.5	Example of alkene functional groups side chain or terminated polysiloxanes, (a) Vinyl dimethylsiloxy terminated polydimethylsiloxane; (b) methacryloxypropyl dimethylsiloxy terminated polydimethylsiloxane; (c) Vinyl methylsiloxy, trimethylsiloxy terminated; (d) (Methacryloxypropyl) methyl siloxane, dimethylsiloxane copolymer, trimethylsiloxy terminated. (Chandrasekhar, 2005)	10
Figure 2.6	Addition polymerization of vinyl and hydride functional polysiloxane in the presence of platinum catalyst and heat.	11
Figure 2.7	Chalk-Harrod mechanism for hydrosilylation of alkenes catalysed by late transition metal complexes (Marciniak, 2009).	12
Figure 2.8	De-activation and re-activation of Karstedt platinum complex catalyst by inhibitor.	13
Figure 2.9	Free-radical polymerization between vinyl-terminated methylsiloxy and polydimethylsiloxane, catalyzed by peroxide. (Licari, 2003)	14
Figure 2.10	Structure conformations of silsesquioxanes (Kuo et al, 2011)	17
Figure 2.11	Anatomy of a T8-POSS molecule (Koo, 2006)	18
Figure 2.12	Comparison between C60 (left) and octamethyl POSS (right) in approximately 1 nm in diameter (Hartmann & Dearmitt, 2011)	19

Figure 2.13	Example of monofunctional POSS: Methacryloxypropyl POSS substituted with seven non-reactive isobutyl groups (Li et al, 2005).	20
Figure 2.14	Chemical structure of acrylopropyl POSS (left) and octaphenyl POSS (right) (Hartmann-Thompson, et al, 2010).	21
Figure 2.15	Examples of incompletely caged POSS systems (Hartmann-Thompson et al, 2011).	21
Figure 2.16	Synthesis of monosubstituted octasilsesquioxane, where R = non-reactive groups; R' = reactive organic groups (Gnanasekaran, et al, 2009).	22
Figure 2.17	Type I polysilsesquioxane; Type II polysilsesquioxane (bridged polysilsesquioxanes). The R can be range from hydrogen to macromolecules.	23
Figure 2.18	Key properties aspects of POSS technology (Koo, 2006)	25
Figure 2.19	Low-power LEDs package with hemispherical encapsulant. These types of LEDs emit a few lumens, and it only require a few milliwatts of drive power (Schubert, 2006)	26
Figure 2.20	Cross section view of the basic high-power LEDs package. The package is encapsulated with silicone based encapsulant and packaged with heat sink element. (Khan, 2013)	27
Figure 2.21	Total reflections in LED material layer, where the refractive index: $n_1 > n_2$ . (Winkler, H. et al 2014)	28
Figure 2.22	Light extraction efficiency ratio for GaN and GaP semiconductor as a function of the encapsulant index of refraction. (Cheng et al, 2011)	29
Figure 2.23	The concept of high refractive index (n) nanoparticle loaded encapsulant (Mont, et al, 2008)	30
Figure 3.1	Methacrylate based poly(siloxane-silsesquioxane) with POSS moieties	35
Figure 3.2	Chemicals structure of diphenylsilanediol	36
Figure 3.3	Chemicals structure of 3-methacryloxypropyltrimethoxy silane	37
Figure 3.4	Chemical structure of trisilanol phenyl-POSS	37
Figure 3.5	Chemical structure of Ashby Karstedt platinum-catalyst	39

Figure 3.6	Chemical structure of phenyltris(hydrogendimethylsiloxy) silane	40
Figure 3.7	Synthesis of methacrylate based poly(siloxane-silsesquioxane) resin containing phenyl-POSS moieties through condensation reaction. The aromatic rings are excluded in the diagram for clarity.	44
Figure 3.8	The cured PSSQ hybrid materials obtained by crosslink PSSQ with tris(dimethylsiloxy)phenylsilane, catalyzed platinum catalyst through hydrosilylation reaction. The aromatic rings are excluded in the structure for diagram clarity.	45
Figure 3.9	a) Teflon mold; b) Teflon-glass sandwich	46
Figure 4.1	Non-hydrolytic condensation reaction between silanol and methoxy groups	53
Figure 4.2	Synthesized PSSQ resins, SQ10	54
Figure 4.3	The cured PSSQ samples (3.0mm thick): SQ00 (left), SQ10(center) and SQ20(right), showing that the POSS content doesn't affect on the optical transparency of the samples.	55
Figure 4.4	FTIR spectrum for PSSQ resins	58
Figure 4.5	<sup>1</sup> H-NMR spectra for SQ00, SQ10 and SQ20 PSSQ resin samples	60
Figure 4.6	<sup>29</sup> Si NMR of representative SQ10 (10% POSS) sample compared with that of sample SQ00 (0% POSS). R= methacryloxypropyl, R'=phenyl.	63
Figure 4.7	FTIR spectrum for PSSQ hybrid materials (before cure and after cure)	68
Figure 4.8	DSC curve of SQ samples containing different POSS moieties measured at a heating rate 10°C/min.	70
Figure 4.9	Enthalpy of the SQ samples	71
Figure 4.10	Refractive index versus trisilanolphenyl-POSS content in PSSQ resins	72
Figure 4.11	Plot of $(n^2 - 1)/(n^2 + 2)$ versus density for PSSQ samples	74
Figure 4.12	Cured hardness (shore A) of methacrylate based PSSQ hybrid materials	76

Figure 4.13	Percent of swelling by volume against PSSQ hybrid materials	77
Figure 4.14	Glass transition temperature versus trisilanolphenyl-POSS content in PSSQ hybrid materials	78
Figure 4.15	CTE ( $\alpha$ -1 and $\alpha$ -2) of the PSSQ hybrid materials	80
Figure 4.16	TGA curve for PSSQ hybrid materials (from 250 to 800°C)	82
Figure 4.17	Decomposition temperature (5%) versus SQ samples	82
Figure 4.18	DTG curves of SQ00, SQ10 and SQ20	84
Figure 4.19	Decomposition residue yield content in PSSQ hybrid materials	85
Figure 4.20:	Light transmittance behavior with increasing POSS content showing before (black line) and after ageing (red lines) at 180 °C for 100 hours	86
Figure 4.21	Percentage of light output degradation at 450nm of methacrylate based PSSQ hybrid materials after heat aging at 180°C for 50, 75 and 100 hours.	87
Figure 4.22	Percentage of light output degradation at 450nm of methacrylate based PSSQ hybrid materials after heat aging at 150°C for 150 hours and 300 hours.	88
Figure 4.23	Yellowing index of methacrylate based PSSQ hybrid materials after heat aging at 180°C from 0 to 100 hours	89
Figure 4.24	Yellowing index of methacrylate based PSSQ hybrid materials after heat aging at 150°C from 0 to 100 hours	89
Figure 4.25	Present the visual observation of yellowing effect of samples SQ00, SQ10 and SQ20 as compared to the original unaged sample after degradation at 180 °C for 100 hours.	91

## LIST OF ABBREVIATIONS

ASTM	American Standard Testing Method
ISO	International Standard Organisation
JEDEC	Joint Electron Device Engineering Council
PSSQ	Poly(siloxane-silsesquioxane)
SQs	Silsesquioxanes
DPSD	Diphenylsilanediol
MPTS	3-methacryloxypropyltrimethoxysilane
Ba(OH) <sub>2</sub> .H <sub>2</sub> O	Barium hydroxide, monohydrated
POSS	Polyhedral oligomeric silsesquioxanes
TiO <sub>2</sub>	Titanium dioxide
ZrO <sub>2</sub>	Zirconium dioxide
UV	Ultra-violent
VIS	Visible
IR	Infra-red
FTIR	Fourier transform infrared spectroscopy
NMR	Nuclear magnetic resonance
TGA	Thermogravimetry analyzer
TMA	Thermomechanical analyzer
GPC	Gel permeation chromatography
PTFE	Polytetrafluoroethylene
HCl	Hydrochloric acid

## LIST OF SYMBOLS

T <sub>g</sub>	Glass transition temperature
CTE ( $\alpha$ -1)	Coefficient of thermal expansion below glass transition temperature
CTE ( $\alpha$ -2)	Coefficient of thermal expansion above glass transition temperature
ppm.K <sup>-1</sup>	Coefficient of thermal expansion
ppm	Part per million
M <sub>w</sub>	Weight average molecular weight
M <sub>n</sub>	Number average molecular weight
PD	Polydispersity
RI	Refractive index
T <sup>5</sup> <sub>d</sub>	Decomposition temperature at 5%
W.m <sup>-1</sup> .k <sup>-1</sup>	Thermal conductivity
SG	Specific gravity
°C	Degree Celsius
K	Kelvin
$\sigma$	Standard deviation
%	Percentage
wt%	Weight percent
Mol%	Mole by percentage
nm	Nanometer
Ph	Phenyl
Me	Methyl
Et	Ethyl
Pt	Platinum
Si	Silicon
T <sub>8</sub>	Fully condensed caged POSS
T <sub>7</sub>	Trisilanol POSS

# SINTESIS DAN KAJIAN SIFAT-SIFAT RESIN METAKRILAT POLI(SILSESQUIOSAN-SILOKSAN)

## ABSTRAK

Polisiloksan kini telah digunakan sebagai kanta optik, pengkapsulan optoelektronik dan bahan elektronik dalam industri elektronik. HB LED (diod pemancar cahaya kecerahan tinggi) adalah lampu yang berpotensi untuk menggantikan mentol pijar, neon dan halogen. Untuk meningkatkan kecekapan HB LED ini, bahan berasaskan polisiloksan untuk pengkapsulan atau kanta LED memerlukan reka bentuk optik yang baik, pelepasan haba yang baik, indeks biasan yang tinggi untuk kecekapan pengekstrakan cahaya dan pemancaran cahaya yang cemerlang, serta rintangan cahaya dan kekerasan yang tinggi untuk melindungi LED daripada tekanan mekanikal. Resin silikone yang biasanya digunakan dalam pengkapsulan LED atau pembungkusan hanya mempunyai indeks biasan 1.40-1.54, kekerasan dan kestabilan terma yang rendah. Dalam kajian ini, bahan hibrid metakrilat poli(silsesquiosan-siloksan) (PSSQ) yang mempunyai kestabilan haba dan indeks biasan yang tinggi ( $>1.55$ ) telah dihasilkan dan dicadangkan sebagai bahan yang berpotensi untuk pengkapsulan LED dan pembungkusan elektronik. Resin PSSQ yang berasaskan metakrilat mengandungi kandungan trisilanolfenil-POSS yang berbeza telah disintesis melalui tindak balas pemeluwapan, diikuti oleh fabrikasi bahan hibrid PSSQ ini melalui tindak balas penambahan. Struktur kimia, berat molekul, sifat optik dan sifat haba bahan hibrid PSSQ tersebut telah diuji oleh Spektroskopi Fourier Transformasi Inframerah (FTIR),  $^1\text{H}$ -Nuklear Resonans Magnetik (NMR),  $^{29}\text{Si}$ -Nuklear Resonans Magnetik (NMR), Kromatografi Permeasi Gel (GPC), Refraktometer Abbe, Spektrofotometer UV/VIS, Durometer, Kalorimeter

Pengimbasan Pembezaan (DSC), Analisis Termomekanis (TMA) dan Analisis Termogravimetri (TGA). Spektrum FTIR menunjukkan bahawa resin PSSQ yang disintesis mempunyai tahap pemeluwapan yang tinggi. Bahan hibrid PSSQ yang dihasilkan telah menunjukkan kejelasan optik yang tinggi, dengan pemancaran cahaya lebih daripada 95% dalam lingkungan gelombang cahaya 400-1000nm. Kandungan POSS bahan hybrid PSSQ yang tinggi memberi kekerasan yang tinggi dan indeks biasan yang tinggi. Begitu juga, bahan hibrid PSSQ diperkukuh dengan kandungan POSS yang tinggi menunjukkan kestabilan terma yang baik pada ujian penuaan suhu tinggi, suhu penguraian yang tinggi, serta Tg lebih tinggi.

# **SYNTHESIS AND PROPERTY STUDIES OF METHACRYLATE BASED POLY(SILOXANE-SILSESQUIOXANE) RESINS**

## **ABSTRACT**

Nowadays, polysiloxane is widely used as optical lenses, optoelectronic encapsulation and electronic packaging materials in electronic industry. Typical HB LEDs (high brightness light emitting diodes) is a potential lamp to replace existing incandescent, fluorescent and halogen bulbs. As for development of such high efficiency HB LEDs, the polysiloxane based LED encapsulation materials or lenses requires an excellent optical design, good heat dissipation, high refractive index for maximum light extraction efficiency and excellent light transmittance, as well as light resistance and high hardness to protect the LEDs from mechanical shock. However, most of the commercial silicone resin employed in LEDs encapsulation or packaging is known to have a refractive index range from 1.40 to 1.54 only, low hardness and poor thermal stability. In this research study, thermally stable and high refractive index (>1.55) methacrylate based poly(siloxane-silsesquioxane) (PSSQ) hybrid materials were fabricated and proposed as a potential material for optoelectronic and LEDs packaging materials. The methacrylate based PSSQ resins containing different portion of trisilanolphenyl-POSS were synthesized through condensation reaction, followed by the fabrication of these methacrylate based PSSQ hybrid material through hydrosilylation reaction. The chemical structure, molecular weight, optical properties and thermal properties were investigated by Fourier Transform Infrared (FTIR) Spectroscopy, <sup>29</sup>Si-Nuclear Magnetic Resonance (NMR), Gel Permeable Chromatography (GPC), Abbe refractometer, UV/Visible Spectrophotometer, Thermomechanical Analyzer (TMA) and Thermogravimetric

Analysed (TGA). The FTIR spectra showed that the synthesized PSSQ resins have high degree of condensation. The fabricated PSSQ hybrid materials were shown excellent optical clarity, with light transmittance at least 96% over the wavelength 400 – 1000nm. The PSSQ hybrid material with higher POSS content gives higher hardness and higher refractive index (1.56). Similarly, PSSQ hybrid material with higher POSS content shown excellent thermal stability, high discoloration resistance at high temperature aging test, higher decomposition temperature, higher Tg and lower CTE.

# CHAPTER 1

## 1.0 INTRODUCTION

### 1.1 Research Background

High power light emitting diode (LED) packaging, consist of a transparent encapsulant or lens for the light to escape from the semiconductor and a thermal path for heat dissipation, and package in a polyphthalamide plastic leaded chip carrier (PLCC) or directly mounted on a metal core printed circuit board (MCPCB). All high power LEDs generates more heat compared to low power LEDs. Typical high power high brightness light emitting diodes' (HB LED) encapsulation material requires high optical transparency, high refractive index, chemical inertness, high temperature stability, good radiation resistance, hermeticity, etc (Schubert, 2006).

High refractive index encapsulant is required for high power LEDs, as to give better light extraction and light transmission efficiency. Ideally, the refractive index should be close to 1.70 in order to be compatible with the LED dies (Aanegola, et al, 2013).

Most of the LEDs encapsulants are based on hydrocarbon polymers. One of the commonly used LEDs encapsulant is epoxy resin. However, the epoxy resin tends to discoloration and loses its transparency after prolonged exposure to temperatures greater than 120°C and exposure to shorter wavelengths, such as blue, violet and ultraviolet.

Since 2000s, the silicones or polysiloxanes has been used to overcome the limitation of epoxy based encapsulant. Most of the polysiloxanes has high thermal stability, up to 190°C, which is significantly higher than epoxies. Beside this, high flexibility of the polysiloxanes provides lower mechanical stress on the semiconductor chip in LEDs package (Schubert, 2006).

## **1.2 Problem statements**

Most of polysiloxanes in the market are based on methyl group with low refractive index range from 1.40 to 1.42, this will reduce the light output and light extraction efficiency of the high power LEDs. Hence, in order to increase the refractive index of polysiloxane, phenyl group has been partly substituted to the polysiloxane chain. Unfortunately, high phenyl content in polysiloxane will reduce its high temperature discoloration resistance, optical clarity and mechanical property, with maximum refractive index only up to 1.54. Beside this, there is limited report for phenyl polysiloxane materials with a high refractive index (over 1.55) and high transparency accompanied by resistance to yellowing at high temperature, with lower CTE (Kim et al, 2010; Zhao et al, 2014).

Increase refractive index can be done by loading the polysiloxanes with high refractive index surface treated metal oxide nanoparticles, such as titanium dioxide (TiO<sub>2</sub>) and zirconium dioxide (ZrO<sub>2</sub>) nanoparticles. This method leads to increase in refractive index but suffer from poor optical clarity and chemical compatibility. A special and complicated surface treatment process is required for the ZrO<sub>2</sub> nanoparticles is required in order to form a stable nanoparticles suspension in resin. (Williams et al, 2013). High temperature yellowing resistance of the phenyl polysiloxane can be improved by adding small amount of antioxidant, however, this

method will only protect the phenyl silicone temporary, because antioxidant will be depleted after prolonged exposure to high temperature.

### **1.3 Research Objectives**

This project aims to establish a new synthetic route to incorporate partially caged structure phenyl-POSS into the methacrylate based oligosiloxane in order to produce a high refractive index, thermally stable and high transparency hybrid material. Based on the problem statements, the research objectives are as follows:

- 1) To synthesis LED encapsulant of methacrylate based poly(siloxane-silsesquioxane) resins containing POSS moieties
- 2) To study the thermal and optical properties of cured methacrylate based poly(siloxane-silsesquioxane) resins containing POSS moieties

## CHAPTER 2

### 2.0 Literature reviews

#### 2.1 Introduction to Polysiloxanes

Chemically, polysiloxanes are inorganic polymers that consist of alternate silicon and oxygen atoms backbone structure, linked to organic side groups such as aliphatic or aromatic hydrocarbons, forming a general  $(-R_1R_2SiO-)$  as represented in Figure 2.1. The term ‘siloxane’ was derived from the words **silicon**, **oxygen**, and **alkane**. In the market, the polysiloxanes is referring as silicones.

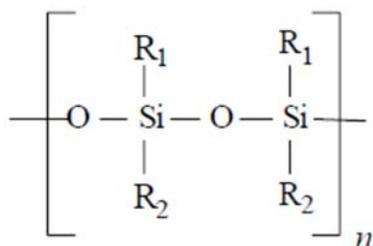


Figure 2.1: General structure for a linear chain polysiloxane

Generally, the polysiloxanes can be classified into fluids, greases, rubbers and resins form. Polysiloxanes have found in many and diverse applications, due to its highly thermal and radiation stability, water repellency, anti-adhesive characteristics, low toxicity and stable over a wide temperature range (Chanda et al, 2009).

##### 2.1.1 Nomenclature of Polysiloxanes

There are 4 types of construction of silicone polymers backbone nomenclature, as illustrated in the Table 2.1. The most widely studied polysiloxane is poly(dimethylsiloxane) (PDMS), which contains methyl groups as the substituents