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Development and Characterization of Low Dielectric Constant Polymers for Microelectronic Applications

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Abstract

This project aims to synthesize and characterize a series of bismaleimide (BMI) polymers based on maleic anhydride and diamines containing flexible aliphatic and aliphatic-ether units of various molecular lengths. The reaction of diamines with maleic anhydride was carried out by a two-step procedure that included a ring-opening addition to give bismaleamic acid intermediates, followed by a cyclodehydration reaction to form BMI monomers. BMIs containing an aliphatic main chain (A-BMI) and BMIs containing the aliphatic-ether main chain (O-BMI) were obtained. The effects of varying the chain length of the aliphatic and aliphatic-ether on the resultant BMI polymer systems were evaluated.

The reaction of synthesis was investigated using Fourier Transform Infrared Spectroscopy (FTIR). The structural analysis was performed by FTIR and NMR spectroscopy. Their curing behaviors were characterized by Differential Scanning Calorimetry (DSC) and rheometry. Thermo-Gravimetric Analysis (TGA) and Thermal Mechanical Analyses (TMA), Dielectric Thermal Analysis (DEA), and tensile test were utilized to characterize the properties of the cured polymers.

Results showed that the introduction of aliphatic and aliphatic-ether groups to BMI resin not only significantly reduces the dielectric constant ($\epsilon = 2.0\sim 2.6$ for A-BMI polymers, $\epsilon = 2.9\sim 6$ for O-BMI polymers at 100 kHz), but also effectively increases the toughness of the cured resin, compared with the aromatic BMI, 4,4-bismaleimidodiphenylmethane.

The presence of methylene ($-\text{CH}_2-$) and ether ($-\text{O}-$) groups in the BMI also affect the reactivity of the double bonds in maleimide ring. The thermodynamic effect makes A-BMI monomer less reactive but makes O-BMI monomer more reactive with the increasing of length of main chain.

For A-BMI polymers, their thermal, dielectric and tensile properties were all affected by the chain length of A-BMI and the odd even effect. FTIR and NMR show that when the CH_2 length is odd, the packing density is lower. A-BMI is more stable as the chain length increase. BMI-3, BMI-5 and BMI-7 having odd number of CH_2 had lower melting points compared with those having even number of carbons. An even number of carbons on the main chain apparently results in better molecular packing, and hence higher melting temperatures are observed for these compounds. Increasing the length of the backbone chain lowered the melting points of BMIs, leading to a large processing temperature range between melting temperature and onset temperature of cure. As the chain length increases, the peak curing temperature, gel temperature of the A-BMI also increased. All the A-BMI polymers studied were stable up to 450°C in both air and nitrogen and possessed high glass transition temperatures up to 400°C . BMI-3,5,7 with odd number of carbons have lower tensile strength than those with even ones.

For O-BMI polymers, their thermal, dielectric and tensile properties are all affected by the chain length of O-BMI. O-BMI monomers with longer chain length have lower gel temperatures and shorter gel times. As the chain length increases, the peak curing

temperature, curing enthalpy, glass transition temperature and degradation temperature of O-BMI all decrease. Three factors including the inductive effect, chain mobility and thermodynamic effect make the O-BMI monomer more reactive thus leading to a lower curing temperature as the length of chain was increased. Meanwhile, because the amount of reactant function group decreases with increase in the chain length, the curing heat decreases. The higher the crosslink density of polymer, the higher the glass transition temperature of polymer. Introduction of an ether group and long chain into two maleimide groups would decrease its crosslink density. Therefore, the glass transition temperatures of O-BMI polymers decrease with increasing the length of main chain. The longer the length of main chain, the larger the probability of random scission. Thus, as the length of the main chain increased, the thermal degradation temperatures of O-BMI polymers decreased. The magnitude of the dielectric constant increased with increasing length of the main chain. Both polarity and mobility of O-BMI polymers resulted in an increase in the dielectric constants at temperatures between 0°C and 200°C as the length of the main chain was increased.

The A-BMI and O-BMI as additives to modify C-BMI was carried out to study thermo-hygro-mechanical and electrical properties of the copolymer systems. BMI-6 and BMI-230B were chosen to blend with C-BMI. The dielectric constant and toughness (from tensile test) of the BMI-6, BMI-230B and C-BMI copolymer were improved.

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Table of contents

	Page
Abstract	I
Acknowledgement	IV
Table of Contents	V
List of Figures	IX
List of Tables	XIV
List of Equations	XVI
List of Acronyms	XVII
Chapter One Introduction	1
1.1 Background	1
1.1.1 The application of polyimide in microelectronics	8
1.1.2 The application of bismaleimide in microelectronics	10
1.2 Objectives and Scope	16
Chapter Two Literature Review	17
2.1 The chemistry of bismaleimide	17
2.1.1 The synthesis of bismaleimide	17
2.1.2 The curing of bismaleimide monomer	21
2.1.3 Michael addition reaction of BMI	22
2.1.4 The copolymerization of bismaleimide	23
2.2 Principle of structure-property relationships of BMI	24

2.2.1	Factors influencing melting point, glass transition temperature	25
2.2.2	Thermal stability	27
2.2.3	Dielectric properties	28
2.2.4	Mechanical properties	32
2.2.5	Gelation	33
2.2.6	Odd vs. even effect	34
2.2.7	Functional groups used in bismaleimides	37
Chapter Three	Proposed Programme	40
3.1	Required BMIs for packaging materials	40
3.2	Preparation of required BMIs and their desired properties	41
Chapter Four	Research Methodology	43
4.1	Raw Materials	43
4.2	Experimental Approach	44
4.3	Sample Preparation	48
4.4	Analytical procedures	59
Chapter Five	Synthesis and Properties of A-BMI Systems	76
5.1	Phase (I): Synthesis of the A-BMI	76
5.1.1	Synthesis of the intermediate A-BMAs	76
5.12	DSC analyses of bismaleamic acids (A-BMAs)	77
5.13	Synthesis of the A-BMIs	82
5.2	Phase (II): Characterization of the A-BMI systems	90

5.2.1	FTIR and NMR analyses	90
5.2.2	DSC analyses of bismaleimides (A-BMIs)	98
5.2.3	Gel points of A-BMIs	105
5.2.4	TGA analyses of A-BMIs	108
5.2.5	Glass transition temperature and CTE of A-BMI polymer	113
5.2.6	Dielectric properties of A-BMI polymers	116
5.2.7	Tensile properties of A-BMI polymers	127
5.2.8	Moisture absorption of A-BMI polymers	131
5.3	Summary	134
Chapter Six	Synthesis and Properties of O-BMIs	135
6.1	Phase (I): Synthesis of the O-BMIs	135
6.2	Phase (II): Characterization of the O-BMI systems	139
6.2.1	FTIR analyses of O-BMI monomers	139
6.2.2	Thermal curing of O-BMI monomers	140
6.2.3	Gel Points of O-BMI monomers	144
6.2.4	TGA analyses of O-BMI polymers	145
6.2.5	TMA analyses of O-BMI polymers	148
6.2.6	Dielectric properties of O-BMI polymers	150
6.2.7	Tensile properties of O-BMI polymers	157
6.2.8	Toughness of BMI-230 polymer	159
6.2.9	Moisture absorption of O-BMI polymers	159

6.3	Summary	161
Chapter Seven	The blends of the BMI systems	162
7.1	The characterization of blending of BMI-6 and BMI-230B systems	163
7.2	The A-BMI and O-BMI as additives to modify C-BMI	166
7.3	The characterization of blending of BMI-6, BMI-230B and C-BMI	175
Chapter Eight	Conclusions	182
Chapter Nine	Future Work	185
Reference		189
Appendix I	Synthesis	199
Appendix II	FTIR analyses	204
Appendix III	NMR analyses	209
Appendix IV	DSC analyses	214
Appendix V	DEA analyses	218
Appendix VI	TGA & TMA analyses	222
Appendix VII	Gel points	224
Appendix VIII	Data analyses	231

List of Figures

- 1.1 The aliphatic and aromatic chain structures of bismaleimides
- 1.2 The cross-linking reaction of bismaleimide
- 2.1 Maleic anhydride reacts with diamine to form BMI
- 2.2 Reactions which take place during the maleimide synthesis
- 2.3 Maleic anhydride reacts with isocyanate to form BMI
- 2.4 The Michael addition reaction of BMI
- 2.5 Intermolecular distances of the terminal C atoms
- 2.6 The planar zigzag conformation and helical structure
- 4.1 Outline of the development and characterization of BMI
- 4.2 Synthesis of a bismaleimide compound
- 4.3 Synthesis of a bismaleimide compound
- 4.4 The formation of O-BMIs by two-stage reaction
- 4.5 The structures of the synthesized O-BMI monomers
- 4.6 A typical spectrum of bismaleimide monomer
- 4.7 A typical plot of conversion to form BMA
- 4.8 A typical plot of heat flow versus temperature by DSC
- 4.9 The plot of conversion vs time of O-BMI-230B
- 4.10 The plot of conversion vs temperature of O-BMI-230B
- 4.11 Typical TGA thermogram on A-BMI monomer
- 4.12 Typical TGA thermogram on cured bismaleimide

-
- 4.13 Typical TMA thermogram on cured BMI
 - 4.14 A typical plot of dielectric constant of BMI-230B
 - 4.15 A typical dielectric relaxation plot of BMI-600
 - 4.16 A typical rheological plot of G' , G'' versus time
 - 4.17 A typical stress-strain plot of the BMI polymer
 - 5.1 FTIR spectrum of a typical bismaleamic acid (BMA-8)
 - 5.2 The plot of the conversion vs time to form BMA-8
 - 5.3 DSC analysis of A-BMAs
 - 5.4 The effect of chain length on melting points of A-BMAs
 - 5.5 Effect of the odd number of C on the melting point of A-BMAs
 - 5.6 Effect of the even number of C on the melting point of A-BMAs
 - 5.7 FTIR spectrum of BMI-8
 - 5.8 The plot of cyclisation reaction to form BMI-8
 - 5.9 Reactions which take place during maleimide synthesis
 - 5.10 ^{13}C NMR spectrum of BMI-6
 - 5.11 ^1H NMR spectrum of BMI-2
 - 5.12 FTIR spectrum of BMI-8
 - 5.13 Effect of the main chain length on the frequency shift of $\text{C}=\text{C}$ in A-BMI
 - 5.14 Effect of the even number of C on the frequency shift of $\text{C}=\text{C}$ in A-BMI
 - 5.15 Effect of the odd number of C on the frequency shift of $\text{C}=\text{C}$ in A-BMI
 - 5.16 Effect of the CH_2 on the frequency shift of $\text{C}=\text{O}$ in A-BMI
 - 5.17 Effect of the odd number of C on the frequency shift of $\text{C}=\text{O}$ in A-BMI

-
- 5.18 Effect of the even number of C on the frequency shift of C=O in A-BMI
 - 5.19 Effect of the CH₂ on the chemical shift of H-C=C in A-BMI
 - 5.20 The melting point and heat curing of A-BMI monomer
 - 5.21 The effect of chain length on melting points and curing temperatures
 - 5.22 The effect of chain length on gel point of A-BMI monomer
 - 5.23 The effect of chain length on gel temperature of A-BMI monomer
 - 5.24 Typical TGA thermograph of uncured BMI-8 in air
 - 5.25 Typical TGA plot of the BMI-8 polymer
 - 5.26 Effect of chain length on degradation on cured A-BMIs
 - 5.27 Effect of chain length on Tg
 - 5.28 The effect of chain length on Tg and CTE of the A-BMI polymers
 - 5.29 A typical dielectric constant plot of BMI-8
 - 5.30 The effect of chain length on dielectric constant of A-BMI polymers at 1Hz
 - 5.31 A typical dielectric relaxation plot of BMI-4
 - 5.32 The effect of chain length on the dielectric loss of A-BMI polymers at 1 Hz
 - 5.33 A typical stress-strain curve of BMI-8 polymer
 - 5.34 The effect of chain length on tensile properties of A-BMI polymers
 - 5.35 The effect of chain length on tensile properties of A-BMI polymers
 - 5.36 The effect of chain length on moisture absorption of A-BMI polymers
 - 6.1 FTIR spectrum of a typical O-BMI (BMI-230B) monomer
 - 6.2 ¹H NMR spectrum of BMI-230B
 - 6.3 Effect of chain length on the frequency shift of C=O in O-BMIs

-
- 6.4 The typical heat curing of BMI-400B
 - 6.5 Effect of chain length on the curing temperatures of O-BMIs
 - 6.6 The typical curing kinetics of the BMI-400B
 - 6.7 Effect of chain length on gel temperature and gel time of O-BMIs
 - 6.8 Typical TGA thermograph on cured BMI-230B
 - 6.9 Effect of chain length on the decomposition temperature of O-BMI polymers
 - 6.10 Effect of chain length on Tg and CTE of O-BMI polymers
 - 6.11 A typical plot of dielectric constant of BMI-230B
 - 6.12 A typical dielectric relaxation plot of BMI-600
 - 6.13 Effect of chain length on dielectric constants of O-BMI polymers
 - 6.14 Effect of chain length on the dielectric relaxation of O-BMI polymers
 - 6.15 The stress-strain relationship of BMI-230B
 - 6.16 The stress-strain relationship of BMI-400B
 - 6.17 Effect of chain length on moisture absorption of O-BMIs
 - 7.1 A typical DEA plot of BMI blending
 - 7.2 A typical stress strain relationship of B90
 - 7.3 Effect of the A-BMI content on dielectric constant of the blending
 - 7.4 Effect of the A-BMI content on Tg of the blending
 - 7.5 Effect of the A-BMI content on CTE of the blending
 - 7.6 Effect of the A-BMI content on Td of the blending
 - 7.7 Effect of the A-BMI content on moisture absorption of the blending
 - 7.8 Effect of the O-BMI content on toughness of the blending

-
- 7.9 Effect of the O-BMI content on Tg of the blending
 - 7.10 Effect of the O-BMI content on CTE of the blending
 - 7.11 Effect of the O-BMI content on Td of the blending
 - 7.12 Effect of the O-BMI content on moisture absorption of the blending
 - 7.13 Effect of the BMI-6 content on K & moisture absorption of the blending
 - 7.14 Effect of the BMI-6 content on thermal properties of the blending
 - 7.15 Effect of the BMI-230B content on the properties of the blending
 - 7.16 Effect of the BMI-230B content on the Tg & Td of the blending

Figures in Appendix

1. The conversion vs time to form BMA and BMI
2. FTIR spectra of BMA and BMI compounds
3. NMR spectra of BMI compounds
4. DSC analyses of BMA and BMI compounds
5. DEA analyses of BMI polymers
6. TGA and TMA thermogram on BMI
7. The rheological analyses of BMI

List of Tables

- 1.1 Ideal requirements for electronics packaging materials
- 2.1 The functional groups and their α values
- 2.2 The Intermolecular distances of the terminal C atoms
- 4.1 A-BMI code and its main chain
- 4.2 Typical amounts of reactants used in the preparation of bismaleimides
- 4.3 Typical amounts of reactants used in the preparation of O-BMIs
- 4.4 O-BMI code and the relative chain
- 4.5 Characteristic FTIR absorption peaks of bismaleamic acid
- 4.6 Characteristic FTIR absorption peaks of bismaleimide
- 5.1 Effect of chain length on melting point of bismaleamic acids (BMA)
- 5.2 The effect of diamine chain length on the formation of A-BMA & A-BMI
- 5.3 Comparison about the yield of A-BMIs
- 5.4 Characteristic NMR absorption peaks of A-BMI
- 5.5 The effect of CH₂ on the reactivity of maleimide double bond and C=O
- 5.6 ¹H NMR chemical shifts of the A-BMI function
- 5.7 Melting, curing temperatures and curing heat of A-BMI systems
- 5.8 The Effect of chain length on curing time of A-BMI
- 5.9 Gel Temperature and Gel Time of A-BMI
- 5.10 Uncured A-BMIs: vaporization and decomposition temperatures
- 5.11 Effect of chain length on decomposition of the cured A-BMIs

-
- 5.12 A-BMI polymers: Tg and CTE
 - 5.13 Dielectric constant of A-BMI polymer
 - 5.14 Dielectric loss peak of A-BMI polymer
 - 5.15 Summary of tensile properties of A-BMI polymers
 - 5.16 Effect of chain length on moisture absorption of A-BMIs
 - 5.17 The molar mass of A-BMIs
 - 6.1 The effect of diamine chain length on the formation of O-BMAs and O-BMIs
 - 6.2 Comparison about the yield of O-BMIs
 - 6.3 The curing temperatures and curing heat of O-BMI monomers
 - 6.4 The effect of chain length on the curing time at the temperature of 230°C
 - 6.5 Gel Time and temperature of O-BMI monomers
 - 6.6 Comparison of O-BMIs: weight loss temperature and decomposition
 - 6.7 Tg and CTE of the O-BMI polymer
 - 6.8 Dielectric constant of O-BMI polymer
 - 6.9 Dielectric loss peak of O-BMI polymer
 - 6.10 Summary of tensile properties of O-BMI polymers
 - 6.11 Comparison of toughness of BMI-230B and C-BMI
 - 6.12 Effect of chain length on moisture absorption of O-BMIs
 - 7.1 The properties of blended materials
 - 7.2 The properties of the blend systems (C-BMI blended with A-BMIs)
 - 7.3 The properties of blend systems
 - 7.4 The properties of blend systems

7.5 The properties of blend systems

7.6 The properties of the blended BMI-6, BMI and C-BMI systems

Tables in appendix: The molar mass and properties of compounds

List of Equations

Equation 2-1	Bell–Evans–Polanyi relation
Equation 2-2	Clausius-Mossotti equation
Equation 2-3	α value in Clausius-Mossotti equation
Equation 4-1	reaction equation
Equation 4-2	percentage yield
Equation 4-3	normalized absorbance
Equation 4-4	extent of reaction (α)

List of Acronyms

A-BMI	bismaleimide with alkylene main chain, including BMI-2,3,4,5,6,7,8
Ac ₂ O	acetic anhydride
BMA	bismaleamic acid
BMA-2	intermediate bismaleamic acid to form BMI-2
BMA-3	intermediate bismaleamic acid to form BMI-3
BMA-4	intermediate bismaleamic acid to form BMI-4
BMA-5	intermediate bismaleamic acid to form BMI-5
BMA-6	intermediate bismaleamic acid to form BMI-6
BMA-7	intermediate bismaleamic acid to form BMI-7
BMA-8	intermediate bismaleamic acid to form BMI-8
BMI	bismaleimide
BMI-2	ethylenebismaleimide
BMI-3	1,3-bismaleimidopropane
BMI-4	1,4-bismaleimidobutane
BMI-5	1,4-bismaleimidopentane
BMI-6	1,6-bismaleimidoheptane
BMI-7	1,4-bismaleimidoheptane
BMI-8	1,8-bismaleimidoheptane
C-BMI	Commercial BMI, 4,4'-Bismaleimideodiphenylmethane
CTE	coefficient of thermal expansion

DEA	dielectric thermal analyzer
DMA	dynamic mechanical analyzer
DMF	N,N'-dimethylformamide
DSC	differential scanning calorimetry
FTIR	fourier-transform infra-red
Hc	height of the characteristic transmittance peak
Hc,t	the corresponding height of the characteristic transmittance peak at time t
Hr	height of the standard reference peak
Hr,t	the corresponding height of the standard reference peak at time t
KBr	potassium bromide
NaAc	sodium acetate
NMR	nuclear magnetic resonance
O-BMI	bismaleimide with oxyalkylene main chain, including BMI-230B,400B, 600,900,2000,2000B,4000B
Pm	molar polarization
PTFE	polytetrafluoroethylene
Td	onset degradation temperature
Tg	glass transition temperature
TGA	thermogravimetric analysis
Tm	melting point
TMA	thermomechanical analysis
To, Tp, Te	extrapolated onset, peak and end curing temperature, respectively

T_{v-max}	maximum vaporization temperature
V_m	molar volume
ΔH	heat of cure
α_1, α_2	coefficients of thermal expansions below and above T_g
α	The extent of reaction (Chapter 3)
α	the ratio of the molar polarization to the molar volume (Chapter 2)
ϵ	dielectric constant

Chapter 1 Introduction

1.1 Background

The continuous advancement of microelectronics in all fields of technology has become a basic fact of our daily life. Organic polymeric materials have long played significant roles in the microelectronics industry because of their processability, attractive mechanical properties, and relatively low cost. A variety of polymers have been proposed for use as materials with low dielectric constants for applications in microelectronics. Polyimides, epoxy, silicones, heteroaromatic polymers, fluoropolymers and hydrocarbon polymers without any polar groups which are widely used today [1-3] will be reviewed briefly.

Silicones

With a main chain of repeating Si-O and hydrocarbon side groups, silicone, possesses excellent thermal stability and flexibility that are superior to most other materials. It is used for encapsulation, but is not as popular as epoxies. Polydimethylsiloxane provides a very low glass transition temperature material, but is suitable for use at temperatures up to 200°C.

Epoxies

The main advantage of epoxy is low cost, ease of processing, and electrical properties, which have made epoxy resins very attractive in electronic applications. Epoxy resins are

widely used for formulating the molding compounds for encapsulation. However, the relatively higher thermal expansion of epoxy induces internal stress in the package during its use. Inorganic fillers such as fused silica have added to lower the thermal expansion. Also, epoxy compounds are too brittle, and tends to fail physically during usage and handling. The incorporation of a small amount of an elastomeric material, such as silicone elastomeric, carboxyl terminated butyldiene (CTBN) type domain particles, to the rigid epoxy can drastically reduce the elastic modulus, and thermal stress and increase the toughness of the epoxy material. Epoxy has also been used for interlayer dielectrics.

Polyimide

The superior thermal stability (up to 500°C), mechanical and electrical properties of polyimide have made possible its use in many high performance applications, from aerospace to microelectronics. It is used as chip carriers, laminates, insulation, moldings, coatings and interlayer dielectrics. Bismaleimides are an important class of addition type polyimides and are well known for their excellent processability and balance of thermal, electrical and mechanical properties. They have been evaluated as potential replacement materials for epoxy resins where high temperature performance is required. Bismaleimides bridge the temperature performance gap between epoxy and polyimides. Whilst epoxy resins are usually limited to service temperatures of about 200 °C, bismaleimides are capable of performing at temperatures up to 300 °C [4].

Heteroaromatic polymers

In general these types of polymers tend to exhibit even higher thermal stability and higher

glass transition temperatures than the purely phenyl base polymers of similar structure. Besides the well known polyimides there are poly(benzoxazole)s, poly(phenyl quinoxaline)s (PPQs) and poly(arylene ether oxazole)s as examples of polymers with particularly high stability at high temperatures. The quinoxaline group is not very polar, so the dielectric constants of PPQs are often rather low, even without the incorporation of fluorine.

Hydrocarbon polymer

Polymers containing nothing but carbon and hydrogen exhibit nearly 0% moisture uptake and low dielectric constants as is known for polyethylene ($\epsilon = 2.3$) or polystyrene ($\epsilon = 2.6$). However, these polymers are not stable at high temperatures above 120 °C

Fluorocarbon polymers

The polymers with the lowest dielectric constants are undoubtedly fluoropolymers. These materials generally do not take up any water and have very low dielectric constants. In fact, it is the only group of polymers having dielectric constants less than 2.3. Unfortunately, the use of aliphatic fluoropolymers is limited by their low thermal stability. Another limiting factor is their poor adhesion properties. The coefficients of thermal expansion of fluorocarbon polymers are also relatively high.

Developments in plastic packaging materials play a very important role in the growth of the microelectronics industry. The purpose of encapsulation is to protect the electronic components from adverse environments, thermal shock, temperature cycle during actual

life applications, to improve handling in later assembly processes, prevent impurities and contaminations, and increase the long term reliability of the electronics with a reasonable cost. Apart from a low dielectric constant, some of the key requirements for electronics packaging material are given in Table 1.1.

Table 1. 1 Ideal requirements for electronics packaging materials [5,6]

Materials property	Requirements/Consideration
Dielectric constant	As low as possible (2.0~3.5), frequency independent
Dielectric loss	As low as possible (below 0.01), frequency independent
Mechanical strength	High mechanical strength and resistance to thermal shock
Coefficient of thermal expansion (CTE)	Large CTE mismatch leads to stresses between two adjacent dissimilar materials
Residual stress	As low as possible either by matched CTE or low modulus
Elongation-at-break	Should be large, > 10%
Thermal stability	High stability with little or no outgasing on heating
Glass transition temperature (T _g)	High, the CTE is higher at temperatures above T _g
Water uptake	As low as possible
Compatibility	No detrimental chemical reaction with other materials
Planarization	As high as possible
Processability	High

As indicated above, the first requirement of a packaging material is that it must have a low dielectric constant. The dielectric properties of the insulating layers in a high density interconnect is important because it affects the performance and speed of the active circuitry. The dielectric constant should be low such that good insulation exists between

the active circuitry. Polarity in the dielectric material limits both the signal propagation velocity and the maximum allowable interconnect density on a chip. Lower dielectric permittivity allows closer spacing between interconnect lines with minimum cross talk. The increased packing density of interconnect wiring, enables higher device layout density on the substrate which contributes to increased operating speeds by virtue of shorter overall wire lengths. In short, the use of insulating layers with lower dielectric constant materials contributes synergistically to both higher circuit density and speed. So, the application of new low ϵ polymers will enable the development of future generations of lower cost, higher performance integrated circuits.

Typically, dielectric constants should be low (between 2.0 and 3.5) over a very wide frequency range [7, 8]. Materials having a low dielectric loss reduce signal attenuation. The dielectric loss tangent, $\tan \delta$, should be below 0.01 and independent of frequency. However, many of the conventional polyimide resins and bismaleimide-based cured resins have high dielectric constants of 3.4 or higher.

On the other hand, fluorinated polyimides are attractive because of their low dielectric constants, which can be as low as 2.5 [9-12]. These materials have low water uptake and excellent adhesion, but are sensitive to solvents and show a significant reduction in modulus at their glass transition temperature (290°C). However, they are not employed as chip-level packaging materials, mostly due to their relatively high cost, high CTE's, and problems with solvent resistance [5].

Polymers with very low dielectric constants such as polyethylene do not meet the combined thermal and mechanical requirements for application in electronic devices, nor do they have the desired adhesive characteristics [1]. Generally, non-fluorinated aromatic polyimides which have good thermal and mechanical properties have dielectric constants between 3 and 4. On the other hand, the more expensive, fluorinated polyimides have dielectric constants between 2.6-3.0 [1]. Therefore, there is a need to develop a new class of non-fluorinated aromatic polyimides which have good thermal and mechanical properties and low dielectric constant of below 3.0.

The second requirement for any packaging material is its mechanical integrity throughout large temperature variations, adverse environmental conditions, as well as direct mechanical abuse that it may be subjected to service conditions. Even the smallest mechanical failure as a result of cracking, crazing, or delamination of a small area can lead to eventual electrical failure. The mechanical properties that are required to minimize the danger of mechanical failure are low thermal mismatch and intrinsic stress, high strength, large elongation at break, and good adhesion between all materials that share one or more interfaces in the package.

The third requirement is thermal properties. The manufacture of electronic components involves many high temperature steps. It is, therefore, necessary to know the thermal properties such as thermal stability and glass transition temperature of polymers. One important consideration for package design is the minimization of thermal stress caused by the mismatch in the coefficients of thermal expansion (CTE) of the two materials that are

in contact. Thermally induced stress can cause the chip or packaging to bend or crack, or result in loss of adhesion. The CTEs of conductor metals, chips and substrates are usually low (between 2 and 20 ppm). Therefore, a polymeric dielectric with low a CTE would have some obvious advantages. Segment mobility and regularity of the structure are two factors that result in a high CTE. Alternately, a lower modulus will reduce overall stress caused by thermal mismatch.

The fourth requirement for polymers used in electronics application is their chemical resistance to environmental influences such as various process solvents and metal etchants. Exposure to such materials can lead to increased stresses, adhesion loss and solvent induced cracking. Chemical resistance depends on the chemical structure of the polyimide. Partially fluorinated and aliphatic polyimides tend to be most susceptible to attack by organic solvents. However, they exhibit a relatively low water uptake. Water uptake in polyimides is a major concern as it increases the dielectric constant and can lead to adhesion loss, corrosion, increased stress, changes in the mechanical behavior, molecular weight breakdown by hydrolysis or blistering during heating.

Finally, planarization (i.e. the ability to produce a flat surface over rough features) is also needed in electronics applications, particularly if several layers of signal lines are deposited on top of each other. The degree of planarization obtainable for a given polymer depends on solubility, solid content, solution viscosity and flow [5]. Polymer flow during cure can lead to increased planarization.

1.1.1 The application of polyimide in microelectronics

A wide variety of polymers have been evaluated for use in microelectronics applications, however, polyimides have emerged as the favored class of materials. Polyimides have been widely utilized as packaging material and dielectric layers for the electronic and microelectronic industry because of their outstanding characteristics such as low dielectric constant ($\epsilon = 3.5$) [5,6].

Polyimides may be categorized into two different groups according to their synthesis route: (a) condensation type and (b) addition type resins. Condensation-type polyimides exhibit excellent high temperature thermal and mechanical properties, but have unattractive processing characteristics. The structure of condensation-type polyimide results from reaction between a diamine and a dianhydride in a polar aprotic solvent such as dimethylformamide. Viscous solutions of polyamic acid are obtained that are chemically or thermally transformed to the polyimide. However, these thermostable polymers obtained by condensation are relatively costly to produce and there are process problems related primarily to the elimination of water or volatile matter. During chemical transformation, the release of water or volatile creates porosity that impairs the mechanical properties and aging characteristics of the materials [13]. A second problem associated with this class of polyimides is poor flow, that is, the temperatures required for cyclization of the polyamic acid precursors and fusion are quite close. Poor flow properties can adversely affect consolidation of the polyimide material [14].

Addition type polyimide resins are produced from bisimides bearing reactive end groups. One of the most important types of bisimides is bismaleimides [15]. Addition polyimides are usually low molecular weight resins containing unsaturated moieties such as maleimido, ethynyl, or nadimido end groups for subsequent crosslinking reactions [16]. Volatile condensates are not produced during curing, and the production of a void-free product is possible. Due to the high crosslinking density, addition polyimides generally possess higher stiffness and dimensional stability than condensation polyimides with equivalent segmental structures. Processability is another important advantage attributed to the initial low molecular weight of these addition type polyimide. Therefore, the current project will focus on addition type polyimides.

One of the problems with most polyimides is their poor processability caused by limited solubility in organic solvents and high melting and softening temperatures, thus narrowing down their applicability [17]. To overcome such a difficulty, polymer structure modification becomes necessary. Much effort has been achieved in designing and synthesizing new dianhydrides and/or diamines, thus, producing a great variety of soluble and processable polyimides for various purposes. On the other hand, a low dielectric constant is one of the most attractive properties of polyimide materials for microelectronics applications. It was expected that a low dielectric constant could be achieved either by having aliphatic repeating groups with low polarity or fluorine substituents in a molecular skeleton. As is well known, the strong electronegativity of fluorine results in very low polarizability of the C–F bonds. Much attention has been focused on the preparation of fluorine-containing aromatic condensation polymers. However, the fluoro-polyimides may

have low adhesion strength, low glass transition temperature, low mechanical strength or high thermal expansion coefficient (CTE). Moreover, they are expensive [18]. It could be advantageous to develop relatively inexpensive non-fluorine polyimides that have low dielectric constant and good processibility.

1.1.2 The application of bismaleimide in microelectronics

Bismaleimides (BMIs) are a leading class of thermosetting polyimides and have received increasing attention in the past years. The need for bismaleimide resins arose because of the poor high temperature performance of epoxies. BMI systems are capable of performing at temperatures up to 300°C and are therefore a useful class of materials with a temperature performance range between that of epoxies and polyimides. The major applications for BMI structural composites are in aerospace industry. BMI composites are also used in printed circuit boards. The structure of BMI monomer contains the reactive maleimide end group and spacer group [19]. The maleimide moiety is a five-membered imide ring containing a carbon-carbon double bond, an aliphatic or aromatic spacer group is included between the maleimide functional groups. The maleimide double bond is highly electron deficient due to the two adjacent electron withdrawing carbonyl groups attached to maleimide ring. Aliphatic bismaleimides can be used to produce flexible polymers, while aromatic bismaleimides are used to produce polymers with more rigid backbones. BMIs based on aromatic diamines are crystalline materials with high melting points. The most widely used BMI is 4,4'-bismaleimidodiphenyl methane as shown in Figure 1.1.

4,4'-bismaleimidediphenyl methane (Melting point 158 °C)

1,6'-bismaleimideo-2,2,4-trimethylhexane (Melting point 127 °C)

Figure 1.1 the aliphatic and aromatic chain structures of bismaleimides

Bismaleimides are typically prepared by the reaction of maleic anhydride with diamine compounds through the cyclization of the maleamic acid intermediate [20]. Figure 1.1 shows two examples of BMI. A typical bismaleimide compound has two maleimide double bonds in the molecule which can undergo a homopolymerization by a free radical mechanism under the application of heat, photo-irradiation, or in the presence of a radical initiator, to yield a cured product having a three-dimensional network structure. When the molecular make-up of main chain is changed, physical properties such as the melting temperature will be changed together [21]. BMI-based polymers have found popular use in high temperature polymer and composites mainly because of its good mechanical properties, thermal and dimensional stability.

The lack of volatile emissions during cure permits BMIs to be processed more easily than conventional condensation-type polyimides that often result in volatile by-products. As such, it can be used as a heat resistant insulating material. Furthermore, since no reaction byproduct such as condensation water is produced in the crosslinking cure reaction, the crosslinking cure reaction of the bismaleimide compound is advantageous in manufacturing various structural materials, and molding materials [7]. In addition, bismaleimide-based cured resin has been used for a multi-layered wiring substrate (such as 4,4'-bismaleimido- diphenyl methane). In summary, BMI resins offer the following advantages:

- high temperature stability
- comparatively good processability and non-volatility
- high tensile strength and modulus, good dimensional stability [22]
- lower dielectric constant (3.5) compared with most of other polymers.

However, BMI is disadvantageous in many aspects. Most of the current bismaleimide compounds developed so far have a dielectric constant of more than 3. However, Murarka reported the need for a dielectric constant of $\epsilon = 3$ for 0.25 μm minimum interconnect space and $\epsilon = 2$ for 0.18 μm . Thus the use of traditional dielectrics at very small interconnect dimensions would degrade signal propagation speed, and increase power consumption and cross-talk [1]. Therefore, polymers with the dielectric constants between 2~3 should be developed for microelectronics applications. The dielectric constants of polymers are strongly influenced by their chemical structure. Polymer structures should have low

polarity and low polarizability to achieve low dielectric constants. Generally, molecules that have polar groups (permanent dipoles) in their chains have higher dielectric constants, dielectric losses as well as increased moisture absorption [23]. Polyethylene has a dielectric constant of about 2.2, and this is attributed to CH₂ group which is less polar. Introducing fluorine atoms into polymers is a popular way of achieving low polarity. Polytetrafluoro-ethylene (PTFE) despite its strong polar C-F group (1.39D) also has a low dielectric constant about 2.1. The reason for this lies in the strong electronegativity of fluorine resulting in very low polarizability of the C-F bonds. Misra [12] reported that octafluoro- benzidine bismaleimide and its reaction products with fluorinated diamines had dielectric constants of $\epsilon = 2.84\sim 2.9$. Generally, the presence of a phenyl ring group results in higher polarity than (C-C) repeating units [24].

Unmodified BMIs suffer from brittleness due to their high cross-link densities. They are high modulus, low strength materials with a very low elongation at break mainly due to their high crosslink density and rigid aromatic ring [25]. One approach to toughen BMIs involves the incorporation of a flexible extended chain into the backbone of the BMI structure to increase the freedom of thermal expansion (due to the increased degree of freedom) and the tensile elongation (due to the reduced crosslink density). It was reported [16] that the introduction of ester groups into the backbone of the bismaleimide would benefit flexibility with little effect on reactivity or thermal stability in the resultant BMIs. However, most investigations were based on the aromatic BMIs with two bismaleimidophenyl groups connected by a central group such as -CH₂-, -O-, and -SO₂-.

Figure 1.2 The cross-linking reaction of bismaleimide

The copolymerization of BMI with other monomers (see Figure 1.2) could also increase the toughness of polymer [16]. One such chain-extended copolymerization uses a Michael addition reaction of a diamine or nucleophilic compound with an electrophilic maleimide double bond. Another approach for developing toughened BMIs is to copolymerize them with an olefinic compound using the Diels-Alder reaction [16]. BMIs are known to be dienophilic and readily react with a good diene partner, such as vinylbenzene, propenylphenoxy, allylphenyl or allylphenoxy.

Many bismaleimides polymerize at the temperature of or just above the melting point of the monomer. Generally, the temperature difference between melting and onset of polymerization is small. As a result it is difficult to maintain the uncured resin in a fluid state, and the accompanying difficulty in attaining a homogeneous melt leads to processing difficulties unless solution processing is employed. Therefore, BMI is scarcely used alone. Instead, it is often prepolymerized with diamines, and reactive elastomers, in order to increase the molecular weight and lower the melting point of the monomer. Only

through such modification, can BMI be used as a molding material. However, the addition of the second component results in a composition having a higher dielectric constant than BMI if it was used alone [7].

In order to meet the requirement of low dielectric constant, good processing performance, good mechanical properties, high glass transition temperature (T_g) and good thermal stability [26-28], it is necessary to develop a new BMI system. This is the focus of the current work. Because bismaleimide polymers are important primarily for their thermal stability, which usually results from aromaticity in the structure, the majority of bismaleimides are prepared from aromatic diamines. However, aliphatic diamines can also provide benefits in improved processability, flexibility, solubility and dielectric properties [29]. In order to achieve a polymer structure with a low dielectric constant, repeating units with low polarity and low polarizability have to be used. As such, less polar groups (CH_2 and OCH_2) were selected as the main chain to obtain BMIs with low dielectric constants in this project.

From the view point of molecular design, introducing flexible linkage into bismaleimides can effectively improve the toughness. Therefore, the purpose of this work is to synthesize a series of bismaleimides and study the effect of varying aliphatic or aliphatic-ether chain length on the properties of bismaleimide systems, this is also the novelty of this work. And in this project, bismaleimides were prepared from aliphatic or aliphatic-ether diamines with varying chain lengths. The aliphatic or aliphatic-ether group contains a kind of $-\text{CH}_2-$ repeating unit which is a less polar group. Therefore, aliphatic bismaleimide or A-BMI

which have $\text{-CH}_2\text{-}$ repeating unit was expected to have a low dielectric constant. On the other hand, BMI with both $\text{-CH}_2\text{-}$ and the ether group was expected to have improved toughness and a low dielectric constant.

1.2 Objectives and Scope

- The objective of this research work is to synthesize and evaluate the effect of aliphatic and aliphatic-ether chain extender on the properties of a bismaleimide polymer. The properties of interest include molecular structure, thermomechanical behaviors and electrical conductivity.

The scope of this project is:

- To synthesize bismaleimide monomers containing aliphatic and aliphatic-ether main chain
- To evaluate the effect of molecular structure on the properties
- To characterize their curing behavior
- To characterize their thermal, mechanical and electrical properties
- To study their processing behavior of the synthetic bismaleimide monomers
- To develop BMIs which have a low dielectric constant of below 3.0 and good mechanical properties, which are suitable for use as a packaging material.

Chapter 2 Literature Review

This chapter is divided into two parts, namely, the chemistry of bismaleimide and theory of structure and property relationships.

2.1 The Chemistry of Bismaleimide

2.1.1 The synthesis of bismaleimide

Generally, bismaleimide can be prepared by two chemical routes. One approach is to react maleic anhydride with diamines while the other one involves reacting maleic anhydride with a diisocyanate compound [30-32].

Figure 2.1 Maleic anhydride reacts with diamine to form BMI

The synthesis of a bismaleimide from an maleic anhydride and a diamine involves two reaction steps. Figure 2.1 showed the formation routes of bismaleimides where R represents the main chain between two polymerizable maleimide groups. The first step

forms a maleic acid which is subsequently converted to the corresponding bismaleimide through an intramolecular cyclization (imidization) step with the release of water condensate. The first reaction is usually performed at room temperature in dimethylformamide (DMF) or acetone solvents. In the presence of acetic anhydride and sodium acetate, the maleic acid totally disappears in 40 minutes at 50°C, and the imide and isoimide rings are formed as shown in Figure 2.2 [33].

Figure 2.2 Reactions which take place during the maleimide synthesis

At long reaction times, the concentration of isoimide rings decreases and that of imide rings increases. Isoimide rings disappear completely after 150 minutes. The yield of the bismaleimide is in the range of 65-75% [16]. The various side reactions during the chemical imidization are responsible for the low yield in BMI. The side product acetamide was observed for the chemical cyclodehydration. The product was precipitated with

distilled water and washed with a solution of NaHCO_3 until neutral pH. Then the product was dried in an oven at 60°C . Numerous publications [4, 11, 15] have appeared in the past describing the synthesis and characterization of various bismaleimides. Main chain R represents an appropriate chemical structure between two polymerizable maleimide groups. For example, by introducing into the bismaleimide an ether group that has a high flexural property, the flexibility of the resultant bismaleimide can be improved. One such compound is bismaleimidophenoxyphenylpropane. This compound gives a cured product with low modulus of elasticity and a high breaking strength and hence can be used alone as a molding material [7]. Therefore, one approach of modification is to introduce an appropriate chemical structure between two reactive maleimide groups. The increased chain length of a bridging segment provides a decreased cross-linking density in the thermoset and gives [16]

- An increased coefficient of thermal expansion due to an increased degree of freedom.
- An increased tensile elongation because of the reduced cross-linking density.
- A reduced tensile strength and modulus.

Conversion of poly(amic acid)s to the corresponding polyimides is commonly performed thermally in the solid state. This method is suitable for the preparation of thin specimens such as films, coatings, fibers, and powders in order to allow the diffusion of by-product and solvent without forming bristles and voids in the final polyimide products. Grenier-Loustalot reported [30] that the endothermic ring dehydration occurred simultaneously with the melting of the products, while the cross-linking reaction occurred at a higher temperature. After ring closure, BMI is formed thermally. Although the thermal

transformation method has been reported to be useful for synthesis of BMI in the solid state, most researchers use the chemical imidization approach to synthesize BMI. FTIR spectroscopy is widely used to monitor the thermal imidization of poly(amic acid) film [31], the chemical dehydration of amic acid and the maleimide polymerization. This is achieved by monitoring the disappearance of the NH absorption, the appearance of carbonyl vibrations near 1720 cm^{-1} , and the appearance of the C=C-H at 3099 cm^{-1} and C-N-C band at 1137 cm^{-1} peaks during synthesis. Therefore, the formation and the reaction of BMI can be conveniently monitored by FTIR.

The BMI monomer can also be prepared by reacting diisocyanate with maleic anhydride in a one-step reaction in the presence of a catalyst (e.g. Triethylamine) at $65\text{--}70^\circ\text{C}$ as shown in Figure 2.3 [32].

Figure 2.3 Maleic anhydride reacts with isocyanate to form BMI

The isocyanate-terminated PU prepolymer was dissolved in DMF and added to the solution of maleic anhydride and catalyst. The reaction took place under dry nitrogen atmosphere. Main chain R represents an appropriate chemical structure between two maleimide groups.

2.1.2 The curing of bismaleimide monomer

The maleimide double bond is highly electron deficient due to the two adjacent electron-withdrawing carbonyl groups so that BMI exhibits a high reactivity. A few curing reactions, such as thermal polymerization, addition reactions, and Diels-Alder reactions, have been developed to increase the application performance of BMI polymer. The most important curing reaction of BMI monomer is its homopolymerization at elevated temperature [16]. The double bond of the maleimide is very reactive and homo- and co-polymerization can be achieved by simply heating the monomer to between 150-400°C. The homo-polymerization reaction of BMI monomer produces no volatile by-products and provides void-free thermosets [4]. The BMI monomers thermally set to rigid, solvent-resistant, highly cross-linked thermosets.

BMI monomers are well known to crosslink by free radical polymerization. There are three structural features that affect the reactivity of BMI monomers [19], namely, the inductive effect, the effect of chain mobility and the steric effect of monomer molecules. In the inductive (polar) effect, the BMI reactivity is modified by the presence of electron withdrawing or donating groups on the nitrogen substituent. The long range inductive effect of aromatic groups might lead to increased electron withdrawal from the maleimide bonds, making the aromatic BMI more reactive [19]. Chain mobility, which is an important factor governing the crosslinking reaction. The reaction activation E_a decreases as the backbone chain length increases and thereby the reactivity increases [33]. In the steric effect of monomer molecules, the steric restrictions caused by incorporating short chains into the network make the BMI less reactive.

Heuts reported [34] the factors that govern the free-radical polymerization and monomer reactivity are generally summarized in the following four features: (1) polar effects; (2) steric effects, for example, 1,2-disubstituted alkenes do not readily homopolymerize (although they might copolymerize quite readily), which could possibly be attributed to steric hindrance; (3) (resonance) stabilization effects, these effects can arise if delocalization of the unpaired electron in the reactant and product radicals is possible. If the reactant radical has a highly delocalized electron, it will be relatively stable and have relatively low reactivity; (4) thermodynamic effects, which can be ascribed to differences in the relative energies between reactants and products, lowering or increasing the reaction barrier. For many reactions, including propagation and transfer reactions, an approximate linear relationship exists between the activation energy, E_a , and reaction enthalpy, ΔH_r , the so-called Bell–Evans–Polanyi relation [34]:

$$E_a = \rho \Delta H_r + C \quad \text{Equation (2-1)}$$

where ρ and C are constants.

During polymerization of BMI the maleimide disappears as the substituted succinimide forms. The disappearance of the absorption band located at 1150cm^{-1} (C-N-C) and the appearance of succinimide absorption (C-N-C) at 1180cm^{-1} could be monitored by using FTIR. The co-polymerization of BMI monomers will be described in section 2.1.4.

2.1.3 Michael addition reaction of BMI

Bismaleimides can also undergo a chain extension reaction, known as Michael reaction [13], with primary and secondary amino compounds. Because the brittleness of the cured

product arises from its extensively cross-linked structure, hence many efforts have been made to toughen BMIs [35-43] by reducing the cross-linking density of the polymers without adversely affecting other desirable properties. In Michael addition reaction, chain extenders are introduced into the BMI resins to reduce cross-link density and improve mechanical properties. The approach of modification by the Michael addition reaction is shown in Figure 2.4 [44-46].

Figure 2.4 The Michael addition reaction of BMI: R, R' represent different structure

The kinetics and mechanism of the cure of a bismaleimide-diamine thermoset was also studied [47,48]. Generally, the performance of the cured resin depends on [16]

- The structures of the original BMI resin and the diamine extender.
- The ratio of the BMI to the diamine modifier.
- The curing conditions.

2.1.4 The copolymerization of bismaleimide

The simplest method of BMI modification is the use of two or more monomers in a thermosetting compound. High performance BMI resins are based on rigid aromatic structures, i.e. bis(4-maleimidophenyl)methane and, thus, possess high melting points and a narrow processing window. An approach of modification uses a eutectic mixture to improve the processability and the performance of the final thermoset. A BMI eutectic

mixture is a blend of BMI resins with an optimized composition at which the melting point is minimized [4,16]. For example, Compimide 353 (Trade mark) is a low-melt heat-curable eutectic mixture which is composed of three BMI species and has a melting point of approximately 70°C.

Copolymerization is possible with a wide range of functional groups due to the variety of chemical reactions possible through the maleimide group. The copolymerization of BMI with allyl phenyl compounds by means of an Ene/Diels-Alder reaction has been found to be one of the most effective methods. The copolymerization of urethane-modified bismaleimide and bismaleimide has been reported to improve the toughness [32,49,50]. The blending of polyimide and bismaleimide to form the semi-interpenetrating polyimide network was also studied [51]. Owing to the mechanical properties of polymer materials with interpenetrating network structures are superior to those of ordinary polymers. In particular, the maximum tensile strength of interpenetrating polymer networks (IPNs) is much higher than that of the constituent polymers.

2.2 Principle of structure-property relationships of BMI

The chemical, physical and mechanical properties of the thermoset polymers are determined mainly by three factors: the chemical structure of the monomer, the morphology and the cross-link density of the polymer [52]. Investigation of these factors by experimental or theoretical means should hopefully lead to a better understanding of structure-property relationships in BMI.

2.2.1 Factors influencing melting point, glass transition temperature

It is necessary to solve the processing difficulty of conventional bismaleimide resins as they have a tendency to initiate curing and polymerize at temperature only slightly above their melting temperatures. The narrow processing gap causes BMI to cure without fully melting to give a powder product first, unless solution processing is employed [16]. However, solution processing should be avoided in packaging applications. Hence, it is of interest to synthesize a BMI with a larger processing gap between the melting and polymerization onset temperatures. To achieve this, the melting point can either be suppressed or the onset temperature of polymerization can be raised.

The melting point (T_m) and glass transition temperature (T_g) are important in determining the mechanical and thermal properties of polymers. These two temperatures determine the temperature range in which the polymer can be employed. In general, melting point and glass transition temperatures are both affected in the same manner by the changes in structural regularity and symmetry, bond flexibility, packing ability and the intermolecular forces of polymer chains [53-55].

Molecular symmetry of polymer chains plays an important role in determining glass transition temperature and melting point. If it is regular and orderly, it will pack into crystals easily. In addition, the aromatic rings like to stack together in an orderly fashion, making the crystal even stronger.

T_m and T_g , is related to the flexibility of the polymer backbone, polymers with main

chains containing long aliphatic linkages have a low T_g or low melting point. Because the longer length of the $-(CH_2)_n-$ chains in the structure result in less efficient packing [23, 56, 57]. For example, a new aromatic BMI bearing a long alkylene chain (C6,C8,C16) had melting point of 45°C [58]. Excessive flexibility in a polymer chain as in polysiloxanes and natural rubber leads to an inability of the chains to pack [53].

The T_g values change depending on how easily the chains move [59]. A polymer that has high segmental chain mobility will have a very low T_g, while one that doesn't move so well will have a high one. The more flexible the backbone chain is, the higher the segmental chain mobility, and the lower its T_g will be. Flexibility of the chain segments is determined by the degree of freedom with which different segments along the chain backbone can rotate around the covalent bonds. Linear polymer chains made of C-C, C-O, single bonds have a high degree of freedom for rotation. The flexible side groups, which serve to hold the chains apart, free their motions and decrease the T_g. On the other hand, the presence of aromatic or cyclic structure in the chain backbone or of bulky side groups on the backbone C atoms hinders the freedom for rotation to increase the T_g. The less restriction to rotate, the more flexible are the chain segments, and hence, the higher their segmental mobility. A crosslinking reaction hinders the free rotation of end groups and thus, increases the glass transition temperature. For the aromatic BMI, the glass transition temperature is maximized at the completion of the cross-linking reaction and is above 300°C [16]. The high glass transition temperatures offered by BMIs are attributed to the aromatic backbone and the high crosslinking density.

Intermolecular forces can be a big help for a polymer if it wants to form crystals. The presence of polar and hydrogen bonding groups favors crystallinity because they make possible dipole-dipole and hydrogen bonding intermolecular forces. It is better to form strong hydrogen bonds. This strong binding holds crystals together. At same time, stronger intermolecular forces lead to a higher T_g .

2.2.2 Thermal stability

The thermal stability of a polymer is also dependent on the chemical structure of polymer. The resistance to heat and aggressive environments is directly related to the bonding energy of the different elements in the polymer chain. The breaking of chemical bonds under the influence of heat is the result of overcoming bond dissociation energies. Polymers are highly thermally sensitive due to the limited strength of the covalent bonds that make up their structures. Scission in polymer chain can occur either randomly or by a chain-end process. The degradation of polymers to form smaller molecules may proceed by random scission or specific scission. The presence of oxygen traces in polymers acts as a catalyst or initiator in thermal or thermo-oxidative decomposition. Thermoplastics possess higher oxygen permeability compared to thermosets, because the cross-linking bonds in the latter restrict the diffusion of oxygen.

The chain of the heat resistant molecule should incorporate a high energy bond. Aliphatic structures are sensitive to thermooxidative cleavage, and therefore impart low thermo-stability to the polymer. Aromatic structures or heterocyclic systems are the best candidates for the requirement of high energy bonds. Aromatic rings are generally resistant

to thermooxidative attack. Hence, many polymers designed for high temperature use contain aromatic units [6]. The thermal resistance of the polyimide is decreased because of the existence of the long methylene chain due to the fact that a long chain of atoms may facilitate the random chain scissions [60]. In addition, structural abnormalities, such as branch points, existing along the chains also cause thermal instability [61]. The groups such as -O-, -S-, -CONH-, and -CO- are less stable than aromatic rings, the least stable linking units are alkylene linkages, -SO₂-, -NH-, and chlorine-containing groups. Cross-linking generally resulted in stability improvement.

The thermal degradation of the crosslinked aliphatic and aromatic bismaleimides has been studied [62,63]. The aliphatic BMIs show the lowest stability due to the cleavage of aliphatic bridges giving many fragments containing succinimide or maleimide groups. The decomposition of aromatic BMIs can be attributed to the cleavage of succinimide ring followed by carbon monoxide evolution. Bis(4-maleimidophenyl)methane, which is an aromatic BMI, has a very high decomposition temperature at 500°C in nitrogen. The major applications for BMI structural composites are in the aerospace industry and also for printed circuit boards in the electronic industry.

2.2.3 Dielectric properties

Both the chemical and physical factors play key roles in the electrical properties of polymers. The chemical aspect is concerned with the design and synthesis of new polymers that will exhibit the desired electrical properties, such as high or low dielectric constant, low dielectric loss, high resistivity, or any other special electrical property [24, 64].

In order to achieve a polymer structure with a low dielectric constant, repeating units with low polarity and low polarizability have to be used. The segmental mobility of polymer molecules affects the polarization of the dipoles and hence affects the dielectric constant. The incorporation of aliphatic groups is known to result in low dielectric constants because of low polarity and high hydrophobicity. Another effective approach to decrease the dielectric constant is to introduce fluorine substituents or perfluoroalkyl groups into polyimide materials. As is well known, the strong electronegativity of fluorine results in very low polarizability of the C–F bonds [17]. The low polar group (CH₂) and (OCH₂) can be introduced in BMIs as main chain to study their effect on dielectric constant.

In order to design low dielectric compounds, it is necessary to predict the dielectric constant of the desirable polymer. The dielectric constant of the polymer can be calculated by employing the Clausius-Mossotti equation (2-2) [65]:

$$\epsilon = \frac{(1 + 2\alpha)}{(1 - \alpha)} \quad \text{Equation (2 - 2)}$$

$$\alpha = \frac{P_m}{V_m} \quad \text{Equation (2 - 3)}$$

where P_m is the molar polarization and V_m is the molar volume. Here, α is the ratio of the molar polarization to the molar volume.

The Clausius-Mossotti equation is, however, applicable only to nonpolar or weakly polar polymers. From the above equation, it is clear that lowering α reduces ϵ . Therefore, by selecting constituent groups with small α values (such as non-polar hydrocarbons),

compounds with lower ϵ values can be designed. The relationship between the chemical structure of the constituent groups and α values are given in Table 2.1. For example, when α values are less than 0.4, ϵ is expected to be less than 3.0. Generally, the maleimide group has a dipole moment and a somewhat high α value of about 0.8. Introducing methyl groups with small α valued groups can dilute the maleimide group.

Table 2.1 the functional groups and their α values [66]

	$-\text{CH}_3$	$-\text{CH}_2-$	$-\underset{ }{\text{CH}}-$		$-\text{O}-$		$-\text{CONH}-$	$-\text{OH}$
α	0.24	0.29	0.38	0.38	0.52	0.82	1.04	2.06

Fluorine-containing aromatic polyimides have been attractive for use in the microelectronics industry as insulating layers because of their low dielectric constant, good thermal and mechanical properties over the processing temperature range [9-12,67]. Misra [26] synthesized the fluorine-containing aromatic bismaleimide, but octafluorobenzidine bismaleimide has a high melting point at 282°C and initial curing temperature at 285°C. In addition, the fluorinated polyimides exhibit low water absorption [67], because moisture level in polymer will significantly affect the electrical properties. A polymer with low polarity and low polarizability was expected to have a lower water uptake. The moisture absorption of bismaleimide resin was also studied [68], the experimental findings reveal that both hydrogen bonding and the nature of the network strongly affect the hygrothermal diffusion behavior of the bismaleimide resin.

Dielectric loss is caused by the lag in dipole orientation under an alternating electric field. Under the influence of an alternating electric field, the polar molecules of a system rotate toward an equilibrium distribution in molecular polarization. Dielectric losses will be obtained when the motion of the polar molecules is not sufficiently rapid for the attainment of equilibrium with the applied field. Some electrical energy would be transformed into heat and the medium would be heated up, aged and even damaged. Dielectric loss peaks are those associated with either the glass transition or local reorientational processes. Most polymers exhibit more than one region of dielectric loss. The largest loss peak (α peak) usually occurs at high temperature and is associated with the glass transition. The second loss peak (β peak) may occur in the glassy state and is associated with shorter range motions such as side-group rotations or local mode motions. Orientation polarization is strongly temperature-dependent. As the temperature of the material is increased, the random motion of the dipoles increases. At temperatures below T_g , where the polymer matrices are rigid, the interactions between the dipoles and the external field are limited. However, at higher temperatures, increased molecular motions facilitate the interaction between dipoles and the external field, thus absorbing more energy. At temperatures near the T_g , steep increases in dielectric losses occur. When the temperature is increased above T_g , the segmental motion of the polymer molecules become enhanced. The dielectric properties thus change with increased segmental mobility [23].

The polymer chain can be considered as a series of kinetic units; each of these units moves in an independent manner and involves the cooperative movement of a number of consecutive chain atoms. Dielectric relaxation analysis can contribute to the understanding

of the cooperative motion, because it is concerned with the movement of dipoles. The dielectric spectrum reflects the state of the molecular dynamics of the segments or group of segments. The motion of $(-\text{CH}_2-)$ and $(-\text{CH}_2\text{CH}_2\text{O}-)$ has been reported [59,69-71]. The segmental movement involving six carbon atoms by rotation about two chain bonds $(-\text{CH}_2-)$ is called crankshaft motion which occur at $-120\sim-70^\circ\text{C}$. The kinetic unit of $-\text{CH}_2\text{CH}_2\text{O}-$ in PET could vibrate locally in a range of temperature from -63 to 160°C [69].

2.2.4 Mechanical properties

The intermolecular forces and crosslink are important factors to determine the mechanical properties of thermoset polymers. The higher the chain interaction, the higher the mechanical strength of polymer. An increase in the crosslink density initially increases the tensile strength, but beyond a maximum value it subsequently decreases. As the crosslink density increases in a polymer, there is a decrease in the segmental mobility and flexibility of the polymer chains themselves. High crosslinking reduces the number of conformations that the polymer can adopt upon being loaded. As a crack grows to a failure, the polymer can dissipate only a small amount of energy, leading to low ultimate tensile strength.

Cured poly(bismaleimide) is extremely brittle because of its highly crosslinked structure and aromatic nature. A great deal of work has been done to achieve greater fracture toughness in BMI resins [72-80]. There are three approaches to decrease brittleness. The first approach is to use diamines, dithiols, allylphenols or reactive flexible oligomers as chain extenders for BMIs to decrease their crosslinking densities of the cured BMI resins

[44, 81, 82]. The second approach is to utilize engineering thermoplastics and elastomer to serve as toughness modifiers for the BMI network [83, 84]. A third approach is to introduce the different backbone chain structure into two maleimide groups. For example, the BMI includes a siloxane segment in the main chain [39, 85-86], or sulphone ether bonds [41, 87], or ether bonds [42, 77, 88]. It is hoped that longer segments between crosslinking points would reduce the brittleness of the polymer. However, introducing such tougheners usually causes a lowering of the thermo-oxidative stability of the final products [89]. In order to enhance the toughness of BMI resins whilst maintaining favorable properties at elevated temperatures, much effort has been given to the development of long chain aromatic diamines. It has been demonstrated that the introduction of phenoxy units to the BMI structure decreased the brittleness of the cured resins significantly without a reduction in their heat resistant properties [15].

2.2.5 Gelation

A gelation is a continuous network of macroscopic dimensions immersed in a liquid medium exhibiting no steady-state flow. During the course of thermosetting polymerization, the monomer (a viscous liquid) is transformed into a polymer mixture--an elastic material of infinite viscosity and essentially infinite weight average molecular weight. The onset of gelation marks the division of the polymer mixture into two parts: a gel phase, which is insoluble in all non-degrading solvents (including the monomer), and a sol phase, which consists of small molecules and can be extracted from the gel. Gelation occurs at different conversions depending on the system and the polymerization conditions. Polymerization continues beyond the gel point. The amount of gel increases at the expense

of the sol. It was considered [90] that during gelation a material changes from one in which molecular connectivity extends from a single molecular scale to one in which molecular connectivity extends throughout the entire sample. The crossover of G' and G'' has been suggested as a criterion for gelation. However it is frequency dependent in most polymer systems and is observable in polymer fluids where significant molecular entanglements are present.

2.2.6 Odd vs. even effect

The melting points of the compounds with even numbers of C atoms are relatively higher than those of the compounds with odd numbers. Mostly, “packing effects” are given as an explanation for such an alternation in melting points. The crystal packing of *n*-alkanes has been reported [91]. The differences in the packing (odd/even) could be understood in terms of variations in the main axis of the molecules. The length of the main molecular axis increases by a constant value of 1.268 Å with each additional CH₂ group. Therefore the intermolecular distances between the end groups, namely the CH₃ groups, are responsible for the alternation in the densities. The end groups of the odd and even numbered *n*-alkanes are not able to approach to the same distances. The methyl groups situated opposite to each other try to adopt a staggered conformation. Such an arrangement has indeed been found for the triclinic even numbered *n*-alkanes. But for odd numbered ones, a similar conformation was only possible on one side, on the other side the methyl groups had very long distances and the methyl groups were not really situated opposite to each other. This arrangement had larger gaps as shown in Figure 2.5. Thus, the even numbered *n*-alkanes had optimal intermolecular contacts at both ends, whereas the odd ones possessed these at

one end, and at the other end the distances were longer. This leads to a less dense packing for the odd *n*-alkanes and as a consequence, to relatively lower melting points. The distances between the methyl C atoms of adjacent groups are listed in Table 2.2.

Figure 2.5 Intermolecular distances of the terminal C atoms [91]

Table 2.2 Intermolecular distances of the terminal C atoms [91]

No. of C atoms	Distance 1 (Å)	Distance 2 (Å)
6	3.623	3.623
7	3.605	3.734
8	3.617	3.617
9	3.606	3.737

For the even numbered *n*-alkanes they are equal. For the odd numbered *n*-alkanes two different distances were found, one of them corresponded to those of the even numbered members, and on the other side, where the gaps exist, the distances were longer. Thus the melting point odd/even alternation of *n*-alkanes could be explained by the interaction of methyl groups.

The phenomenon of the odd even effect has also been known to be present in polymers. A polymer with an even numbered methylene spacer shows a higher T_m value than the neighboring polymers with odd numbered methylene spacers [92]. This odd-even effect was attributed to the zigzag packing of the polymer chains. Polymers with an even number of methylene spacers possess planar zigzag packing of the methylene chain while polymers with an odd number of methylene spacers possess non-planar zigzag packing which leads to a lower standard of packing [92]. Figure 2.6 shows the planar and non-planar zigzag conformation.

Figure 2.6 The planar zigzag conformation and helical structure [92]

The planar zigzag conformation is produced by all trans states which is in minimum energy state. The planar zigzag conformation which seems to offer minimum intramolecular interaction results in a compact molecule, which allows efficient molecular packing in the crystal. PTFE which has a helical structure is an example of molecules which is not compact. The atomic radius of the fluorine atom is so large that the PTFE chains cannot

orient themselves into a low-energy planar zigzag conformation typical of many other polymers. PTFE forms a helical structure, which is thought to stress and weaken the C-C bond comprising the backbone, which may account for its tendency towards chain scission. A single PTFE chain is shown in Figure 2.6. As the temperature of the polymer increases the helical structure loosens and begins to approximate a planar-zigzag conformation. Bunn reported [93] the odd even effect of polymers with the dipolar end groups. The dipolar groups of even molecules (where the dipoles are oppositely directed in a zigzag molecule) are very close. The interaction of the dipolar groups may stiffen the even molecules and therefore give this configuration additional stability. For odd ones the dipoles would be parallel and therefore would repel each other to increase the flexibility, decreasing the stability of the zigzag configuration. Goldfarb reported [94] the melt temperatures of the linear bismaleimides follow an odd-even chain length effect. The higher melting temperatures are observed for the BMIs with an even number of carbons on main chain.

2.2.7 Functional groups used in bismaleimides

The relationship between the molecular structure of polymers and their properties has been mentioned in the earlier sections. The three categories of functional groups mostly commonly used as main chain in BMIs are:

- ◆ Rigid groups like benzene ring,
- ◆ Flexible groups such as $-\text{O}-$, $-\text{CH}_2-$, siloxanes ...,
- ◆ Polar groups mainly $-\text{CO}-$, $-\text{SO}_2-$,

- ◆ Nonpolar groups like $-\text{CH}_2-$.

The stiffening effect of the $-\text{SO}_2-$ group largely exceeds that of the $-\text{CO}-$ group which only carries one oxygen and the T_g of polyethersulfones are roughly 75°C higher than that of corresponding polyetherketones [6]. It must be stressed that one main purpose of the polymer backbone is to maintain the linearity of molecular connections and thereby to generate material flexibility, strength, oxidation stability and synthetic accessibility. For most polymers it is the side groups that determine properties such as solubility and surface chemistry [61].

The aliphatic carbon-carbon bond

Using the non-polar group (CH_2) as main chain of BMI could obtain the BMI polymers with low dielectric constant and enhanced toughness. Meanwhile, the carbon-carbon single bond is the unit that confers appreciable flexibility to a polymer chain and thereby enhances toughness of the polymer. This flexibility is a consequence of the inherently low barrier to torsion of the carbon-carbon bond. The main weakness of the aliphatic carbon-carbon chain unit is its sensitivity to thermo-oxidative cleavage. This property is a consequence of the ability of the bond to undergo free radical cleavage reactions, and it is exacerbated when the side groups are hydrogen atoms.

The carbon-oxygen bond

BMI monomers with $-\text{CH}_2\text{CH}_2\text{O}-$, and $-(\text{CH}_3)\text{CHCH}_2\text{O}-$ groups as main chains can improve their chain flexibility. Oxygen atoms in a hydrocarbon chain allow skeletal torsional mobility and materials flexibility. If the nearby side groups are sufficiently small

(i.e. hydrogen) to allow an interaction between the skeletal oxygen atoms and water, the polymers are hydrophilic or water soluble.

Chain flexibility can be increase by substituting carbon-carbon bonds with carbon-oxygen or carbon nitrogen linkages. The cohesive energy of a methylene group is 2.85kJ/ mol whilst that of an ether group is 12.1kJ/mol. but ether groups have a lower rotational potential energy barrier than methylene [64]. Thus, the flexibility of the molecule with carbon-oxygen linkages is better than that with carbon-carbon bonds, i.e. polyethylene ($T_m=144^{\circ}\text{C}$), with its relatively high rotational potential energy barrier for the $-\text{CH}_2-$ bond rotation, thus has a higher melting temperature than the ether-oxygen-containing polytetrahydrofuran $(-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{O})_n$, with $T_m\sim 35^{\circ}\text{C}$. Therefore, BMI polymers with the ether group are expected to improve the toughness of the polymers.

Chapter 3 Proposed Program

3.1 Required BMIs for Packaging Materials

The rapid growth of the number of components per chip, the rapid decrease of device dimension, and the steady increase in IC chip size have imposed stringent requirements, not only on IC physical design and fabrication, but also on electronic packaging and interconnects. This trend toward miniaturization has prompted the current investigation on the development of bismaleimides for board fabrication and encapsulation applications. It is apparent from chapters 1 and 2 that the encapsulant must have a low dielectric constant to reduce the device propagation delay. It is known that materials with a dielectric constant of $\epsilon = 3$ are required for 0.25 μm minimum interconnect space [1]. The use of traditional dielectrics which have higher ϵ in circuitry with very small interconnect dimensions would degrade signal propagation speed, and increase power consumption and cross-talk [1]. In addition, encapsulants must also have suitable mechanical and thermal properties, such as minimal post-processing residual stress and thermal coefficient of expansions (CTE), which are close to that of the adjacent materials.

Bismaleimides have been evaluated as the potential replacement for epoxy resins where high temperature performance is required. Bismaleimides bridge the temperature performance gap between epoxy and polyimides. Epoxy resins usually cannot withstand

the severe environment (260°C for duration of up to 30s) encountered in processing during surface mounting. Bismaleimides possess excellent thermal stability and high glass transition temperature (T_g) compared with epoxies. However, BMIs can be self polymerized through their reactive maleic double bonds to give highly cross-linked brittle polyimides, which is their major disadvantage. This disadvantage can probably be overcome by introducing an appropriate chemical structure between two polymerizable maleimide groups. Because the precursor diamine is readily available at low cost, 4,4'-Bismaleimideodiphenylmethane (C-BMI) which is prepared using this precursor and is based on 4,4'-diaminodiphenylmethane, is the most widely used aromatic BMI resin [13]. However, the cured C-BMI products are extremely brittle because of their highly crosslinked structures. In contrast, BMIs bearing aliphatic (A-BMI) and aliphatic-ether (O-BMI) chain are expected to have higher toughness due to the flexibility of the aliphatic and aliphatic-ether chain. The toughness of both the A-BMI and O-BMI synthesized in the present work will be assessed.

3.2 Preparation of Required BMIs and Their Desired Properties

Two series of the BMI systems will be synthesized including: (a) bismaleimide systems with aliphatic main chain (A-BMI) and (b) bismaleimide systems with aliphatic-ether main chain (O-BMI). The reason for selecting either aliphatic or aliphatic-ether as the main chain was because both contain a kind of $-\text{CH}_2-$ repeating unit which is a low polar group. Since A-BMI has $-\text{CH}_2-$ repeating unit, it would be possible to have a low

dielectric constant. On the other hand, O-BMI with both $-\text{CH}_2-$ and the ether group would have an improved toughness and a low dielectric constant.

Therefore, in this project, bismaleimide systems containing aliphatic (A-BMI) and aliphatic-ether (O-BMI) main chain will be synthesized and evaluated. The effects of varying the chain length of the aliphatic and aliphatic-ether diamines on the properties of resultant bismaleimide systems will be also studied. The aliphatic-chain diamines that were studied include ethylenediamine, 1,3-diaminopropane, 1,4-diaminobutane, 1,5-Diaminopentane, 1,6-hexanediamine, 1,7-diaminoheptane and 1,8-diaminooctane. The aliphatic-ether-chain diamines include poly(propylene glycol) -block-poly(ethylene glycol)-block- poly(propylene glycol) bis(2-aminopropyl ether) which had number average molecular weights M_n of 600, 900 and 2000g/mol, and poly(propylene glycol) bis(2-amino- propyl ether) which had M_n of 230, 400, 2000 and 4000g/mol. The synthesis of the aromatic BMIs starting from aromatic diamines has been reported in the literature [4,15]. However, the synthesis of the aliphatic and aliphatic-ether BMIs has not been reported. Techniques to monitor the percentage conversion and purification of the produced BMI will be developed in the synthesis of A-BMI and O-BMI. It is expected that BMI with a low dielectric constant of $\epsilon = 3$ or lower could be obtained and that an increased toughness could be achieved by incorporating aliphatic and aliphatic-ether repeating groups.

Chapter 4 Research Methodology

4.1 Raw Materials

In order to synthesize the two series of the BMI systems outlined in section 3.2, diamines with different number of -CH₂- and -OCH₂- repeating units were selected. The materials used were:

1. Maleic Anhydride (MerckTM, Germany, purity 99%)
2. Ethylenediamine (FlukaTM, Sigma-Aldrich, purity 99%) No of -CH₂- : 2
3. 1,3-Diaminopropane (FlukaTM, Sigma-Aldrich, purity 99%) No of -CH₂- : 3
4. 1,4-Diaminobutane (FlukaTM, Sigma-Aldrich, purity 99%) No of -CH₂- : 4
5. 1,5-Diaminopentane (TCITM, Japan, purity 95%) No of -CH₂- : 5
6. 1,6-Hexanediamine (MerckTM, Germany, purity 98%) No of -CH₂- : 6
7. 1,7-Diaminoheptane (AldrichTM, Sigma-Aldrich, purity 98%) No of -CH₂- : 7
8. 1,8-Diaminooctane (MerckTM, Germany, purity 98%) No of -CH₂- : 8
9. Sodium Acetate (MerckTM, German purity 99%)
10. Acetic Anhydride (MerckTM, Germany, purity 99%)
11. Dimethylformamide (MerckTM, Germany, purity 99.8%)
12. Poly(propylene glycol) -block-poly(ethylene glycol)-block- Poly(propylene glycol) bis(2-aminopropyl ether), Mw=600, 900, 2000g/mol, Poly(propylene glycol) bis(2-aminopropyl ether), Mw=230, 400, 2000, 4000g/mol from Sigma-Aldrich

Maleic anhydride, diamines, solvents and catalysts were used as received. 4,4'-

Bismaleimidodiphenylmethane (C-BMI) from Aldrich was used as received.

4.2 Experimental Approach

The objective of this research work was to develop and characterize a series of BMI polymers based on aliphatic and aliphatic-ether diamines and maleic anhydride. The effects of varying the chain length of the aliphatic and aliphatic-ether diamines on the

Figure 4.1 Outline of the development and characterization of BMI

resultant bismaleimide systems will also be evaluated.

Diamines of the following molecular weights were chosen, i.e. approximately 60-150, 230, 400, 600, 900, 2000 and 4000 g/mol. It was expected that a low dielectric constant and increased toughness could be achieved by incorporating aliphatic and aliphatic-ether repeating groups with low polarity in a molecular skeleton. An outline of the research approach is given in Figure 4.1. The experimental work includes two phases: (a) synthesis and (b) characterization of the BMI.

The bismaleimides were synthesized by a two-step reaction: the first step was the reaction of maleic anhydride with diamine to form the corresponding bismaleamic acid. The second step was the cyclization of the amic acid to form bismaleimide, performed at low temperature (50°C). The degree of conversion in samples processed for different durations was characterized using Fourier Transform Infrared Spectroscopy (FTIR) and Nuclear Magnetic Resonance Spectroscopy (NMR).

Subsequently, the processability, curing behavior, thermal, mechanical, dielectric and rheological properties of the various BMI systems were evaluated. The processability of the resins will be determined by their solubility in various solvents, melt viscosity (flowability), and processing window (the temperature range between melting point and onset temperature of curing). Poor processability is a common concern for a high performance thermoset resin, such as poly (bismaleimide) resins where the resin becomes

flowable only at elevated temperatures, the processing of the resin is difficult because of its rapid curing reaction. A wide processing window is therefore desirable for optimum processing design and performance control. A Differential Scanning Calorimeter (DSC) and rheometer were used to measure the melting point, curing temperature and gel point of the synthesized BMI monomer.

By studying the curing behavior, some understanding of the processing procedure of BMI polymers can be obtained. Generally, the thermal properties of a polymeric material are characterized by its glass transition temperature (T_g), coefficient of thermal expansion (CTE) and thermal decomposition temperatures. The above properties were measured using a Thermal Mechanical Analyzer (TMA) and a Thermal Gravimetric Analyzer (TGA) respectively. The minimization of thermal stress that can be attributed to the mismatch in the coefficients of thermal expansion (CTE) of the two materials in contact is one of important considerations for packaging materials.

Mechanical properties are commonly defined by tensile, compression, and flexural characteristics under various conditions and are described by the ultimate strength (yield and break strengths), modulus (stiffness), and extensibility. Impact resistance and fracture energy (toughness) are also important mechanical properties that should be considered. Tensile test and toughness were carried out to characterize the mechanical properties of the cured BMI polymers. Packaging materials should have high mechanical strength and resistance to thermal shock.

Since the BMI polymers could also be used as microelectronic packaging materials, they should possess low dielectric constants. This is because signal propagation speed and wiring density in multichip packaging are increased when the dielectric constant is lower. Dielectric measurements were performed using a DEA (dielectric thermal analyzer).

Phase (I): Synthesis of the A-BMI systems and O-BMI systems

In phase 1, BMI systems with different chain lengths of aliphatic and aliphatic-ether diamines in the main chain were synthesized. In all, 14 compounds of BMIs have been synthesized in this project. FTIR and NMR were used to determine the structure of these BMIs.

Phase (II): Characterization of the A-BMI systems and O-BMI systems

In phase 2, the curing properties, thermal, dielectric and tensile properties of A-BMI and O-BMI were evaluated. Differential Scanning Calorimetry (DSC) was used to determine the melting points and curing temperatures of BMI monomers, and to define the processing window and curing conditions. A rheometer was used to determine the melt viscosity and gel point of A-BMI and O-BMI. The decomposition temperatures of BMI polymers were determined by Thermo Gravimetric Analysis (TGA). In addition, Thermal Mechanical Analyses (TMA) was used to determine the glass transition temperatures and thermal expansion coefficients of the fully cured polymers. The dielectric constant, α , β and γ transitions were measured by Dielectric Thermal Analyser (DEA). The tensile strength and toughness of the polymers was examined by stress-strain measurements.

4.3 Sample Preparation

Phase (I): Synthesis of the A-BMI and O-BMI systems

1. Synthesis of the A-BMI systems:

The synthesis route for the A-BMI compounds is summarized as follows:

Stage 1: The preparation of the bismaleamic acid intermediates

Stage 2: The cyclisation reaction of the A-bismaleamic acid to A-bismaleimides

Figure 4.2 Synthesis of a bismaleimide compound [16]

Seven aliphatic bismaleimides were synthesized from the reaction of maleic anhydride with seven different diamines, namely, ethylenediamine, 1,3-diaminopropane, 1,4-

diaminobutane, 1,5-Diaminopentane, 1,6-hexanediamine, 1,7-Diaminoheptane, 1,8-diaminooctane. Details are summarized in Table 4.1.

Table 4. 1 A-BMI code and its main chain

Bismaleimide code	Bismaleimide type	bismaleamic acids code	Main chain
BMI-2	ethylenebismaleimide	BMA-2	-(CH ₂) ₂ -
BMI-3	1,3-bismaleimidopropane	BMA-3	-(CH ₂) ₃ -
BMI-4	1,4-bismaleimidobutane	BMA-4	-(CH ₂) ₄ -
BMI-5	1,5-bismaleimidopentane	BMA-5	-(CH ₂) ₅ -
BMI-6	1,6-bismaleimidoheptane	BMA-6	-(CH ₂) ₆ -
BMI-7	1,7-bismaleimidoheptane	BMA-7	-(CH ₂) ₇ -
BMI-8	1,8-bismaleimidooctane	BMA-8	-(CH ₂) ₈ -

A detailed procedure for the synthesis of the BMIs is described as follow:

Stage 1: The synthesis of A-bismaleamic acid intermediate

The stoichiometry of this reaction, based on the ratio of maleic anhydride to diamine equivalent weight, is fixed at 2:1. Typical amounts of maleic anhydride and diamines used in the preparation of bismaleamic acids are shown in Table 4.2. Initially, 0.0795 mol of the diamine was accurately weighed to 5 mg and dissolved in a five-necked 500ml reaction flask containing 150 ml of N,N-dimethylformamide (DMF). The reaction flask was equipped with a stirrer, a pressure equalizing dropping funnel, a temperature controller, nitrogen inlet and a reflux condenser as shown in Figure 4.3. A solution containing 0.159 mol of maleic anhydride dissolved in 150 ml of DMF was added drop-wise from a dropping funnel over 5 minutes at the ambient temperature (typically 25°C).

Table 4.2 Typical amounts of reactants used in the preparation of bismaleimides

Reactants	Molar mass (g/mol)	Amount used		Reactants	Amount used	
		mol	g		mol	g
Maleic anhydride	98.06	0.159	15.57	BMA-2	0.075	19.22
Ethylenediamine	60.10	0.0795	4.78	BMA-3	0.075	20.27
1,3-Diaminopropane	74.13	0.0795	5.89	BMA-4	0.075	21.32
1,4-Diaminobutane	88.15	0.0795	7.01	BMA-5	0.075	22.37
1,5-Diaminopentane	102.18	0.0795	8.12	BMA-6	0.075	23.42
1,6-Hexanediamine	116.21	0.0795	9.24	BMA-7	0.075	24.48
1,7-Diaminoheptane	130.24	0.0795	10.35	BMA-8	0.075	25.53
1,8-Diaminooctane	144.26	0.0795	11.47

Figure 4.3 Synthesis of a bismaleimide compound**A. Determination of percentage conversion of A-bismaleamic acid**

After adding the maleic anhydride solution, the reaction mixture was heated and

maintained at 50°C in a thermo-regulated bath and stirred continuously. Samples were removed periodically (every 30 minutes) for FTIR analysis in order to monitor the progress of the reaction. The reaction was stopped when there were no further changes in the intensity of the C=O peak at $1700\pm 10\text{ cm}^{-1}$. This typically took about 2 hours. The solution was allowed to cool before proceeding on to the next stage where A-bismaleamic acid was prepared.

B. Calculation of reaction yield

The reaction mixture described above was then precipitated in deionised water. The intermediate bismaleamic acid precipitate was filtered and washed several times with deionised water before being dried in an air oven for 24 hrs at 50°C [45]. The final product was accurately weighed to determine their yields. Samples were analyzed using FTIR to determine their final molecular structure [30]. Assuming two reactants, A and B, form the product C according to the equation (1) given below

The actual yield of the product is determined experimentally whilst the theoretical yield is determined by chemical calculation. The yield of bismaleamic acid C can be calculated using Equation (4-2) where

$$\text{Percentage yield of C} = \frac{\text{Actual yield of C}}{\text{Theoretical yield of C}} \times 100\% \quad \text{Equation (4 - 2)}$$

Stage 2: The cyclization reaction of A-bismaleamic acid to A-bismaleimides

The intermediate A-bismaleamic acid dissolved in 250 ml DMF was placed in the reaction flask as shown in Figure 4.3. The cyclization was carried out in the presence of an acetic anhydride and sodium acetate, the maleic acids completely cyclised to give bismaleimides at 50°C.

A. Determination of percentage conversion

A 500 ml five-necked flask was charged with 0.075 mol dried bismaleamic acid and two catalysts: 2g of sodium acetate, and 40 ml of acetic anhydride. Cyclization of the bismaleamic acids was carried out at 50°C under continuous stirring. Samples were removed every 30 minutes and precipitated in deionised water. The precipitate was filtered and washed several times before being dried in an oven at 50°C for 24 hrs. The dried samples were then analyzed using FTIR. Typically the reaction lasted about 2~6 hours until no further changes in the intensity of the C-N-C peak at $1127\pm 10\text{ cm}^{-1}$ was detected.

B. Preparation of A-BMI

A 500 ml five-necked flask was charged with 0.075 mol dried bismaleamic acid, 2g of sodium acetate and 40 ml of acetic anhydride. Cyclization of the bismaleamic acid was carried out at 50°C for 5 hrs and stirred continuously. The reaction mixture was precipitated in deionised water. The bismaleimide precipitate was filtered and washed several times with deionised water and sodium bicarbonate solution until neutral pH

before being dried in an oven at 50°C for 12hrs. The final products were weighed to calculate their yields and analyzed for their molecular structures by FTIR and NMR.

2. Synthesis of the O-BMI systems:

The bismaleimides (O-BMI) were prepared according to a two-step method shown in Figure 4.4.

Figure 4.4 The formation of O-BMIs by two-stage reaction

Stage 1: The synthesis of bismaleamic acid intermediate of O-BMI

Typical amounts of maleic anhydride and diamines used in the preparation of bismaleimides are shown in Table 4.3. In order to obtain a proper yield of O-BMI, a

different molar amount of diamine was used in the experiments because the molar mass of the aliphatic-ether diamine ranged from 230g/mol to 4000g/mol. A appropriate amount of the diamine was weighed and dissolved in 150 ml of N,N-dimethylformamide (DMF) in a five-necked 500ml reaction flask equipped with a stirrer, a dropping funnel, a temperature controller, nitrogen inlet and a reflux condenser as shown in Figure 4.3. The pre-determined amount of maleic anhydride dissolved in 150 ml of N,N-dimethylformamide (DMF) was added drop-wise via a dropping funnel over 5 minutes at room temperature. The mixture was then heated and stirred at 50 °C for 2 h. Samples were removed periodically (every 30 minutes) and analyzed using FTIR to determine the percentage conversion in order to ascertain whether the reaction is completed.

Table 4.3 Typical amounts of reactants used in the preparation of O-BMIs

Formulations	Maleic anhydride		Diamine	
	mol	grams	mol	grams
BMI-230B	0.159	15.57	0.0795	18.285
BMI-400B	0.159	15.57	0.0795	31.8
BMI-600	0.159	15.57	0.0795	47.7
BMI-900	0.0795	7.785	0.03975	35.775
BMI-2000	0.03975	3.8925	0.019875	39.75
BMI-2000B	0.03975	3.8925	0.019875	39.75
BMI-4000B	0.019875	1.946	0.0099375	39.75

Stage 2: The cyclization reaction of aliphatic-ether amic acid to form O-BMIs

After stage 1, the catalysts of sodium acetate and acetic anhydride were added into the

flask. The reaction was carried out at 50 °C for 6 hours. Samples were also removed every 30 minutes and analyzed using FTIR to determine the percentage conversion. It was found that the reaction took 6 hours to complete reaction at 50 °C. Most of DMF was removed using a rotary evaporator from the reacted mixture. The mixture subsequently dissolved in 100 ml chloroform, the solution was then washed with distilled water several times and dried using a rotary evaporator. A brown liquid was obtained. The synthesized aliphatic-ether BMIs were labeled as BMI-230B, 400B, 2000B, 4000B for those with methyl side group and BMI-600, 900, 2000 for those without methylene side group shown in Figure 4.5 and Table 4.4. In Figure 4.5, the number of repeat units (n) comes from the product specification of the diamine.

Figure 4.5 The structures of the synthesized O-BMI monomers

Table 4. 4 O-BMI codes and the relative chain

	Bismaleimide code	Oxyalkylene chain	No. of repeat unit
1	BMI-230B	$-\text{[OCH}_2\text{CH(CH}_3\text{)]}_n-$	2.6
2	BMI-400B	$-\text{[OCH}_2\text{CH(CH}_3\text{)]}_n-$	5.6
3	BMI-600	$-(\text{OCH}_2\text{CH}_2)_b-$	8.5
4	BMI-900	$-(\text{OCH}_2\text{CH}_2)_b-$	15.5
5	BMI-2000B	$-\text{[OCH}_2\text{CH(CH}_3\text{)]}_n-$	33
6	BMI-2000	$-(\text{OCH}_2\text{CH}_2)_b-$	40.5
7	BMI-4000B	$-\text{[OCH}_2\text{CH(CH}_3\text{)]}_n-$	68

Phase (II): Characterization of the A-BMI and O-BMI systems

In phase (II), all the samples (A- & O- bismaleamic acids, A- & O- BMI monomers and polymers) were characterized using FTIR, NMR, DSC, TGA, TMA, DEA and rheometer.

1. DSC analyses

DSC analyses were carried out to provide crucial information about melting and curing reaction such as melting point, exothermal-start, exothermal-peak and exothermal-end temperatures and exothermal enthalpy. Before BMI monomers was characterized using DSC, the bismaleamic acid and A-BMI samples were dried in oven at 50°C for 24 hours while the O-BMI samples were dried in oven at 50°C for 48 hours.

2. FTIR, NMR, TGA, TMA, Rheological and tensile analyses

FTIR and NMR were used to determine the structure of the A- & O- BMI monomers.

TGA and rheometer were used to characterize uncured BMI monomers to obtain their vaporization and gelation properties respectively. The fully cured A- & O- BMI polymers were characterized using TGA, TMA and tensile tester to obtain their thermal and mechanical properties. The uncured and cured BMI samples were prepared as follows:

A. The uncured A-BMI and O-BMI monomers

The uncured A-BMI monomers were dried in oven at 50°C for 24 hours before they are characterized using FTIR, NMR, TGA and rheometer. The O-BMI monomers were dried in vacuum oven at 50°C for 48 hours before FTIR, NMR and rheological analysis.

B. The A-BMI polymers

BMI-3, 5, 6, 7, 8 were individually placed in 20 mm diameter metal pan and heated in oven to 180 °C for 1 hr until the BMIs melted thoroughly before curing at 220 °C for 10 hrs. Because of their high melting point, BMI-2, 4 were heated in the oven directly to 220 °C and was kept at isothermal condition for 10 hrs. The curing condition was chosen based on the DSC analyses. There was a gap between onset temperature and peak temperature of cure, any temperature between the gap can be chosen for curing temperature. If too high a curing temperature (i.e. exotherm-peak temperature) was chosen, the reaction rate will proceed too quickly and a large amount of heat will be released in a short period of time, causing the BMI to crack. For this reason, a lower curing temperature (220 °C) with longer curing time (10 hrs) was chosen in this

experiment. The DSC curve showed that the curing exotherm of BMI disappeared after 10 hrs at 220°C, indicating the completion of curing.

C. The O-BMI polymers

The O-BMIs were cured as follows: O-BMI monomer was placed in 20 mm diameter metal pan and heated in an oven to 230 °C for 10 hr and then to 260 °C for 3 hours.

3. DEA analyses

The dielectric constant and dielectric loss as a function of temperature were obtained using the TA DEA 2970 Dielectric Analyser. The test was conducted as follows:

A. The A-BMI polymers

A sample of A-BMI powder was placed onto the ceramic single surface sensor such that the powder covered the sensor to an approximate height of 1.0 mm. Then the sensor with A-BMI powder was placed in oven and heated to the required temperature (i.e. 180°C for BMI-3,5,6,7,8, and 220°C for BMI-2,4). The compounds at that temperature melted and were spread evenly on the sensor surface using a wooden rod. The compounds were cured in oven at 220 °C for 10 hours.

B. The O-BMI polymers

For the O-BMI system, the compounds were coated directly onto the sensor using a wooden rod at room temperature. The compounds were cured in an oven at 230 °C for 10 hours and 260 °C for 3 hours.

4.4 Analytical procedures

The analytical equipment and procedures used for characterizing the samples are described in this section:

- (a) Nuclear Magnetic Resonance (NMR) Spectroscopy, Bruker Spectrometer 500MHz
- (b) Fourier Transform Infra Red Spectrometer (FTIR), Nicolet 560 FTIR
- (c) Differential Scanning Calorimeter (DSC), TA Instrument model 2920 DSC
- (d) Thermal Gravimetric Analyzer (TGA), TA Instrument model 2950 TGA
- (e) Thermal Mechanical Analyzer (TMA), TA Instrument model 2940 TMA
- (f) Dielectric Analyzer, TA Instrument model 2970 DEA
- (g) Rheometer, HAAKE RS-150
- (h) A Micro and Lloyd tensile tester
- (i) Moisture absorption

(a) Nuclear Magnetic Resonance (NMR) Spectroscopy

^1H and ^{13}C NMR were used to determine the chemical structure of the monomers synthesized. Samples were dissolved in deuterated solvents, CDCl_3 , at a solid concentration of 2~10%. The NMR spectra obtained on a Bruker Spectrometer operating at 500 MHz. ^1H and ^{13}C NMR spectra were referenced against tetramethylsilane (TMS) at 0 ppm. The ^{13}C NMR spectra showed that the BMI compounds exhibited a carbonyl resonance around 168-170 ppm, and the maleimide double bond resonance at 133 ppm [30]. The region of aliphatic carbons is around 0~60 ppm [30]. In the ^1H NMR spectra of

BMI, a sharp singlet due to the proton of the double bond appeared at 6.7 ppm (4H, CH=CH) [91, 93].

(b) Fourier Transform Infra Red Spectrometer (FTIR)

FTIR analysis carried out using a Nicolet 560 FTIR spectrometer to monitor the changes in the various functional groups of the sample. A small amount of the solid sample was ground with anhydrous KBr powder and the fine powder mixture was then pressed into discs. For solution samples, the spectra were obtained using an Attenuated Total Reflectance (ATR) diamond accessory. All the samples were scanned 40 times at 4 cm⁻¹ resolution. A typical FTIR spectrum of the BMI is shown in the Figure 4.6, and the characteristic FTIR absorption peaks of bismaleamic acid and BMI are given in Tables 4.5 & 4.6, respectively.

Quantitative analysis on the rate of reaction was conducted using the peak height ratio method. The CH₂ , characteristic absorption between 2960 and 2850 cm⁻¹ was used as the internal reference as it was found in both bismaleamic acids and bismaleimides and was unaffected during the reaction. The amount of amic acid formed was monitored by measuring the peak height of the characteristic C=O absorption at 1700±10 cm⁻¹. The cyclization reaction of the bismaleamic acid to BMI was monitored by studying the characteristic C-N-C peak height at 1127±10 cm⁻¹. The normalized absorbance heights of the characteristic peaks were calculated using Equation (4-3).

$$\text{Normalized absorbance } A_c = \frac{H_c}{H_r} \times 100\% \quad \text{Equation (4 - 3)}$$

Where H_c and H_r are the heights of the characteristic absorbance peaks and the internal reference peak respectively as shown in Figure 4.6. The extent of reaction (α) at any time, t , was calculated from the peak height of the characteristic (c) and reference (r) peaks at infinitely long time, $H_{c,o}$ and $H_{r,o}$ respectively, and their corresponding values at time t , $H_{c,t}$ and $H_{r,t}$ respectively, according to the Equation (4-4) [95]:

$$\alpha = 1 - \frac{\left(\frac{H_{c,t}}{H_{r,t}} \right)}{\left(\frac{H_{c,o}}{H_{r,o}} \right)} \quad \text{Equation (4 - 4)}$$

Figure 4. 6 A typical spectrum of bismaleimide monomer (BMI-8)

Table 4.5 Characteristic FTIR absorption peaks of bismaleamic acid

Functional group	Characteristic absorption (cm ⁻¹)
N-H	3300 [39], 3390 [13]
N-H	1560-1530, 1270-1250, 650-630 [30]
-CH ₂ - (reference)	between 2960 and 2850 cm ⁻¹ at least two peaks [96]
-OH	3340, 3482 [85]
C=O	1710 [97]

Table 4.6 Characteristic FTIR absorption peaks of bismaleimide

Functional group	Characteristic absorption (cm ⁻¹)
-CH ₂ - (reference)	between 2960 and 2850 cm ⁻¹ at least two peaks [96]
-C=C- of maleimide ring	3100, 830, 690 [98]
C-N-C of maleimide ring	1127 [99, 100]
C=O	1710, 1730, 3446 [96]

Figure 4.7 A typical plot of conversion to form BMA

The conversion of the various reactive groups of the samples was plotted against reaction time and typical plot of conversion rate versus time for a bismaleamic acid (BMA) obtained by FTIR spectrum is shown in the Figure 4.7.

(c) Differential Scanning Calorimeter (DSC)

Differential Scanning Calorimeter (DSC) TA 2920 was used to monitor the melting and curing properties of the samples. The instrument measures the heat capacity and monitors heat flow during endothermic and exothermic transitions or reactions. About 5 mg of

sample was weighed accurately to $\pm 0.01\text{mg}$ in an aluminum test pan and hermetically sealed before being placed in the DSC cell. The sample was heated from room temperature (25°C) to 350°C at a heating rate of $10^\circ\text{C}/\text{min}$. Nitrogen gas at a flow rate of $50\text{ cm}^3/\text{min}$ was passed continuously into the test cell throughout the experiment. Figure 4.8 shows a typical DSC thermograph indicating the melting point (T_m), extrapolated onset temperature (T_o), peak temperature (T_p) of curing and the exothermic heat (ΔH) evolved. The melting and onset temperatures were used to define the processing window ($T_o - T_m$) while the onset and peak temperatures were used to define a suitable isothermal cure temperatures (between T_o and T_p) for optimizing the curing profiles of BMI systems. After T_p , the cure exotherm reduced gradually and disappeared finally (i.e. $\Delta H \approx 0$) to indicate the completion of cure.

Figure 4. 8 A typical plot of heat flow versus temperature by DSC

Figure 4.9 shows the percentage conversion vs. time of BMI. For example, the full cure was achieved at 230 °C for 8 hrs. The curing at 220 °C for 24 hrs for BMI monomer was chosen in this study. DSC can also provide valuable information about the rate (kinetics) of reaction. The curing kinetics of the BMI systems were studied in order to understand and control the curing reaction. The kinetic approach normally requires three or more experiments at different heating rates, between 1 and 10°C/minute. In this study, 2, 5 and 7°C/minute were used to test the BMI samples. The samples were heated to 350°C at a rate of 2, 5, 7°C/min individually. TA Instruments currently offers the software package to process the data to obtain the plots of cure kinetics of BMI systems. For the modeling of the cure kinetics, the rate of reaction is assumed to be the product of two functions, $k(T)$ and $f(x)$. The temperature dependent function or rate constant, $k(T)$, is:

$$k(T) = Z \text{ EXP}(-E_a/RT) \text{ (the Arrhenius equation)}$$

where E_a is the activation energy, Z is the pre-exponential factor, R is the universal gas constant (8.314 J/mol deg), and T is the absolute temperature (K). It is understood that at higher temperatures the reaction rate is greater.

The second function, a function of the concentrations of the reactants $f(x)$, gives the dependence of the reaction rate on the extent of reaction. Naturally, as the reactants are used up, the rate decreases. This function is expressed as:

$$f(x) = (1-x)^n$$

where n is the reaction order and x is the fraction reacted. Adherence to this equation is referred to as n -th order behavior. The TA kinetics software automatically assesses the

extent of reaction (or the partial areas of cure) and then performs a best-fit to the above equations in order to extract the kinetic parameters. From this, the values of the activation energy of cure, E_a , the pre-exponential factor, Z , and the order of reaction, n , are determined.

One highly useful plot, for process control purposes, is the degree of cure versus time under isothermal conditions. These predictive plots are displayed in Figure 4.9 at various isothermal cure temperatures. Another important plot that the TA kinetics software provides is the conversion time as a function of temperature. Figure 4.10 shows the typical plot of conversion time vs. temperature of BMI.

Figure 4.9 The plot of conversion vs time of O-BMI-230B

Figure 4.10 The plot of conversion vs temperature of O-BMI-230B

(d) Thermal Gravimetric Analyzer (TGA)

TGA analysis was carried out on a TA 2950 TGA system to determine the thermal stability of the bismaleimide samples. Approximately 10 mg of sample was placed on the platinum pan and heated from room temperature (25°C) to 600 °C at a heating rate of 20° C/min. The samples were tested for their thermal stability in both dry air and purified nitrogen gas at a flow rate of 50 cm³/min. TGA was also used to determine the maximum vaporization temperature (Tv-max) and onset temperature of decomposition (Td-onset) of uncured BMI samples (See Figure 4.11). The percentage weight loss versus temperature of cured sample was obtained as shown in Figure 4.12. The onset degradation temperature (Td) and the sample 10% weigh loss temperature were tabulated.

Figure 4. 11 Typical TGA thermogram on A-BMI monomer

Figure 4. 12 Typical TGA thermogram on cured bismaleimide

(e) Thermal Mechanical Analyzer (TMA)

The coefficient of thermal expansion (CTE) and the T_g of the cured BMIs were determined using a TA 2940 TMA system. The effect of varying the chain length of the diamine on the T_g and the CTE of cured BMI samples were evaluated. The cured BMI was cut into dimensions of approximately 5mm x 5mm and 3mm (thickness) and ground to ensure surface flatness. The TMA system was fitted with a flat-bottomed quartz expansion probe. A static load of 5mN was applied on the sample and the dimensional change in the sample when heated from room temperature (25°C) to 425 °C at a heating rate of 10 °C/min was measured.

Figure 4.13 Typical TMA thermogram of cured BMI

The CTE values below and above the T_g of the sample, i.e. α_1 and α_2 respectively and the T_g for each of BMI type was tabulated. A typical TMA thermogram of a cured BMI

is shown in the Figure 4.13.

(f) Dielectric Analyzer, TA Instrument model 2970 DEA

The dielectric constant and dielectric loss of BMI polymer as a function of temperature were obtained using TA DEA 2970 Dielectric Analyser as shown in Figure 4.14-15. When performing dielectric measurements, the sample is placed in contact with a disposable ceramic single surface sensor. The well prepared sensor was then cooled down to $-140\text{ }^{\circ}\text{C}$ to observe the relaxation transition (They are called α and β transition in order of decreasing temperature) of the cured resin and then heated to $280\text{ }^{\circ}\text{C}$ at a rate of $5\text{ }^{\circ}\text{C}/\text{min}$. The following frequencies were applied to the resin during the analysis: 1, 10, 100, 1000, 10k and 100k Hz. The DEA cell was purged with dry nitrogen adjusted to a flow rate of 80 ml/min.

Figure 4.14 A typical plot of dielectric constant of BMI-230B

Figure 4.15 a typical dielectric relaxation plot of BMI-600

(g) Rheometer, HAAKE RS-150

The viscosity of BMI monomer as a function of temperature and time was obtained using a HAAKE RS-150 rheometer. The rheometer, fitted with a pair of 20mm disposable aluminum parallel plates, was used to determine the gelation times and temperatures of the BMI samples. Approximately 4 ml of the liquid sample (or equivalent solid sample) was applied between parallel plates. The gap between the parallel plates was preset at 0.5mm. Frequency and stress sweeps were conducted to select the proper parameters. All measurements were conducted in the oscillatory mode at a frequency of 4.7 Hz and a shear stress of 5000 Pa. The optimized frequency and shear stress values were determined by rheometer (HAAKE RS-150).

Figure 4.16 A typical rheological plot of G' , G'' versus time

For determination of the gelation point of BMI, the parallel plate sensors were preheated to the required temperature before introducing the test sample. The sample was then heated until the gel point was obtained. The gelation times were determined at various isothermal temperatures. The gelation temperatures were obtained at certain temperature ranges, namely 30-280°C. The sample was placed between parallel plates of 25 mm diameter and a gap of 0.5 mm. The data were collected at a frequency of 4.7 Hz and a shear stress of 5000 Pa in the oscillatory mode. The heating rate was 3 °C/min. The gelation point of the sample was indicated by the crossover point of the shear storage modulus (G') and shear loss modulus (G'') plot as shown in Figure 4.16. At this point, the initial network of the BMI was formed.

(h) Tensile Test

A Micro™ specimen tester was used to evaluate the tensile stress-strain properties of the cured BMI samples. 5 specimens were tested for each data point. Specimens approximately 15x5x0.2 mm were used in this study. The gauge length was fixed at 8 mm (the distance between the clamp) and the strain rate was set at 0.001mm/sec. The test was conducted at room temperature. Figure 4.17 shows a typical stress-strain curve of a pure BMI specimen. The tensile modulus of the sample was calculated from the slope of the linear portion of the stress-strain curve. The following equation was employed:

$$\sigma = E \epsilon \quad \text{Equation (4-5)}$$

Where E is Young's modulus; σ , the stress; ϵ , the strain.

The stress σ is a measure of the force per unit area:

$$\sigma = F / (WB) \quad \text{Equation (4-6)}$$

and the strain or elongation is defined as the extension per unit length:

$$\epsilon = d / l \quad \text{Equation (4-7)}$$

Where d is the displacement; F, the load at the displacement d; l, the span; and W and B, the width and the thickness of specimen, respectively.

The toughness of a material was taken to be the area under a stress-strain curve. The stress is proportional to the tensile force on the material and the strain is proportional to its length. Thus, the area under the curve then is proportional to the integral of the force over the distance the polymer stretches before breaking. This integral can be taken to be

the energy required to break the sample. The toughness is a measure of the energy a sample can absorb before it breaks.

Figure 4.17 A typical stress-strain plot of the BMI polymer

A LLOYD™ LR10K tensile tester is used to determine the sample toughness. Samples approximately 30mm x 10mm x 4mm were used in this study. The samples were subjected to a three-point bend and a 5 kN loading cell is used. The strain rate was set at 0.1mm/s. The flexural toughness was calculated from the area under the stress-strain curve.

(i) Water absorption

Water absorption experiments were performed on thin bismaleimide films that were dried for two days at 100 °C in a vacuum oven prior to contact with water. These rectangular

samples had nominal length of 30 mm, a width of 10 mm, and a thickness of 0.06 mm. This sample geometry was chosen in order to have a relatively high surface area to volume ratio to assist in the attainment of water absorption equilibrium. Absorption experiments were performed at 50 °C and were considered complete after 14 days of immersion in deionized water. At the end of the experiment, the samples were quickly removed from the water, blotted dry, and immediately weighed to determine the total water uptake.

Chapter 5 Synthesis and properties of the A-BMI systems

5.1 Phase (I): Synthesis of the A-BMI

5.1.1 Synthesis of the intermediate A-BMAs

The A-BMI synthesis was monitored using FTIR, by measuring the characteristic functional groups present in bismaleamic acid and maleimide compounds. The structures of A-BMIs were confirmed by NMR analysis shown in later part of this section.

Figure 5. 1 FTIR spectrum of a typical bismaleamic acid (BMA-8)

The quantitative evaluation of the reaction to form amic acid was conducted by following the appearance of characteristic peak at $1540 \pm 10 \text{ cm}^{-1}$ (N-H) and the $(-\text{CH}_2-)$ absorption at 2919 cm^{-1} peak was used as the internal reference for BMA-8. Figure 5.1 shows the

FTIR spectrum of a typical of bismaleamic acid (BMA-8). The analysis of these spectra showed that the amic acid appeared very rapidly but stabilized after 1-2 hrs. Figure 5.2 shows the typical plot of conversion vs time to form a bismaleamic acid (BMA-8). The conversion vs time plots for the other BMA samples are shown in Appendix I (Figure 1). The conversion times of BMAs were tabulated in Table 5.2 in section 5.1.3.

Figure 5. 2 The plot of conversion vs time to form BMA-8

5.1.2 DSC analyses of bismaleamic acids (A-BMAs)

The thermal analyses of the intermediate bismaleamic acids (BMA) were investigated using differential scanning calorimetry (DSC) to determine one or more endothermic and exothermic peaks associated with structural or physical changes. Melting endotherms of A-BMAs were observed between 170°C and 191°C as shown in Figure 5.3. One endothermic peak was observed for each BMA and this probably indicated that the BMAs were pure. After melting, there was a small endothermic peak, which was induced

by the heat dehydration reaction, because the imidisation can occur during heating [16]. A common method for the preparation of a polyimide from the amic acid is thermal imidisation which is heating at temperatures higher than the melting point of an amic acid [16]. This is the reason why there were two endothermic peaks, one for melting and the other one for dehydration.

Figure 5. 3 DSC analysis of A-BMAs

Table 5. 1 Effect of chain length on melting point of bismaleamic acids (BMA)

	BMA-2	BMA-3	BMA-4	BMA-5	BMA-6	BMA-7	BMA-8
T _m (°C)	190	180	191	163	180	146	170

The effect of diamine chain lengths on the melting point of the corresponding bismaleamic acid is summarized in Table 5.1 and shown in Figure 5.4. It can be seen that the melting point tends to decrease with increasing chain length, but the melting points of BMA seem to follow the odd even effect. A-BMAs with even CH_2 sequences have higher T_m whilst those with odd sequences have lower T_m . Compounds with an even number of methylene spacers possess planar zig-zag packing of the methylene chain while compounds with an odd number of methylene spacers possess non-planar zig-zag packing which leads to a lower standard of packing [92]. The packing density tends to decrease for bismaleamic acid having an odd number of flexible $-\text{CH}_2-$ groups resulting in lower melting points. FTIR analysis is shown in Section 5.2.1 that when CH_2 length is odd, the packing density is lower.

Figure 5.4 The effect of chain length on melting points of A-BMAs

Roland Boese [91] reported that the even numbered compounds have optimal intermolecular contacts at both ends, whereas the odd ones possess these at one end only and that the distances between the layers at the other end are longer, this leads to a less dense packing for the odd compounds and as a consequence, as shown above, to relatively lower melting points.

Figure 5.5 Effect of the odd number of C on the melting point of A-BMAs

Figure 5.5 and 5.6 show the effect of odd even number of carbon atoms on melting points of A-BMAs. It is observed that the melting points of A-BMAs with the odd numbers of methylene units and the even ones both decrease as the chain length increase. The T_m is related to the flexibility of the backbone, the compounds with main chains containing long aliphatic linkages have a low melting point. As such, the melting points of A-BMAs decrease as the chain length increase. The magnitude of decrease for the odd A-BMI is 34°C (BMI-7~BMI-3), but the magnitude of decrease for the even A-BMI is 21°C (BMI-

8~BMI-4). Because even-membered chains pack together in a uniform fashion more compactly than do odd-membered chains, the change for even A-BMI is small. Figure 5.6 shows that the gap of melting point between 2C and 4C atoms is small. A heavy or strongly bond group will of course damp down the motions at the end of CH₂ sequence, but the forces tending to displace the heavy group must depend on the motions in the CH₂ chain. The motion of short methylene carbon is relatively restricted. Therefore, there is not much change of melting point between 2C and 4C atoms as shown in Figure 5.6. Figure 5.6 also shows that there is greater change between 4C and 6C atoms, and between 6C and 8C atoms. Two factors, intermolecular forces and molecular flexibility, are of equal importance in determining the melting point. As the chains become longer, their flexibility makes the odd even effect progressively smaller until, for long end chains, it becomes unnoticeable. So there is greater change between 4C and 6C atoms.

Figure 5.6 Effect of the even number of C on the melting point of A-BMAs

5.1.3 Synthesis of the A-BMIs

Figure 5. 7 FTIR spectrum of BMI-8

The cyclization reaction of the bismaleamic acid (BMA) to form BMI was monitored by following the appearance of characteristic peak C=C at $1127 \pm 10 \text{ cm}^{-1}$. The (-CH₂-) absorption peak at $2909 \pm 10 \text{ cm}^{-1}$ shown in Figure 5.7 was used as the internal reference.

Figure 5. 8 The plot of cyclisation reaction to form BMI-8

Chapter Five**Synthesis & properties of the A-BMI systems**

Figure 5.8 shows the plot of the cyclisation reaction to form BMI-8. The conversion vs time plots for other BMI samples are shown in Appendix I. The results were tabulated in Table 5.2. The reaction curves to form BMIs stabilized after 2-4 hrs indicating the end of the cyclisation reaction. All the curves show an initial linear trend whose slopes increased with increasing the time. At longer times, the all reaction rates decreased substantially and the curves reached a plateau. The curves stabilized after a period of time, indicating completion of the reaction. From Table 5.2, it was found that the time to form the A-BMA is the same and the time to form the A-BMI is different. The diamine chain length has no effect on the formation of A-BMA and has less effect on the formation of A-BMI. The formation of the bismaleamic acid was a fast exothermic reaction and the formation of the bismaleimide was a slow imidization reaction as reported [16]. Results show similar cyclisation time for increasing chain length.

Table 5. 2 The effect of diamine chain length on the formation of A-BMA & A-BMI

Chain (CH ₂) _n	n=2	n=3	n=4	n=5	n=6	n=7	n=8
Bismaleamic acids (minutes)	30	30	30	30	30	30	30
Bismaleimides (hours)	2	3	3	3	3	3	5

Table 5.3 Comparison about the yield of A-BMIs

Chain (CH ₂) _n	n=2	n=3	n=4	n=5	n=6	n=7	n=8
Bismaleimides	47%	46%	53%	43%	57%	56%	58%

Figure 5.9 Reactions which take place during maleimide synthesis [16]

From Table 5.3, the yields for A-BMI compounds were low, which is consistent with the Liao's work [31]. Various side products are accountable for the reduced yield shown in Figure 5.9 [31]. Liao demonstrated that isoimide was formed as an intermediate that rearranges to the maleimide because of acetate ion catalysis. The isoimide rings disappear completely after 150 minutes. Other by-products are acetanilides, which are formed in

Chapter Five

Synthesis & properties of the A-BMI systems

high percentage when acetic anhydride with no (or low) acetate ion concentration is employed for the chemical cyclodehydration [4]. FTIR and ^1H NMR analyses also allow detection of whether some impurity (isoimide and acetanilides) remain in the purified samples by the presence of dual absorption at $1700\text{ cm}^{-1}(\text{C}=\text{O})$ in the IR spectra and resonance signals at around 9 ppm (NH) in ^1H NMR spectra [33]. The isoimide and acetanilide not to be detected in the IR and ^1H NMR spectra are absent in my samples.

The two-steps method allows control of the formation of the imide by following the disappearance of the amic acid. The temperature is a key controlling condition during synthesis. The first reaction was performed at a temperature of 50°C in a solvent. The formation of fumaric acid which does not cyclize, has to be minimized by working at a low temperature of about 50°C [33].

Imidization from an amic acid is an intramolecular cyclization with a dehydration process. Acetic anhydride and sodium anhydride were used to remove the produced water and accelerate the imidization reaction. In the presence of acetic anhydride, the amic acid disappears at 50°C , whereas the imide ring is formed. The coexistence of the maleic anhydride and amine at high temperatures might allow the Michael addition (See 2.1.3 for Michael reaction) to occur when the reaction is carried out at 140°C for a long duration, which would be undesirable for this system. Therefore, imidization from an amic acid is done at 50°C to avoid the possible Michael reaction between maleic and amine groups that can occur at high temperature.

Chapter Five***Synthesis & properties of the A-BMI systems***

The solution was then poured into cold water. The precipitate was collected by filtration, repeatedly washed with water and dried at 60°C-70°C in a vacuum oven. FTIR spectroscopy was used to monitor the dehydration of amic acid. The disappearance of the NH absorption, the appearance of carbonyl vibrations, and the appearance of C-N-C band at 1400 cm⁻¹ are the most accurate indication in monitoring the formation of BMI.

The structures of A-BMIs were confirmed by Bruker 500MHz NMR ¹³C NMR (CDCl₃) spectrum through the presence of the carbonyl resonance at 169 ppm and the double bond band in maleimide ring at 133 ppm in line with work reported elsewhere [30]. The region of aliphatic carbons is around 25~40 ppm. The ¹H NMR (CDCl₃) showed a sharp singlet for A-BMIs at 6.7 ppm (4H, CH=CH) due to the proton of the double bond. Figure 5.10-11 show the typical NMR spectra of A-BMI. NMR spectra for other A-BMI samples are shown in Appendix III. ¹H NMR spectra are shown in Table 5.4. Figure 5.10 showed one peak at 170.7 ppm is attributed to the carbonyl carbon and another peak at 133.91 ppm is attributed to the C=C carbon of BMI-6. The ¹H NMR spectra of BMI-2 showed two characteristic peaks at 3.75 ppm (CH₂) and 6.70 ppm (CH=CH) in Figure 5.11.

Figure 5.10 ^{13}C NMR spectrum of BMI-6

Figure 5.11 ^1H NMR spectrum of BMI-2

Chapter Five**Synthesis & properties of the A-BMI systems****Table 5.4 Characteristic NMR absorption peaks of A-BMI**

A-BMI	CH ₂ repeating unit	¹ H NMR spectra δ
BMI-2	CH ₂ CH ₂	3.75 (4H, 2CH ₂)
BMI-3	CH ₂ CH ₂ CH ₂	3.5 (4H, 2CH ₂), 1.9 (2H, CH ₂)
BMI-4	CH ₂ CH ₂ CH ₂ CH ₂	3.5 (4H, 2CH ₂), 1.5 (4H, 2CH ₂);
BMI-5	CH ₂ CH ₂ CH ₂ CH ₂ CH ₂	3.5 (4H, 2CH ₂), 1.6 (4H, 2CH ₂), 1.3 (2H, CH ₂)
BMI-6	CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂	3.5 (4H, 2CH ₂), 1.5 (4H, 2CH ₂), 1.3 (4H, 2CH ₂)
BMI-7	CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂	3.5 (4H, 2CH ₂), 1.5 (4H, 2CH ₂), 1.3 (6H, 3CH ₂)
BMI-8	CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂	3.5 (4H, 2CH ₂), 1.5 (4H, 2CH ₂), 1.3 (8H, 4CH ₂)

5.2 Phase (II): Characterization of the A-BMI systems

5.2.1 FTIR and NMR analyses

Figure 5. 12 FTIR spectrum of BMI-8

One of the outstanding properties of bismaleimide is the reactivity of the maleimide double bond. The double bond of the maleimide ring is electron-poor as a result of the adjacent carbonyl groups which have the electron withdrawing effect. Consequently, the reactivity of maleimide double bonds towards nucleophiles is activated compared with a classical ethylene C=C bond. It has been reported that aromatic BMI reactivity was affected by the inductive (polar) effect [19]. The inductive effect of aromatic groups might lead to increased electron withdrawal from the maleimide bonds, making the aromatic BMI more reactive [19]. Therefore, aromatic C-BMI is more reactive. But for aliphatic A-BMI, it is not known whether the distribution of the methylene group and electron density of C=O could modify the reactivity of the maleimide double bond. Because the change of the electron density affects the shift of wave number which can be

measured using FTIR as shown in Figure 5.12, the IR vibration bands of the maleimide ring of the different A-BMIs are tabulated in Table 5.5.

Table 5.5 The effect of CH₂ on the frequency shift of double bond and C=O

A-BMI	2	3	4	5	6	7	8
Double bond C=C (cm ⁻¹)	3104	3087	3091	3085	3087	3085	3089
Carbonyl group C=O (cm ⁻¹)	1706	1704	1697	1708	1692	1700	1693

Figure 5.13 Effect of the main chain length on the frequency shift of C=C in A-BMI

FTIR spectroscopy showed in Figure 5.13 that there was significant odd even effect of methylene groups on the wave number of double bond. When the CH₂ length is odd, the frequency of C=C group is lower than when the chain length is even. These data would seem to indicate that the inductive effect of the aliphatic chain has effect on the electron density of the maleimide double bond. As a result, the reactivity of double bond would be affected by the odd even effect.

Figure 5.14 Effect of the even number of C on the frequency shift of C=C in A-BMI

Figure 5.15 Effect of the odd number of C on the frequency shift of C=C in A-BMI

It was noticed the small but consistent shift of approximately 15-20 cm⁻¹ to lower frequency was observed when BMI-3, BMI-4, BMI-5, BMI-6, BMI-7 and BMI-8 C=C bonds were compared with BMI-2 C=C bond as shown in Figure 5.14 and Figure 5.15. A lowering of these frequencies is characteristic of conjugation with another double bond

structure, such as C=O. Conjugation extends the dipolar character of the carbonyl group to the double bond. The electron-withdrawing C=O group decreases the electron density in both C=O group and conjugated C=C and this results in a lower stretching frequency. Conjugated C=O and C=C are more stable than their non-conjugated counterparts because of the delocalization of the electrons over both the carbonyl group and the C=C double bond. The conjugated C=C stretching frequency decrease as the chain length increase. This suggests that the double bond becomes slightly more single bond character. Therefore, A-BMI should be more stable as the chain length increase.

Figure 5.16 Effect of the CH₂ on the frequency shift of C=O in A-BMI

The effect of the number of carbon on the wave number of carbonyl groups of A-BMIs is as shown in Figure 5.16, it can be seen that the spectra for BMI-3, BMI-5 and BMI-7 with odd number of carbon atoms between imide linkages showed a slightly higher wave number in the carbonyl C=O peak at 1700 cm⁻¹ than those of BMI-4, BMI-6 and BMI-8 with even number of carbon atoms. This implies that there is an odd-even effect. It would

Chapter Five**Synthesis & properties of the A-BMI systems**

be interesting to consider why this increase is observed. The chemical nature of atomic groups adjacent to a carbonyl unit modifies its stretching frequency. The odd-even effect gives rise to the frequency shift between more “ordered and “disordered” fragments of the A-BMI chains. Hans Binder [101] suggested there is correlation between the IR order parameter and the absorption frequency. Wave numbers increase with increasing conformational disorder and decreasing packing density. This reflects a certain distribution of conformational states where the methylene groups in a more disordered conformation absorb at higher frequencies than more “ordered” ones. Hence, each absorption band results from the various microscopic states differing in conformation and/or local packing properties. The carbonyl groups of A-BMI molecules with odd number of carbon atoms absorb at the increased wavenumbers to indicate their more disordered CH_2 groups and decreased packing density. A-BMI molecules with even number of carbon atoms are tightly packed.

Figure 5.17 Effect of the odd number of C on the frequency shift of C=O in A-BMI

Figure 5.18 Effect of the even number of C on the frequency shift of C=O in A-BMI

Figure 5.17 and Figure 5.18 show the effect of the odd or even number of carbon atoms on the frequency shift of C=O in A-BMI. It is observed that the wave numbers decrease in order of BMI-5, BMI-3, BMI-7 for odd ones and BMI-2, BMI-4, BMI-8, BMI-6 for even ones. The carbonyl group C=O is a double bond with a peak at 1700 cm^{-1} , but the C=O bond is not symmetrical and the bulk of the electron density is associated with the more electronegative oxygen. This polarization results in a partial positive charge " δ^+ " on the carbon and a matching partial negative charge " δ^- " on the oxygen. The shifting of C=O bond can occur when the electron density was added and extracted - adding strengthens (higher frequency) and extracting weakens (lower frequency). The shift to lower frequency (i.e. the wave number) implies a decrease of the strength. This indicates that the carbonyl becomes slightly more single bond character. Therefore the stability should increase in order of BMI-5, BMI-3, BMI-7 for odd ones and BMI-2, BMI-4, BMI-

Chapter Five**Synthesis & properties of the A-BMI systems**

8, BMI-6 for even ones. The wave numbers of BMI-6 and BMI-8 can be considered to be equal (within experimental error) in Figure 5.16 suggesting that the stability had reached a plateau for $C \geq 6$.

The structures of A-BMIs were confirmed by Bruker 500MHz NMR ^{13}C NMR (CDCl_3) spectrum through the presence of the carbonyl resonance at 169 ppm and the double bond band in maleimide ring at 133 ppm agrees with work reported elsewhere [30]. The chemical shift region of aliphatic carbons is around 25~40 ppm. The ^1H NMR (CDCl_3) showed a sharp singlet for A-BMIs at 6.7 ppm (4H, $\text{CH}=\text{CH}$) due to the proton of the double bond. Figures 5.10-11 show the typical NMR spectra of A-BMI. NMR spectra for other A-BMI samples are shown in Appendix III. ^1H NMR spectra are shown in Table 5.4. Figure 5.10 showed one peak at 170.7 ppm is attributed to the carbonyl carbon and another peak at 133.91 ppm is attributed to the $\text{C}=\text{C}$ carbon of BMI-6. The ^1H NMR spectra of BMI-2 showed two characteristic peaks at 3.75 ppm (CH_2) and 6.70 ppm ($\text{CH}=\text{CH}$) in Figure 5.11. It was also possible to identify and attribute the chemical shifts for all the compounds synthesized, in particular protons of the maleimide function in NMR. The ^1H NMR spectra of the maleimide double bond at 500MHz for the different A-BMIs are shown in Table 5.6.

Table 5.6 ^1H NMR chemical shifts of the A-BMI function

A-BMI	2	3	4	5	6	7	8
Double bond $\text{HC}=\text{CH}$ (ppm)	6.7014	6.7223	6.6896	6.6834	6.6820	6.6832	6.6845

It can be seen from Figure 5.19 that the aliphatic groups had a slight but noticeable effect on the chemical shifts of maleimide protons.

Figure 5.19 Effect of the CH₂ on the chemical shift of H-C=C in A-BMI

These data indicated again that the inductive effect of aliphatic chain does affect the electronic density of the double bond. It was observed that the chemical shift decreases as the chain length increase. The chemical shift would change depending on the electron density around the proton. If the electron density around the protons increases, the chemical shift decreases. This indicates that the C=C becomes slightly more single bond character (The electron density increases) as chain length increases. Therefore, A-BMI should be more stable as the chain length increase. The chemical shift of BMI-3 is higher than that of other A-BMI suggesting that BMI-3 is more reactive.

In summary, the odd even effect and chain length affect the frequency shift of FTIR and

NMR. It was found that when CH₂ length is odd, the packing density is lower. At same time, A-BMI should be more stable as the chain length increase.

5.2.2 DSC analyses of bismaleimides (A-BMIs)

The thermal and cure behavior of all the BMI samples were investigated by DSC. The DSC profiles of BMIs are shown in Figure 5.20. From Figure 5.20 the endothermic behavior due to melting of the solid A-BMI was observed in the lower temperature region and the exthothermic peak in the higher temperature region. The endothermic peak (T_m) was due to the melting of BMI and the exothermic peak (T_p) due to the curing reaction. The initial thermal curing temperature is denoted by the onset temperature (T_o) of the exothermic peak. The melting, curing temperatures and reaction enthalpy of A-BMI are tabulated in Table 5.7.

Figure 5. 20 The melting point and heat curing of A-BMI monomer

Chapter Five**Synthesis & properties of the A-BMI systems**

The varying trends in the melting points and the curing temperature of BMI systems are shown in Figure 5.21. It can be seen from Figure 5.21 that, in general, BMI systems having longer flexible $-\text{CH}_2-$ groups have lower melting points. This is because the increased chain flexibility and intermolecular cohesive force has a significant effect on the melting point. As the chain length increases, increasing flexible linkages between the two maleimide rings and the decreasing density of polar groups lead to a decrease in the melting point.

Table 5.7 Melting, curing temperatures and curing heat of A-BMI systems

	T_m (°C)	T_o (°C) (onset cure)	$\Delta T = T_o - T_m$ (°C)	T_p (°C) (curing peak)	$-\Delta H$ (J/g)
BMI-2	194	209	15	247	393
BMI-3	171	220	49	249	417
BMI-4	203	228	25	259	480
BMI-5	108	212	103	253	469
BMI-6	136	216	80	261	464
BMI-7	85	215	130	258	413
BMI-8	122	232	110	274	502
C-BMI	159	193	34	219	185

However, the melting temperatures of BMI-3, BMI-5 and BMI-7 with odd carbon chain decrease more significantly than that of BMI-2, BMI-4, BMI-6 and BMI-8 with even carbon chain. This indicates that the melting temperatures follow an odd-even chain-length effect. Francisca and Goldfarb also observed the odd even defect of T_m in polypyromellitimides [92] and in BMI [93] individually. The odd or even number of

Chapter Five***Synthesis & properties of the A-BMI systems***

carbon atoms in hydrocarbon segments of the chain affects the regularity of packing. Monomers with an even number of methylene units possess planar zigzag packing of the methylene chain while monomers with an odd number of methylene units possess non-planar zigzag packing which leads to a loose packing [92]. FTIR analysis in Section 5.2.1 found that when CH₂ number is odd, the packing density is lower. So an even number of carbons on the main chain normally results in higher melting temperatures. BMI-3, BMI-5 and BMI-7 have odd number of carbons so that their melting points reduced most significantly [93].

It is observed from Figure 5.21 that the polymerization onset temperatures (T_o) and peak temperatures (T_p) of these A-BMIs increases with increasing chain length. That is to say that the exothermic peak shifted to a higher temperature as the backbone chain length increases. This is due to the reduced number of reactive groups per volume of A-BMIs. From FTIR analysis in Section 5.2.1, this is because A-BMI should be more stable as the chain length increase. The thermodynamic effect (activation energy) could also explain the phenomenon [34]. The thermodynamic effect can be ascribed to differences in the relative energies between reactants and products, lowering or increasing the reaction barrier. An approximate linear relationship exists between the activation energy, E_{act}, and reaction enthalpy, ΔH_r, the so-called Bell–Evans–Polanyi relationship [34]:

$$E_{act} = \rho \Delta H_r + C$$

where ρ and C are constants.

For A-BMI monomers, their curing enthalpies increase with the length of the aliphatic

chain as shown in Table 5.7, so their activation energies will increase as the length of main chain is increased.

(a) Even No. of C atoms

(b) Odd No. of C atoms

(c) The combined data for Odd and even No. of C atoms

Figure 5. 21 The effect of chain length on melting points and curing temperatures

Chapter Five

Synthesis & properties of the A-BMI systems

Therefore, as the length of main chain increases, the activation energy increases and thereby the reactivity of A-BMI monomer decreases resulting in higher curing temperature. It should be noted that C-BMI monomer with lower reaction enthalpy leads to lower activation energy and thereby lower curing temperature than those of A-BMI monomers.

Three structural features of the bismaleimide are known to affect the reactivity of bismaleimide oligomer [13]: (a) the inductive (polar) effect of the bridging unit on maleimide reactivity; (b) the mobility of the oligomeric molecules up to the point when they become attached to the network; and (c) the steric effect of the oligomeric molecules already attached to the network on the ease of access of other reactive species. It has been argued that the inductive effect is the weakest [13]. The FTIR and NMR analyses in Section 5.2.1 have shown that the inductive effect has effect on the reactivity of BMI. The second factor on mobility of the oligomer molecules is more important. The reaction activation E_a was expected to decrease as the backbone chain length increases and thereby increasing the reactivity [33]. However, DSC analyses show the reverse phenomenon. A-BMI with long flexible chain has high reaction enthalpy and activation energy. Based on this, it can be deduced that the mobility of the A-BMI oligomer is not the main factor that affects the reactivity of A-BMI oligomer. The third factor of steric effect can not be responsible for the differences in the reactivity of the A-BMI monomers because these are linear aliphatic chains. Heuts [34] reported the thermodynamic effect (activation energy) affected free-radical polymerization and monomer reactivity. Hence,

Chapter Five

Synthesis & properties of the A-BMI systems

the increase in curing enthalpies of the A-BMIs with increase in the length of the main chain increase indicated that the reactivity of bismaleimide oligomer was probably due to the thermodynamic effect.

The curing enthalpy evolved per mole of maleimide group increased with increasing molecular chain length of the monomers, possibly because of the increase in chain flexibility. According to the principle of energy minimization, the structure obtained tends to the lowest energy state, but the bond length and angles were usually far from their equilibrium values and because of this, the increase in flexibility decreases the equilibrium value of the cured polymer molecule [53, 61]. This was why the curing enthalpy for A-BMI with more flexible chain was higher.

The DSC was also used to measure the rate (kinetics) of reaction. Figures 4.9 and 4.10 show the typical plot of conversion to cure. The results of the curing time to 99.9% conversion at the temperature of 210°C were tabulated in Table 5.8. The results show that the curing time increases with chain length of the A-BMI molecule. This is because the increase in activation energy of A-BMI with length of aliphatic chain resulted in longer curing times. This is in accordance with the observation that the exotherm peak was shifted to higher temperatures as the length of the backbone chain increased. The FTIR and NMR analyses in this study have also shown A-BMI should be more stable as the chain length increase. In the DSC experiments where only a small amount of sample was used, the heat transfer was efficient and uniform. In order to ensure full curing for the

larger specimen, a curing time of 10 hours at the temperature of 210°C was used to cure the A-BMIs. This curing time was selected based on that reported in the literature [15] for other BMIs.

Table 5.8 Effect of chain length on curing time of A-BMI

A-BMI	2	3	4	5	6	7	8	C-BMI
Time (min)	75	75	90	270	300	330	270	20

It can be seen from Table 5.7 that the melting points of BMI-2, BMI-3, and BMI-4 were higher than that of C-BMI, but the melting points of BMI-5, BMI-6, BMI-7, and BMI-8 were lower than that of C-BMI. This is because BMI-2, BMI-3, BMI-4 have a short chain but BMI-5, BMI-6, BMI-7, BMI-8 have a longer aliphatic chain. Thermodynamically $T_m = \Delta H_m / \Delta S_m$, where ΔH_m and ΔS_m are enthalpy and entropy of melting, respectively. ΔH_m depends on intermolecular forces, whereas ΔS_m depends on the regularity of arrangements and flexibility of polymer chains [92]. BMI-5, BMI-6, BMI-7 and BMI-8 with a longer flexible aliphatic chain probably have more disordered regions resulting in their lower melting points. BMI-2, BMI-3 and BMI-4 which have shorter chains have a higher melting point probably because they have less disordered regions due to the shorter flexible of polymer chains. The lower curing onset temperature (see table 5.7) and the shorter curing time to 99.9% conversion (see Table 5.8) of C-BMI at the temperature of 210°C than those of A-BMIs show the higher reactivity of the former. The long range inductive effect of aromatic groups might have been assumed to lead to increased electron withdrawal from the maleimide bonds, as well as thermodynamic effect making

the C-BMI more reactive [19]. The processing window (T_o - T_m) of C-BMI is 34°C as shown in Table 5.7, except for BMI-2 and BMI-4, A-BMIs have larger processing ranges (49-134°C) than that of C-BMI, at which the material has good fluidity for moldability. The wide processing windows are desirable for the thermoset processing and this can be achieved with the A-BMIs. But the processing window (T_o - T_m) of BMI-2 and BMI-4 is smaller due to their higher melting points mentioned earlier.

5.2.3 Gel points of A-BMIs

The onset of gelation is of critical importance to processing thermoset systems. Gelation is the irreversible transformation of a liquid to a crosslinked elastic gel of infinite molecular weight and defines the upper limit of the processing window. A-BMI begins to become more viscous when heated until it reaches a state when it is no longer a liquid and has lost its ability to flow. This is the 'gel point'. The A-BMI will continue to harden after it has gelled, until, at some time later, it has attained its full hardness and properties. This reaction itself is exothermic, which, in turn, further speeds up the reaction. The whole process is known as the 'curing' of the resin. The gel temperatures and gel times for the A-BMIs are listed in Table 5.9. By comparing the gel time at a fixed temperature, the relative reactivity of A-BMI can be assessed. Gel temperatures and gel times were found to increase with chain length of BMI monomer increasing as shown in Figure 5.22 and 5.23. The FTIR and NMR analyses in this study have shown A-BMI should be less reactive (more stable) as the chain length increase. As the chain size increases, the

thermodynamic effect (activation energy) [34] results in an increase in the gel temperatures and gel times. It can be deduced that the thermodynamic effect leads to the different activation energy and hence affects the reactivity of A-BMI monomers. The results indicated that the thermodynamic effect affects the reactivity of A-BMI monomers.

Table 5.9 Gel Temperature and Gel Time of A-BMI

	Gel time (s) isotherm at 230°C	Gel temperature (°C)
BMI-2	100	210
BMI-3	200	210
BMI-4	210	218
BMI-5	210	215
BMI-6	275	222
BMI-7	360	220
BMI-8	370	230
C-BMI	150	215

Figure 5.22 The effect of chain length on gel point of A-BMI monomer

Figure 5.23 The effect of chain length on gel temperature of A-BMI monomer

There is also a big fluctuation for gel temperature due to odd-even effect as the main chain length increases. This indicates the reactivity is also affected by the odd-even effect. The A-BMI monomers with an even number of methylene units possess a close packing of the methylene chain while monomers with an odd number of methylene units possess a loose packed structure.

It has been shown [34] that the thermodynamic effect (activation energy) is caused by differences in the relative energies between reactants and products. The difference packing leads to the energy difference between reactant and product and this affects the reactivity of the A-BMI monomers. A-BMI monomers with the even-numbered carbon atoms possess higher reaction enthalpies than those of A-BMI monomers with odd ones. Therefore, it can be deduced that A-BMI monomers with the odd-numbered carbon atoms possess higher reactivity, thereby showing a big fluctuation for gel temperature.

Compared to A-BMIs, C-BMI possesses a shorter gel time and a lower gel temperature which can be attributed to its aromatic structure. The inductive effect of aromatic groups and the thermodynamic effect (activation energy) enables the C-BMI to be more reactive [19].

5.2.4 TGA analyses of A-BMIs

TGA analysis of the uncured A-BMI and the cured A-BMI samples were carried out to measure their processing properties and thermal decomposition properties. The focus of the studies on uncured A-BMIs was to determine their vaporization properties before curing. Figure 5.24 shows a typical 2-step weight loss thermograph of uncured BMI-8 in air. All the TGA curves of uncured A-BMIs have two sharp drops (Appendix VI, Figure 1) and the data are tabulated in Table 5.10.

Figure 5. 24 Typical TGA thermograph of uncured BMI-8 in air

Table 5.10 Uncured A-BMIs: vaporization and decomposition temperatures

	Tv-maximum (weight loss by vaporization)		Td-onset (weight loss by decomposition)	
	In air (°C)	In nitrogen (°C)	In air (°C)	In nitrogen (°C)
BMI-2	264 (64% loss)	278 (63% loss)	466	450
BMI-3	268 (41% loss)	293 (44% loss)	471	458
BMI-4	273 (31% loss)	285 (23% loss)	458	449
BMI-5	282 (60% loss)	284 (46% loss)	447	460
BMI-6	270 (29% loss)	291 (23% loss)	443	424
BMI-7	292 (47% loss)	342 (42% loss)	443	443
BMI-8	284 (25% loss)	280 (25% loss)	435	435

The initial weight loss was possibly caused by vaporization of BMI itself and this can be proven further using FTIR. FTIR spectra showed that the vaporized materials possess the same absorption peaks as their respective A-BMI monomers. The thermogram obtained for uncured BMI showed significant vaporization which is not good for processing. Secondly weight loss can also be due to the decomposition of A-BMI. This is responsible for the weight loss at the higher temperatures (Td). The temperatures of second weight loss of the uncured A-BMI monomers were found to be similar to the degradation temperatures of the cured A-BMI polymers.

Figure 5.25 showed a typical TGA plot of a cured A-BMI polymer. Data are tabulated in Table 5.11. The varying trends were shown in Figure 5.18. All the BMI systems showed onsets of degradation at approximately 450°C in dry air and in pure nitrogen.

Figure 5. 25 Typical TGA plot of the BMI-8 polymer

Table 5. 11 Effect of chain length on decomposition of the cured A-BMIs

	Temperature (°C)			
	In air		In nitrogen	
	T _d	T _{10%}	T _d	T _{10%}
BMI-2	443	442	451	453
BMI-3	450	447	456	459
BMI-4	461	458	458	459
BMI-5	449	447	458	460
BMI-6	464	463	461	461
BMI-7	449	447	448	449
BMI-8	445	448	445	449
C-BMI	491	495	492	499

Note: T_{10%}: the temperature at which 10% of weight has been lost.

Increasing the length of aliphatic main chain does not appear to significantly lower the thermal stability. It is interesting to note that the odd-even effect affects the degradation temperatures in air.

From the typical TGA plot shown in Figure 5.25 and the graphs attached in Appendix VI (Figure 1), it can be seen that weight loss began at low temperatures. This can probably be attributed to the evaporation of moisture absorbed by cured BMIs. The decomposition temperatures of these A-BMIs in air have a larger fluctuation than those in nitrogen as shown in Figure 5.26, which implies BMI-3, BMI-5 and BMI-7 are sensitive to thermooxidative degradation due to loose packing.

Figure 5.26 Effect of chain length on degradation on cured A-BMIs

In other words, the differences in chain conformation between A-BMI polymers with

Chapter Five

Synthesis & properties of the A-BMI systems

even-numbered methylene and A-BMI polymers with odd-numbered methylene are believed to be responsible for the observed odd-even effect. The looser packing in the ‘odd’ – type BMIs probably permit higher oxygen diffusion which leads to lower degradation temperatures. The breaking of chemical bonds under the influence of heat is the result of overcoming bond dissociation energies.

Organic substances such as polymers are highly thermally sensitive due to the strength of the covalent bonds that make up their structures. Scission can occur either randomly or by a chain-end process, often referred to as an unzipping reaction. The thermal degradation of BMI is caused by the cleavage of the C-C linkage close to maleimide ring because alkylene linkages are least stable linking units compared with other groups such as -O-, -S- and -CO- [16].

For the same weight of A-BMI sample, the number of the weak C-C bonds close to the maleimide ring proportionally decreased in the cured A-BMIs as the length of the backbone chain of A-BMI increases. The number of weak bonds of A-BMI polymers decreased according to the following order: BMI-2 > BMI-3 > BMI-4 > BMI-5 > BMI-6 > BMI-7 > BMI-8. Thus, cured BMI-2 which has more weak bonds than those of the other cured A-BMIs is expected to have a lower thermal degradation temperature as can be observed in Figure 5.21. Therefore the degradation temperatures of A-BMI polymers

should increase according to the following order: BMI-2<BMI-3<BMI-4<BMI-5<BMI-6<BMI-7<BMI-8 and this general trend were observed for the data in the nitrogen environment from BMI-2 to BMI-6 (see Figure 5.26).

BMI-7 and BMI-8 showed lower degradation temperatures and this seeming discrepancy can be explained. It can be attributed to the fact that BMI-7 with odd-numbered carbon atoms has a loose packing whilst BMI-8 possessed a long flexible main chain. For the thermal degradation in air, it can be seen that BMI-3, BMI-5 and BMI-7 had a lower degradation temperature whereas BMI-2, BMI-4 and BMI-6 had a higher degradation temperature. The loose packing of BMI-3, BMI-5 and BMI-7 is probably responsible for their lower degradation temperatures. BMI-8 possesses a long flexible main chain which made it more susceptible to thermal degradation. A-BMI polymers have lower degradation temperatures than C-BMI because of the aromatic structure in the latter. The high thermal stability of aromatic structures contributes substantially to their high bond strength.

5.2.5 Glass transition temperature and CTE of A-BMI polymer

The glass transition temperatures (T_g) and coefficient of thermal expansion (CTE) of the cured bismaleimide resins were measured by TMA using a penetration probe. Figure 5.27 showed typical TMA plots of the various cured A-BMIs. The results are tabulated in

Table 5.12.

Figure 5.27 Effect of chain length on Tg

Tg for BMI-3 to BMI-8 varied from 413 to 392 °C, with a slight decrease as chain length increased. Tg was not observed for BMI-2 indicating that its glass transition temperature was above its decomposition temperature [102]. The Tg of A-BMIs appeared to be affected by the length of aliphatic main chain. It is known that Tg change depending on the mobility of polymer chains. A polymer chain that has greater mobility will have a lower Tg than those that has lower chain mobility. The more easily a polymer can move, the less heat it takes for the chains to commence wiggling and break out of the rigid glassy state into the soft rubbery state. The more flexible the backbone chain is, the easier the polymer will move, and the lower its Tg will be. A crosslink hinders the free rotation of end groups and thus, increases the glass transition temperature. The crosslink density of A-BMI decrease with the increase of the chain length. Therefore Tg of A-BMI

decreases with the increase of the aliphatic main chain length.

Table 5. 12 A-BMI polymers: Tg and CTE

	Tg (°C)	CTE (α_1) ($\mu\text{m}/\text{m}^\circ\text{C}$)	CTE (α_2) ($\mu\text{m}/\text{m}^\circ\text{C}$)
BMI-2	–	31.5	31.5
BMI-3	413	43.2	152
BMI-4	405	60.2	232
BMI-5	402	85	242
BMI-6	404	89.7	213
BMI-7	388	101	230
BMI-8	392	90.9	239
C-BMI	465	46	173

The CTE values below and above the Tg of the sample are defined as α_1 and α_2 respectively. The CTE values for A-BMI polymers increased significantly with chain length and increase substantially above their Tg.

Figure 5.28 The effect of chain length on Tg and CTE (α_1) of the A-BMI polymers

It is expected that the introduction of long chain between the two maleimide end groups will inevitably decrease the T_g and increase the thermal expansion coefficient and these are consistent with the general trend observed in Figure 5.28. The odd-even effect also affects the glass transition temperature as shown in Figure 5.28. CTE values increase as the number of CH_2 increases except BMI-8. A-BMIs with even number of CH_2 possess higher T_g values than the neighboring A-BMIs with odd number of CH_2 . Clearly, those A-BMI polymers with odd-numbered carbon atoms and were less packed had lower T_g .

Compared to A-BMI polymers, C-BMIs possess a higher T_g and a lower CTE. Because chain stiffness affects chain mobility such as the ease of rotation around the bonds of the polymer backbone, its effect on T_g is easily understood in a simple qualitative sense. If there are bulky groups, such as a benzene ring, in the backbone of the polymer chain, there is a high energy barrier to rotations which would occur at higher temperatures. Hence, it was not surprising that the T_g of C-BMI polymer was higher than those of the A-BMI polymers. Since the CTE is inversely proportional to the bond strength of the material [59], the C-BMI polymer with benzene ring was expected to have low thermal expansion coefficient and this is consistent with the result.

5.2.6 Dielectric properties of A-BMI polymers

Figures 5.29-32 showed the dielectric constant and dielectric loss plots for the various A-BMI samples. The following frequencies were applied to the resin during the analysis: 1, 10, 100, 1000, 10k and 100k Hz. Low frequency of 1 Hz and high frequency of 100k Hz

Chapter Five

Synthesis & properties of the A-BMI systems

were selected to analyze the frequency dependence of A-BMIs. The values of dielectric constants at 1 Hz and 100k Hz were tabulated in Table 5.13. Only the plot of the dielectric constant at 1Hz was shown in Figure 5.30 because the plot of the dielectric constant at 100 KHz is similar with the plot of the dielectric constants at 1Hz.

Figure 5.29 A typical dielectric constant plot of BMI-8

Table 5.13 Dielectric constant of A-BMI polymer

BMI	Dielectric constant (1 Hz /100KHz)							
	50 °C		100 °C		200 °C		275°C	
BMI-2	2.51	2.34	2.29	2.13	2.56	2.13	5.32	2.19
BMI-3	1.98	1.91	1.82	1.77	2.10	1.83	4.04	1.87
BMI-4	2.28	2.23	1.90	1.89	1.95	1.94	2.56	1.97
BMI-5	2.20	1.98	1.86	1.83	1.96	1.88	2.41	1.92
BMI-6	2.08	2.03	1.96	1.94	2.03	1.96	2.55	2.00
BMI-7	2.63	2.52	2.54	2.43	2.87	2.48	4.96	2.55
BMI-8	2.66	2.60	2.57	2.55	2.59	2.56	2.95	2.60
C-BMI	-	-	-	-	-	-	3.41	2.59

Figure 5.30 The effect of chain length on dielectric constant of A-BMIs at 1Hz

There is a big change for BMI-2, BMI-3 and BMI-7 between 1Hz and 100K Hz at 275°C. This variation in dielectric constant is attributed to the frequency dependence of the polarization mechanisms which comprise the dielectric constant. The magnitude of the dielectric constant is dependent upon the ability of the polarizable units in a polymer to orient fast enough to keep up with the oscillations of an alternating electric field. At optical frequencies (10^{14} Hz), only the lowest mass species are efficiently polarized. At lower frequencies, atomic polarization of heavier, more slowly moving nuclei also contribute to the dielectric constant. Atomic polarization of induced dipoles such as a carbonyl group can occur in the infrared (10^{12} Hz) or lower frequency regimes. Dipole polarization is the redistribution of charge when a group of atoms with a permanent dipole align in response to the electric field. In the solid state, alignment of

permanent dipoles requires considerably more time than electronic or atomic polarization, occur at microwave (10^9 Hz) or lower frequencies.

Because C-BMI specimen was very brittle and break easily at below 270°C, no data were collected below this temperature. It can be seen in Figure 5.30 that as the length of the main chain increases, the magnitude of the dielectric constant initially decreases, then remains constant before increasing.

In general, the dielectric constant increases with the polymer's polarity. Thus hydrocarbon polymers have values of 2-3, whilst polar polymers can have values of up to about 10 [64]. The incorporation of aliphatic groups is known to result in low dielectric constants because of low polarity and high hydrophobicity. Therefore, the polarity of A-BMI polymer is expected to decrease with increasing length of the CH₂ units along the main chain. The dielectric constants of A-BMI polymers are expected to decrease according to the following order: BMI-2>BMI-3>BMI-4>BMI-5>BMI-6>BMI-7>BMI-8. This is why BMI-2 has a higher dielectric constant than BMI-3, BMI-4, BMI-5 and BMI-6. BMI polymer's polarity is affected by the polarity of C=O bond. The C=O bond is not symmetrical and this polarization leaves a partial positive charge " δ^+ " on the carbon and a matching partial negative charge " δ^- " on the oxygen. The FTIR spectra shifting of C=O bond can occur when the electron density was added and extracted. From FTIR analysis in Section 5.2.1, the shift to lower frequency of the wave number implies a decrease of the strength. This indicates that the carbonyl becomes slightly more single

bond character and less polarization as chain length increase.

However, the dielectric constant of BMI-7 and BMI-8 were observed to be higher than that for BMI-2. This apparent discrepancy can probably be attributed to the fact that the dielectric constant of a polymer is also determined by the thermal motion of polar groups. The segmental mobility of polymer molecules affects the orientation polarization of the dipoles and hence affects the dielectric constant. In general, crosslinking of a polymer can hinder the orientation of the polar groups and thereby decrease the dielectric constant. The easier the polar group movement, the larger the dielectric constant [103]. In the case of the A-BMI's, the flexibility of the polymer increases with increasing length of the CH₂ units along the main chain. The polar maleimide end groups move more easily with increase in CH₂ chain length. Based on this effect, the dielectric constants of BMI-7 and BMI-8 would be larger than that of BMI-3, BMI-4, BMI-5 and BMI-6 which is in agreement with the data in Table 5.13. The above observations probably suggest that polarity has a larger effect on the dielectric constant of the A-BMIs when the number of CH₂ units in the main chain is small. However, at long chain length when the number of CH₂ units is large, main chain segmental mobility has a greater influence on the dielectric properties of the A-BMI.

A correlation between high free volume and low dielectric constant has been previously reported for polyimides [104]. The increase of the free volume in a polymer decreases the number of polarizable groups per unit volume. The addition

Chapter Five

Synthesis & properties of the A-BMI systems

of pendant groups, flexible bridging units, and bulky groups which limit chain packing density have all been used to enhance free volume in polyimides. Polarizability is the primary variable influencing dielectric constants whereas free volume is a secondary variable which can alter a polymer's polarizability. Enhanced free volume lowers polarization by decreasing the number of polarizable groups per unit volume. In summary, both the polarity and flexibility of molecule affect the magnitude of the dielectric constant.

It is also noted that the dielectric constants of BMI-3 and BMI 5 were slightly lower than that of BMI-4. From FITR analysis, it could be concluded that A-BMI with odd number of carbon atoms has a less polar effect (less packing density) than those with an even number of carbon atoms. The addition of flexible groups which reduces chain packing density to enhance free volume decreases the number of polarizable groups per unit volume. The polarity of BMI-3 and BMI-5 decreases thus resulting in the dielectric constant.

The dielectric constant of C-BMI at 275°C (1 Hz) is 3.4, which is higher than those of BMI-4, BMI-5 and BMI-6 polymers (around 2.5) but lower than those of BMI-2, BMI-3, BMI-7 polymers (around 4~5). According to the Clausius-Mossotti equation mentioned in Chapter 2 (Section 2.2.3), it is clear that C-BMI should have a higher dielectric constant than those of A-BMI polymers and this is consistent with the result for some of the A-BMIs. At 275 °C (See Table 5.13) it can be seen that, C-BMI has a higher

dielectric constant than those of BMI-3 and BMI-7 at a frequency of 100K Hz. However, C-BMI has a lower dielectric constant than BMI-3, BMI-7 at frequency of 1 Hz. This variation in dielectric constant at a different frequency can be attributed to the frequency dependence of the polarization mechanisms. If the frequency is very large, there is no response to a high frequency field. The magnitude of the dielectric constant is dependent upon the ability of the polarizable units to respond fast enough to keep up with the oscillations of an alternating electric field. The results probably suggested at 275°C and 1 Hz the polarizable units of BMI-3 and BMI-7 could respond fast enough but that C-BMI which has a benzene ring responded slower. From Table 5.13, it can be seen that A-BMI which has lower dielectric constant than C-BMI has been successfully synthesized.

Figure 5.31 A typical dielectric relaxation plot of BMI-4

Figure 5.31 show the dielectric relaxation plot of BMI-4. At low frequencies (1 and 10 Hz), the β and γ transitions were observed and the α transition could not be observed. At

Chapter Five**Synthesis & properties of the A-BMI systems**

high frequencies (100 to 100k Hz), only the γ transition was observed.

Dielectric relaxation spectrum reflects the motion state of the segments, or group of segments. In the solid state, alignment of permanent dipoles (bigger movement unit) requires considerably more time than electronic or atomic polarization. The response to a field will depend on the frequency of the electrical field. If the frequency is very large, there is no response to a high frequency field. For this reason, the α transition (bigger kinetic unit) of A-BMI can not be seen in Figure 5.31. This is why only the two transitions β and γ peaks are clearly observed at low frequency in Figure 5.26. The data were tabulated in Table 5.14.

Table 5.14 Dielectric loss peak of A-BMI polymer

A-BMI	Dielectric loss peaks		
	β °C (1 Hz)	γ °C (1 Hz)	γ °C (100 kHz)
BMI-2	18	-113	2.5
BMI-3	15	-108	5.4
BMI-4	8.3	-102	-8
BMI-5	6.8	-95	-9.8
BMI-6	5.8	-92	-10.4
BMI-7	6.3	-81	7.3
BMI-8	-0.6	-78	7.3

To directly compare the results between samples, a single defined frequency was chosen. The β transition of A-BMI at higher frequencies (i.e. 100 Hz-100K Hz) can not be observed. Figure 5.32 is the dielectric loss data at 1Hz. Figure 5.32 shows that the

relaxation transition temperature was relatively sensitive to the length of the main chain. The β transition temperature decreased as the length of the main chain increased. In contrast, the γ transition temperature increased as the length of the main chain increased. The γ transitions were located in the -80 to -120°C range. These γ transitions can probably be attributed to local segmental motion of CH₂ [59,69-71]. The γ transition also follows the odd-even effect and γ transition with an odd number of carbon atoms appeared to shift to higher temperatures. The γ transition was affected by the main chain length and shifted to higher temperatures when the chain length was increased.

Figure 5.32 The effect of chain length on the dielectric loss of A-BMI at 1 Hz

Because the polymer can be considered as a series of kinetic units; each of these moves in an independent manner and involves the cooperative movement of a number of consecutive chain atoms. Some vibration modes depend on chain length, especially for

short chains; some vibration modes are independent of chain length. When the motional unit is smaller or the motional pattern is simpler, the temperature of the loss peak was expected to be smaller and the loss peak shifts to a lower temperature.

In this study, the γ transition depends on chain length and possesses a different motional unit (for BMI-2, with one and two-bond motions, for BMI-8, with three-bond motions), and motional pattern (odd even effect). This follows that crankshaft motion involving 4-6 carbon atoms has three different kinds of kinetic models [59,71]. Such crankshaft motion in polymers has been seen in polyethylene. According to Ronald [105], the three-bond rotation and crankshaft motion are labeled as the so-called type I motion, while both the one and two-bond motions are grouped in his type III motion. The type II motion does not swing the chain but the chain does translate. Now the type I motion should call for high activation energies, because several bonds must be activated almost simultaneously. Jelinski observed two different deuterium NMR spectra of PBT, which indicates the predominant mechanism is the three bond motion in PBT polymer [106].

From Figure 5.32, it was observed that the γ transition shifts to high temperature with increasing chain length. One and two-bond motions can be observed at low temperatures and three-bond motions call for high activation energies to be observed at high temperatures. It was deduced that BMI-2, BMI-3 and BMI-4 with one and two-bond motions show the γ transition at lower temperatures and BMI-5, BMI-6, BMI-7 and BMI-8 with three-bond motions show the γ transition at higher temperatures. Namgoong [106]

analyzed the local motion of the methylene sequence based on the three-bond motion, concluding that the central methylene carbons are more mobile than the terminal methylene carbons in a solid-state polymer. Therefore, γ transition shifts to higher temperature with increasing chain length.

The γ transition also has an odd-even effect as shown in Figure 5.32. The chains with an odd number of carbon atoms possess a higher γ transition temperature and thereby have a larger motion space for the certain motional pattern. This is in accordance with those polymers with odd number of carbon atoms are loosely packed [107]. Polymers with an even number of methylene spacers possess planar zigzag packing of the methylene chain while polymers with an odd number of methylene spacers possess non-planar zigzag packing [92]. The planar zigzag conformation is produced by all trans states which is in a minimum energy state. The planar zigzag conformation which seems to offer minimum intramolecular interaction results in a compact molecule, which allows efficient molecular packing. In other words, the A-BMIs with odd number of carbon atoms possess a less intramolecular interaction. So crankshaft motion occurs and the end-groups move more in the A-BMIs with odd number of carbon atoms. Therefore, the A-BMIs with odd number of carbon atoms possess a higher γ transition temperature.

The β transition peaks located in the 0~20°C range have been attributed to the motion of carbonyl C=O [69,70,108]. In the present work, it has been shown that as the main chain

length increase, the flexibility of main chain increases so that the β transitions shift to lower temperature.

5.2.7 Tensile properties of A-BMI polymers

Figure 5.33 A typical stress-strain curve of BMI-8 polymer

Table 5.15: Summary of tensile properties of A-BMI polymers

	Tensile stress (MPa)	Strain at break (%)	E (GPa)
BMI-2	18 $\pm$ 4	2.2 $\pm$ 0.4	0.82
BMI-3	12 $\pm$ 3	2.1 $\pm$ 0.4	0.63
BMI-4	31 $\pm$ 6	3.8 $\pm$ 0.8	1.05
BMI-5	17 $\pm$ 4	2.2 $\pm$ 0.4	0.78
BMI-6	27 $\pm$ 4	3.7 $\pm$ 0.8	0.85
BMI-7	15 $\pm$ 3	2.6 $\pm$ 0.6	0.63
BMI-8	22 $\pm$ 4	3.2 $\pm$ 0.7	0.85

This section summarizes the effect of the molecular structure on the tensile properties of various samples. Figure 5.33 shows a typical stress-strain curve of the pure BMI-8

specimen. The tensile modulus of the sample was calculated from the slope of the linear portion of the stress-strain curve. Table 5.15 shows the results obtained from tensile tests.

Figure 5.34 The effect of chain length on tensile properties of A-BMI polymers

Figure 5.35 Effect of chain length on the tensile strengths of A-BMI polymers

From Figure 5.34 and Figure 5.35, it is interesting to observe that tensile stress initially

Chapter Five

Synthesis & properties of the A-BMI systems

increased with increasing carbon chain length before it decreased. From Table 5.15, it can be seen that the strain and the modulus also follow this trend. From the previous T_g analysis, T_g increased as the chain length decreased, because molecular weight affects the T_g [52]. As the molecular weight of the monomer decreases, the crosslink density of the cured polymer increases and the T_g increases for materials having similar chemical structures. This can be seen with the products that have very similar structure in the backbone, but vary in molecular weight. Therefore, the crosslink density of A-BMI polymers is expected to increase according the following order: BMI-8, BMI-6, BMI-4, BMI-2 (Even C atoms of A-BMIs) and BMI-7, BMI-5, BMI-3 (Odd C atoms of A-BMIs).

For thermoset materials, polymers with very high levels of crosslinking will lead to brittleness and thereby decrease the tensile strength. An increase in the crosslink density initially increases the tensile strength, but beyond a maximum value the tensile strength subsequently decreases [55]. As the crosslink density increases in a polymer, there is a decrease in the segmental mobility and flexibility of the polymer chains themselves. Thus, the polymer chains are less able to move freely and rotate in the network. So, as the degree of crosslinking increase, the polymer chains would be less able to align themselves in a conformation. High crosslinking density reduces the number of conformations that the polymer can adopt upon being loaded and the polymer would be more brittle but would have higher strength and modulus. Therefore the observed general trend of enhancement in stress and strain as well as modulus with chain length in the A-

BMIs (see Figure 5.35) could be due to increased crosslink density.

From Figure 5.35, it can be seen that BMI-6 and BMI-8 have lower tensile strength than that of BMI-4. Similarly, BMI-7 has lower tensile strength than that of BMI-5, because an increase in the crosslink density initially increases the tensile strength. From the previous T_g analysis, BMI-4 with higher T_g should have higher crosslinking density than BMI-6 and BMI-8 whilst BMI-5 should have a higher crosslinking density than BMI-7. Therefore, BMI-4 and BMI-5 have biggest tensile strengths. After the tensile strength reaches the maximum (BMI-4 and BMI-5), the elongation at break and the tensile strength of BMI-2 and BMI-3 both decrease due to increase of the crosslink density. BMI-2 and BMI-3 with highest crosslinking densities and short chains show the system is highly restricted to move so that the elongation, the strength and Young's modulus of crosslinking networks are drastically reduced. The tensile strength of C-BMI polymer is 12 MPa as reported [49,109]. Because the high crosslink density and two rigid benzene rings of the C-BMI polymer leads to a decrease in the segmental mobility and flexibility of the polymer chains themselves. Therefore, the tensile strength of C-BMI is low.

It can be observed from Figure 5.33 that the A-BMIs exhibit brittle behavior and do not yield and flow before fracture. The changes in stress, strain and modulus follow the odd-even effect as shown in Figure 5.34. A-BMIs with even number of C atoms have higher values in stress, strain and modulus than those of A-BMIs with odd number of C atoms. Bunn reported [93] the odd even effect of polymers with the dipolar end groups. The

interaction of the dipolar groups may stiffen the even numbered molecules and therefore give this configuration additional stability. For odd ones the dipoles would be parallel and therefore would repel each other to increase the flexibility, decreasing the stability of the zigzag configuration. This is in agreement with the observed phenomenon above.

The mechanical property is governed by the intermolecular forces and crosslinking density of the thermoset polymers. The higher the chain interaction, the higher the mechanical strength of polymer. The intermolecular forces for thermoset polymers are determined by the molecular polarity. If polymers have low polarity, then the intermolecular force is low. From DEA analysis, A-BMI polymers with odd-numbered carbon atoms have smaller polarity than those of A-BMI polymers with even ones. It can be concluded that A-BMI monomers with odd-numbered carbon atoms have smaller intermolecular forces than those of A-BMI monomers with even ones. Therefore, an even number of carbons on the main chain may increase intermolecular forces hence higher values in stress, strain and modulus are observed.

5.2.8 Moisture absorption of A-BMI polymers

It is well-known that moisture induces property changes in polymers. Most polymers absorb some water. Moisture absorption will increase an encapsulation material's dielectric constant. Thus, lower moisture absorption is good for encapsulation materials. Table 5.16 shows the results obtained from moisture testing of the A-BMI samples.

Table 5.16 The effect of chain length on moisture absorption of A-BMIs

BMI	BMI-2	BMI-3	BMI-4	BMI-5	BMI-6	BMI-7	BMI-8	C-BMI
Moisture absorption (%)	8.7±0.5	8.8±0.5	7.1±0.5	6.6±0.4	6.6±0.4	5.3±0.3	4.6±0.2	4.8±0.2

Figure 5.36 Effect of chain length on the moisture absorption of A-BMI polymers

Figure 5.36 shows that moisture absorption of A-BMIs decreased as the chain length increased. The moisture absorption of A-BMIs to be divided by the number of CH₂ hydrophobic group also decreased as the chain length increased. Polymer chains with strong polar groups are able to bind water by hydrogen bridges. Some examples are the ketone group (C=O) or the sulphone group (O=S=O) and nitrogen. Imide (-CO-NH-CO-)

Chapter Five***Synthesis & properties of the A-BMI systems***

moieties in bismaleimide are polar groups. These characteristic polar groups contain nitrogen and oxygen as potential proton acceptors to form hydrogen complexes. Water molecules close to polar groups should be able to form hydrogen-bonded complexes with nitrogen and oxygen. The amount of water molecules to be absorbed is dependent on the amount of the polar groups in the certain weight of A-BMI. Table 5.17 shows the molar mass of A-BMIs.

Table 5.17 The molar mass of BMIs

BMI	BMI-2	BMI-3	BMI-4	BMI-5	BMI-6	BMI-7	BMI-8	C-BMI
Molar mass	220.18	234.21	248.23	262.26	276.29	290.32	304.34	358.36

For a given weight of A-BMIs sample, the amount of the polar groups in A-BMIs should decrease as the main chain length increase. Therefore, moisture absorption of A-BMIs decreases with the chain length increase. This is in agreement with the experimental data in Figure 5.36. The decreasing moisture absorption may be also attributed to more moisture repulsive methylene group with chain length increase. C-BMI has lower moisture absorption because of its higher molar mass (shown in Table 5.17) to result in less amount of imide group than those of A-BMIs.

5.3 Summary

A-BMI system was synthesized and characterized. BMI-6 has the best characteristics and properties for use as a polymer for electronics packaging. Dielectric materials must possess a number of important properties. They should retain a low dielectric constant over a wide range of frequencies, be thermally stable, have an adequate glass transition temperature and a low coefficient of thermal expansion (CTE), possess low modulus, high elongation at break and low water absorption.

BMI-6 possesses a low dielectric constant around 2.0 over a very wide frequency range (from 1Hz to 100k Hz) and wide temperature range (from 50 °C to 275 °C). In addition, BMI-6 provides good thermal stability. Its degradation temperature is up to 460 °C in air and in nitrogen. Its glass transition temperature is very high up to 404 °C and CTE is moderate at 89.7 $\mu\text{m}/\text{m}^\circ\text{C}$. Flexible methylene group and loose chain packing are two factors that result in a moderate CTE. Alternatively, a lower modulus will reduce overall stress caused by thermal mismatch. BMI-6 possesses low modulus at 0.85 GPa and moderate elongation at break around 3.7%. Compared to other A-BMI, BMI-6 is attractive with respect to low water uptake. Thus, BMI-6 is a good candidate for use as electronics packaging material. However, its toughness has to be improved further.

Chapter 6 Synthesis and properties of the O-BMI systems

6.1 Phase (I): Synthesis of the O-BMI systems

The structures of the O-BMI synthesized were analyzed by FTIR and NMR. The NMR analysis is shown in a later part of this section. The typical FTIR spectrum was shown in Figure 6.1: the vibrations of carbonyl (C=O) absorption at 1710 cm^{-1} , ($-\text{CH}_2-$) bands between 2880 cm^{-1} and 2980 cm^{-1} , C=C-H of maleimide ring at 3100 cm^{-1} , 830 cm^{-1} , 695 cm^{-1} , -O- bond at 1111 cm^{-1} .

Figure 6.1 FTIR spectrum of a typical O-BMI (BMI-230B) monomer

The chemical structure of bismaleamic acid and bismaleimide was characterized using

Chapter Six**Synthesis & properties of the O-BMI systems**

FTIR. Since the (-CH₂-) absorption peaks between 2960 cm⁻¹ and 2850 cm⁻¹ was not changed and they were used as the internal reference peak to normalize N-H absorbance at 1530±10 cm⁻¹ (formation of BMA) and C-N-C absorbance at 1123±10 cm⁻¹ (formation of BMI). The plots of percentage conversion versus time to form a bismaleamic acid (BMA) and BMI were shown in Appendix II. The reaction times to form BMA and O-BMIs are listed in Table 6.1.

Table 6. 1 The effect of diamine chain length on the formation of O-BMA & O-BMI

	230B	400B	600	900	2000	2000B	4000B
O-BMA (mins)	100	90	60	60	60	60	60
O-BMI (hrs)	8	4	2	2	2	2	2

The reaction curves stabilized after 1 to 2 hrs for BMA formation and after 2 to 8 hours for O-BMI formation. The reaction times to form BMA and BMI with side group CH₃ (230B, 400B, 2000B, 4000B) were significantly affected by the length of the backbone chain. It is possible that the steric effect of CH₃ branch had affected the reactivity. The reaction times to form BMA and BMI without the CH₃ side group (600, 900, 2000) were not affected by the length of the backbone chain.

Table 6. 2 Comparison about the yield of O-BMIs

O-BMI	230B	400B	600	900	2000	2000B	4000B
Yield (%)	68.6	70.7	71	67	71.4	73	64

Chapter Six***Synthesis & properties of the O-BMI systems***

The yield of O-BMI was tabulated in Table 6.2. The yield of O-BMIs also is not so high, the possible reason has been analyzed in the section of synthesis of A-BMI.

The structures of O-BMIs were also confirmed by Bruker 500MHz NMR. The ^1H NMR (CDCl_3) spectrum (Figure 6.2) shows a sharp band for BMI-230B at 6.7 ppm (4H, CH=CH) due to the proton of the double bond.

Figure 6.2 ^1H NMR spectrum of BMI-230B

6.2 Phase (II): Characterization of the O-BMI systems

6.2.1 FTIR analyses of O-BMI monomers

Figure 6.3 show the frequency shift of C=C in O-BMI monomers based on their FTIR spectra. In general, electron withdrawing substituents reduce the electron density at the double bond. The C=C double bond in the maleimide ring is electron-poor due to the presence of two adjacent carbonyl groups, which are the strong electron-withdrawing groups. Comparing the frequency of C=C groups of O-BMIs, the frequency of the C=C double bond decreased as the backbone chain length increased. If the electron density of C=C double bond could decrease, the wave number of C=C group shifts to lower frequency [110]. So the double bond with smaller wave number indicated that the double bond had less electron density. The more electron-poor C=C double bond, the more reactive the C=C double bond [32]. So the O-BMI monomers in figure 6.3 which have a longer main chain would be expected to be more reactive.

Figure 6.3 Effect of chain length on the frequency shift of C=C in O-BMIs

6.2.2 Thermal curing of O-BMI monomers

The thermal behavior of all the O-BMI samples was investigated by differential scanning calorimetry (DSC) in N₂ atmosphere at a heating rate of 10°C/min.

Figure 6.4 The typical heat curing of BMI-400B

From Figure 6.4, it can be seen that one exothermic peak was observed in the high temperature region. No endothermic peak was observed for all O-BMI monomers. The endothermic peaks can be related to the melting for the solid and be related to the vaporization for the liquid. O-BMI monomers are liquid at room temperature. The absence of any endothermic peak indicated that there was no loss of volatiles. The curing onset temperature (T_o), the peak curing temperature (T_p) and reaction enthalpy are tabulated in Table 6.3. Figure 6.5 shows the variation of the curing temperature and

curing heat with chain length of O-BMI monomers.

Table 6.3 The curing temperatures and curing heat of O-BMI monomers

	To (°C) (onset cure)	Tp (°C) (cure peak)	-ΔH (J/g)	-ΔH (kJ/mol)
BMI-230B	280	306	170	66
BMI-400B	244	277	159	89
BMI-2000B	239	273	49	106
BMI-4000B	80	268	27	112
BMI-600	253	289	139	106
BMI-900	250	277	115	122
BMI-2000	188	234	86	186

Figure 6.5 Effect of chain length on the curing temperatures of O-BMIs

The data show that as the chain length increased, the onset curing temperature, curing peak temperature and curing heat of BMI all decreased. The BMI-230B, BMI-400B, BMI-2000B, BMI-4000B with methyl branch and the BMI-600, BMI-900 and BMI-2000 without methyl branch share a similar trend. The above indicated that the backbone chain length significantly affected the reactivity of double bonds of O-BMI monomers. Although the relative amount of function group decreased as chain length increased, the reactivity of O-BMI monomers [13,100] increased due to three factors, namely: (a) the inductive (polar) effect of the bridging unit on maleimide reactivity, which has been discussed in the FTIR analysis in section. 6.2.1. (b) the mobility of the oligomeric molecules up to the point when they become attached to the network, (the mobility of the unreacted monomers increases a lot because more flexible group -O- was involved in them with the increasing chain length resulting in an increase in the reactivity) and (c) the thermodynamic effect (activation energy). Heuts [34] reported that an approximate linear relationship exists between the activation energy, E_{act} , and reaction enthalpy, ΔH_r . For O-BMI monomers, their reaction enthalpies increased as the length of main chain increased, so their activation energies would increase as the length of main chain increased. But this conclusion is direct contradiction regarding curing temperature. Therefore, this approximate linear relationship is not suitable for estimating the activation energy of O-BMI monomer. From section 6.2.1, the O-BMI monomers which have a longer main chain would be expected to be more reactive, so the curing temperature increased with increasing chain length. Meanwhile, because the amount of reactant function group decreased as the chain length increased, the curing heat per gram decreased.

DSC was also used to measure the kinetics of the curing reaction. Figure 6.6 show the typical graph of curing kinetics. The details were tabulated in Table 6.4. The results show that the curing times for BMI-230B, 400B, 2000B, 4000B with methyl side group and for the BMI-600, 900, 2000 without methyl side group decreased as main chain length increased. This is in accordance with the fact that the reactivity of O-BMI monomers was affected by the length of main chain as stated above. Because the O-BMI monomers with longer length of main chain possess higher reactivity, so the curing times decreased as the length of main chain increased. Table 6.4 shows the curing time to 99.9% conversion at the temperature of 230°C.

Figure 6.6 the typical curing kinetics of the BMI-400B

In the DSC experiments where only a small amount of sample was used, the heat transfer was efficient and uniform. In order to ensure full curing in the larger specimen, at curing time of 10 hours at the temperature of 230°C were used to cure the O-BMIs. This curing

time was selected based on that reported [15] in literature for other BMIs.

Table 6.4 Effect of chain length on the curing time at the temperature of 230°C

O-BMI	230B	400B	2000B	4000B	600	900	2000
Time (hours)	7	3	2	3	7	4	1

6.2.3 Gel Points of O-BMI monomers

Table 6.5 Gel time and temperature of O-BMI monomers

	Gel time (s)	Gel temperature (°C)
BMI-230B	900	260
BMI-400B	700	250
BMI-600	500	250
BMI-900	450	240
BMI-2000	100	180
BMI-2000B	50	200
BMI-4000B	-	100
C-BMI	150	215

The gel temperatures and gel times as shown in Table 6.5 and Figure 6.7 respectively were found to decrease with increasing chain length of BMI monomer. Although the concentration of reactant function group decreased with increasing chain length, three

factors are responsible for the increase in the reactivity of the O-BMI monomers [13,103] as discussed in DSC analysis section: (a) the inductive (polar) effect of the bridging unit on maleimide reactivity, (b) the mobility of the oligomeric molecules up to the point when they become attached to the network, and (c) the thermodynamic effect [34]. Therefore, O-BMI monomers with longer chain possess higher reactivity resulting in a decrease in the gel temperatures and gel times.

Figure 6.7 Effect of chain length on gel temperature and gel time of O-BMIs

6.2.4 TGA analyses of O-BMI polymers

Figure 6.8 showed a typical TGA plot of a cured BMI in dry air and in pure nitrogen. Other samples showed similar plots. Data were tabulated in Table 6.6. All the O-BMI systems showed a decrease in onset temperature of degradation in dry air and in pure nitrogen as the chain length increased. Thus, increasing the number of aliphatic C atoms

on the backbone chain appeared to lower the thermal stability. The decomposition temperatures of O-BMI polymers in nitrogen were higher than those of O-BMI polymers in air. This implies that the O-BMI polymers were sensitive to thermo-oxidative degradation. The 10% decomposition temperature of polymers, ranged between 290-370°C, in nitrogen and in air are shown in Figure 6.9.

Figure 6.8 Typical TGA thermograph on cured BMI-230B

Heating a polymer to about 200-400°C will cause thermal vibrations of the molecule resulting in bond scission. This results in thermal degradation of the polymer. The breaking of chemical bonds under the influence of heat is the result of overcoming bond dissociation energies. Scission can occur either randomly or by a chain-end process. Most thermal degradation of polymers is by random scission, which separate rapidly. The longer the length of main chain, the larger the probability of random scission. Therefore,

as the length of main chain increases, the thermal degradation temperatures of O-BMI polymers decreases. This is consistent with the general trend observed in Table 6.6 and Figure 6.9. It is well known that the presence of oxygen traces in polymer decomposition has a catalyst or initiator role in thermal or thermo-oxidative decomposition. Introduction of ether group and long chain into two maleimide groups would decrease its crosslink density and increase free volume of the cured sample, thus increase the thermal expansion coefficient. Because crosslinking restrict the diffusion of oxygen, as the length of main chain increases, the crosslinking density of O-BMI polymers decrease, so O-BMI polymers with longer chain is easier for oxygen to diffuse. Therefore, the degradation temperatures of O-BMI polymers in nitrogen are larger than those in air.

Table 6.6 Comparison of O-BMIs: weight loss temperature and decomposition

	Temperature (°C)			
	In air		In nitrogen	
	T _d	T _{10%}	T _d	T _{10%}
BMI-230B	393±3	371±3	393±3	372±3
BMI-400B	361±3	357±3	364±3	359±3
BMI-600	298±3	317±3	318±3	324±3
BMI-900	300±3	312±3	316±3	322±3
BMI-2000B	317±3	285±3	335±3	328±3
BMI-2000	285±3	293±3	328±3	329±3
BMI-4000B	287±3	298±3	342±3	328±3

Note: T_{10%} : the temperature at which 10% of weight has been lost.

Figure 6.9 Effect of chain length on the decomposition temperature of O-BMIs

6.2.5 TMA analyses of O-BMI polymers

TMA was used to measure the glass transition temperature and CTE and the results were listed in Table 6.7. Because the cured BMI-2000B and 4000B were in a tacky state, they could not be tested. Figure 6.10 shows the effect of chain length on T_g and CTE of O-BMI polymers.

Table 6.7 T_g and CTE of the O-BMI polymer

	T_g (°C)	CTE(α_1) ($\mu\text{m}/\text{m}^\circ\text{C}$)	CTE(α_2) ($\mu\text{m}/\text{m}^\circ\text{C}$)
BMI-230B	148	82	164
BMI-400B	79	92	188
BMI-600	53	95	218
BMI-900	44	125	211
BMI-2000	24	140	919

Figure 6.10 Effect of chain length on Tg and CTE of O-BMI polymers

It was observed that the glass transition temperature decreased and CTE increased with the chain length increase. The presence of crosslinks between chains restricts rotational motion and raises Tg. As crosslinks increase, the polymer chains are less able to align themselves in a conformation. The polymer chains are less able to move freely and rotate in the network. The higher the crosslink density, the higher the glass transition temperature of polymer. Introduction of ether group and long chain into two maleimide groups would decrease its crosslink density and increase free volume of the cured sample, thus decrease the Tg and increase the thermal expansion coefficient. Therefore, the glass transition temperatures of O-BMI polymers decrease with the length of main chain increase.

6.2.6 Dielectric properties of O-BMI polymers

Figure 6.11 A typical plot of dielectric constant of BMI-230B

Figure 6.12 a typical dielectric relaxation plot of BMI-600

Figures 6.11 and 6.12 show the dielectric constant and dielectric loss ($\tan \delta$) for the various O-BMI polymers. The following frequencies were applied: 1, 10, 100, 1000, 10000 and 100000 Hz. At lower frequency (1, 100 and 1k Hz), α and β transitions were observed, γ transition could not be observed. At higher frequency (1k to 100k Hz), only β transition was observed. The response to a field will depend on the frequency of the electrical field. If the frequency is very high, there is no response to a high frequency field. Hence α transition of O-BMI at high frequency (1k to 100k Hz) can not be seen in Figure 6.12. Table 6.8 shows the dielectric constants of O-BMI polymers.

Table 6.8 Dielectric constant of O-BMI polymer

BMI	Dielectric constant (100 kHz)				
	-50 °C	0 °C	50 °C	100 °C	200 °C
BMI-230B	2.62	2.91	2.98	2.82	3.03
BMI-400B	2.66	2.95	3.15	3.33	3.84
BMI-600	2.52	2.9	3.03	3.13	3.84
BMI-900	2.57	3.22	3.58	3.57	4.01
BMI-2000B	2.5	4.2	4.34	4.07	3.63
BMI-2000	2.66	4.13	6.22	5.74	5.03
BMI-4000B	2.3	4.4	2.66	2.41	2.65

Dielectric spectroscopy is sensitive to fluctuations of dipole moments. The comparative data shows that the magnitude of the dielectric constant is very dependent on the concentration of aliphatic-ether in O-BMI polymers. As the amount of aliphatic-ether group increases, the magnitude of the dielectric constant increases at the temperatures

between 0°C and 200°C except for BMI-4000B as shown in Figure 6.13.

Figure 6.13 Effect of chain length on dielectric constants of O-BMI polymers

However, at -50°C there is no significant change in the magnitude of the dielectric constant as the chain length increases. Polymers that have polar bonds in their chains would be expected to have high dielectric constants. The dielectric constant of a polymer is also determined by the thermal motion of polar groups. The easier the orientation of the polar groups, the greater its dielectric constant will be. In the case of the O-BMIs, increasing the amount of aliphatic ether would increase the polarity because aliphatic ether is a polar group. Hence, as the aliphatic ether group was increased, there would be an increase in the segmental mobility and flexibility of the polymer chains. Therefore, the dielectric constant of the O-BMIs at the temperatures between 0°C and 200°C would increase with the main chain length as can be observed in Figure 6.13. BMI-2000 with more aliphatic ether has much higher dielectric constants. BMI-2000B at 50°C has an anomalously higher dielectric constant than that at 100 and 200°C (100 KHz). BMI-2000

and BMI-4000B also have this phenomenon. This anomalous variation in dielectric constant at different temperature can probably be attributed to the temperature dependence of the polarization mechanisms. The magnitude of the dielectric constant is dependent upon the ability of the polarizable units to respond fast enough to keep up with the oscillations of an alternating electric field. The shifts in the dielectric properties with temperature may give rise to maxima in the temperature behavior at constant frequency.

Although BMI-4000B has more aliphatic ether, possibly, its free volume makes the nominal polarity less. Therefore, its lower nominal polarity leads to a lower dielectric constant. A correlation of high free volume and low dielectric constant has been previously reported for polyimides [104]. The introduction of free volume in a polymer decreases the number of polarizable groups per unit volume resulting in lower values for dielectric constant. The addition of pendant groups, flexible bridging units, and bulky groups which limit chain packing density have all been used to enhance free volume in polyimides and are used in this study to examine their effect on dielectric constant. The BMI-4000B polymer has a large free volume due to the pendant -CH₃ groups. In addition, the large pendant -CH₃ groups increase the free volume fraction in the polymer essentially reducing the number of polarizable groups in a unit volume. Therefore, it is not surprising to observe the large reduction in dielectric constant in BMI-4000B.

A dielectric relaxation spectrum reflects the motion state of the segments, or group of segments. Dielectric relaxation is also known as dielectric dispersion and dielectric loss.

Dielectric loss is caused by the lag in dipole orientation behind an alternating electric field. When the polar molecules are very large, or the frequency of alternating field is very high, the rotary motion of the molecules is not sufficiently rapid for the attainment of equilibrium with the field. Dielectric losses will then be generated. From a structural point of view, the dielectric relaxation is orientation polarization, which depends on the internal structures of the molecules and on the molecular arrangement. Most polymers exhibit more than one region of dielectric loss. The largest loss peak (α peak) usually occurs at the high temperature and is associated with the glass transition. The other loss peaks (β , γ peak) may occur in the glassy state and is associated with shorter range motions such as side-group rotations or local mode motions [18].

Table 6.9 Dielectric loss peak of O-BMI polymer

O-BMI	Dielectric loss peaks		
	α °C (1 Hz)	β °C (1 Hz)	β °C (100 kHz)
BMI-230B	267	-101	-10
BMI-400B	161	-93	-11
BMI-2000B	28	-53	-23
BMI-4000B	45	-27	11
BMI-600	82	-88	-33
BMI-900	19	-93	-15
BMI-2000	-6.9	-90	-37

Figure 6.14 Effect of chain length on the dielectric relaxation of O-BMI polymers

The dielectric loss data in Figure 6.12 revealed that, at the lower frequencies, the α and β peaks were clearly observed. These transitions were frequency dependent (which is due to the effects of the molecular dipoles) and shifted to higher temperatures as the measurement frequency was increased. To directly compare results between samples, therefore, a single defined frequency was chosen. Table 6.9 is the comparative data at 1Hz and 100 kHz. The comparative data shows that the relaxation transition temperature was relatively sensitive to the content of aliphatic ether in the chain. From Figure 6.14, the α transition (T_g) decreased as the amount of aliphatic ether increased probably because aliphatic ether is a flexible group. The value of T_g depends on the mobility of the polymer chain - the more immobile the chain, the higher the value of T_g . In particular, anything that restricts rotational motion within the chain should raise T_g . Therefore, the α

transition (T_g) decreases with the increasing amount of aliphatic ether chain.

A very broad relaxation peak called β transition is located in the -80°C to -100°C range. It was reported that the kinetic unit of $-\text{CH}_2\text{CH}_2\text{O}-$ in PET could vibrate locally at temperature of -63°C to 160°C [67]. This β transition can probably be attributed to local segmental motion of $-\text{CH}_2\text{CH}_2\text{O}-$ or $-\text{CH}(\text{CH}_3)\text{CH}_2\text{O}-$. The β transition temperatures of BMI-230B, 400B, 2000B and BMI-4000B appear to be affected by the methyl side group and backbone chain length. But BMI-600, BMI-900 and BMI-2000 show no significant difference in the β transition temperatures. Below T_g , the motion of these individual chains segments becomes frozen with only a small scale molecular motion remaining, involving individual or small groups of atoms. It is possible that the $-\text{CH}_2\text{CH}_2\text{O}-$ group is the basic kinetic unit in the main chain of BMI-600, BMI-900 and BMI-2000. At very low temperatures, only this group can move [67]. Therefore, the β transition temperatures of BMI-600, BMI-900 and BMI-2000 are nearly the same. However the $-\text{CH}(\text{CH}_3)\text{CH}_2\text{O}-$ group may be the basic kinetic unit in the main chain of BMI-230B, BMI-400B, BMI-2000B and BMI-4000B. It is well known that pendant groups have a big effect on chain mobility. Even a small pendant group (CH_3) can act as a fish hook that will catch on any nearby molecule when the polymer chain tries to move like corkscrew. Pendant groups also catch on each other when chains try to slither by each other. As length of the main chain of the O-BMI is increased, more pendant methyl groups can act together to cause a higher steric effect on chain mobility. This probably explains why the β transition

temperatures of BMI-230B, BMI-400B, BMI-2000B and BMI-4000B shifted to high temperatures as the length of main chain was increased.

6.2.7 Tensile properties of O-BMI polymers

Only tensile samples of BMI-230B and BMI-400B could be tested. The samples from BMI-600, BMI-900 and BMI-2000 polymers were too soft and broke very easily when the test samples were fixed for testing. Test samples of BMI-2000B and BMI-4000B were in a tacky state and could not be tested. Figure 6.15 and Figure 6.16 show the stress-strain curves of BMI-230B and BMI-400B. The data are listed in Table 6.10.

Table 6.10: Summary of tensile properties of O-BMI polymers

	Stress (MPa)	Strain (%)	E (GPa)
BMI-230B	34.9	4.5	0.98
BMI-400B	8.2	8.2	0.27

BMI-230B has higher failure stress and lower strain to failure values than those of BMI-400B. Actually, BMI-400B has changed to a tough material, which has a low stress and high strain value. This is attributed to crosslink density. An increase in the crosslink density initially increases the tensile strength, but beyond a maximum value it subsequently decreases because the very high level of crosslink highly restricted the chain mobility of the system, leading to low ultimate tensile strength [53].

The ether group involved in O-BMI plays an important role in improving the toughness

of O-BMI polymers. BMI-400B has a longer flexible main chain than that of BMI-230B, so the crosslink density of BMI-400B polymer is smaller than that of BMI-230B polymer. Therefore, less crosslink density and longer flexible main chain of BMI-400B polymer lead to its lower stress and higher strain compared with BMI-230B polymer.

Figure 6.15 the stress-strain relationship of BMI-230B

Figure 6.16 the stress-strain relationship of BMI-400B

6.2.8 Toughness of BMI-230 polymer

The area under the load-elongation curve was used as a measure of the toughness. Table 6.11 shows the toughness of BMI-230B.

Table 6.11 Comparison of toughness of BMI-230B and C-BMI

	Toughness (MPa)
BMI-230B	50±5
C-BMI	25±3

O-BMI is expected to have high toughness because the ether bonds between crosslinking points would reduce the brittleness of the polymer [42,77,88]. It can be seen from Table 6.11 that BMI-230B which has the flexible OCH₂ group does indeed have better toughness than C-BMI.

6.2.9 Moisture absorption of O-BMI polymers

Table 6.12 shows the results obtained from moisture testing of the O-BMIs samples. No data could be obtained for BMI-2000, BMI-2000B and BMI-4000B because the samples of these BMIs were almost dissolved in water.

Table 6.12 The effect of chain length on moisture absorption of O-BMIs

BMI	BMI-230B	BMI-400B	BMI-600	BMI-900	C-BMI
Moisture absorp. (%)	4.9	6.8	41.3	85.5	4.81

Figure 6.17 Effect of the chain length on moisture absorption of O-BMIs

It can be seen from Figure 6.17 that the moisture absorption of O-BMIs increased with the chain length. The moisture absorption of O-BMIs to be divided by the number of CH_2 group also increased slightly with the chain length. This is to be expected since moisture absorption depends on the polarities in a polymer to form hydrogen bonds. Besides ether bridges the O-BMI polymers contain polar groups such imide ($-\text{CO}-\text{NH}-\text{CO}-$) moieties. Thus, water molecules close to the polar groups would be able to form hydrogen-bonded complexes with the nitrogen and oxygen atoms. The chain length increased the ether groups of O-BMI polymer increased. This was the reason why moisture absorption for cured O-BMI system was observed to increase in the following order: BMI-230B < BMI-400B < BMI-600 < BMI-900. It was observed that the moisture absorption of BMI-230B was nearly the same as that of C-BMI as shown in Table 6.12.

6.3 Summary

In order to achieve a polymer structure with a low dielectric constant in the current work, less polar groups (CH_2 and OCH_2) were selected in the main chain. Meanwhile, to improve its toughness flexible linkages were introduced into the bismaleimides. The objective of this part of the project was to obtain a tough polymer that has low ϵ (less than 3). It can be seen that these requirements are met in BMI-230B. A-BMIs have low dielectric constants whilst BMI-230B has balanced properties of a low dielectric constant and improved toughness. The incorporation of a small amount of ether group to the BMI has drastically reduced the elastic modulus and increased the toughness of the BMI material.

The superior thermal stability of BMI-230B is up to 393°C in air and in nitrogen. BMI-230B possesses a moderate CTE at $82\ \mu\text{m}/\text{m}^\circ\text{C}$ and a moderate glass transition temperature at $148\ ^\circ\text{C}$. This new type of toughed BMI-230B has great potential application to modify BMI systems as described in Chapter 7.

Chapter 7 The Blends of the BMI systems

The unmodified aromatic C-BMI here refers to bis(4-maleimidophenyl)-methane. The aromatic C-BMI has excellent mechanical properties and heat resistance but suffers low elongation to failure and poor toughness. Electrical properties of the unmodified C-BMI such as dielectric strength, volume resistivity, dielectric constant, and dissipation factor are suitable for the fabrication of electronic components. In this Chapter, characterization of the unmodified aromatic and aliphatic and aliphatic-ether BMI blending samples will be carried out to study the processability, thermo-hygro-mechanical and electrical properties of the copolymer systems. We hope that, in doing so, the mixture of these BMIs will improve the dielectric properties and increase fracture toughness.

A-BMIs exhibited high vaporization during processing, and they needed to be processed under pressure to reduce vaporization and hence obtain void-free material. In order to obtain materials with low volatility, longer chain diamine was used to synthesize O-BMIs with higher molecular weights. Liquid O-BMIs with higher molecular weights and lower volatility can offer better processability. Generally, aromatic BMI monomers have relatively high melting points and relatively low cure temperatures. They do not flow easily in the uncured state and therefore are processed via solution polymerization. As a

result, solvent retention is a problem during cure. As such, a liquid BMI should make the processing easier.

The dielectric constants of the A-BMI with alkylene-chain are very low (lower than 3). Generally, the dielectric constant of an electronics packaging material such as aromatic BMI is higher. Blending A-BMI as additives with aromatic C-BMI will be expected to decrease the dielectric constant of copolymer. It was able to achieve enhanced toughness and processability by blending O-BMI as additives with aromatic C-BMI to optimize the various performance of material.

7.1 The characterization of blending of BMI-6 and BMI-230B systems

BMI-6 is the best A-BMI and BMI-230B is the best O-BMI. Compared with C-BMI, BMI-6 has a lower dielectric constant and BMI-230B has a better toughness. The balanced performance could be obtained by blending BMI-6 with BMI-230B. The BMI-6 was blended with various levels of BMI-230B such as 20%, 30%, 50% 70%, and 90% (weight %) as shown in Table 7.1. The blended material with 20% BMI-230B is coded as B20. Figures 7.1 and 7.2 show the typical plot of blending samples of B90. Comparing the thermal properties and toughness, it can be concluded that the varying tendencies of the values in Table 7.1 was the balanced point of these two contributions. The dielectric constant increased as the BMI-230B content increased because the amount of the polar aliphatic ether increases.

Figure 7.1 A typical DEA plot of BMI blending

Figure 7.2 A typical stress strain relationship of B90

Table 7.1 The properties of the blended materials

	B20	B30	B50	B70	B90	C-BMI
BMI-230B Weight Content (%)	20%	30%	50%	70%	90%	0%
Dielectric constant (50°C, 100 kHz)	2.3	2.4	2.5	2.8	2.9	3.4
Toughness (MPa)	30	36	40	45	48	25
T _g (°C)	322	290	250	173	140	465
CTE	87	85	85	84	84	46
T _d (°C)	441	430	420	400	400	491
Moisture absorption (weight %)	6.0	5.9	5.6	5.3	5.0	4.8

It was observed that the glass transition temperatures and decomposition temperatures decreased and CTE changed less with BMI-230B content increase. The polymer with ether group is able to rotate freely in the network. So the glass transition temperatures decreased with BMI-230B content increase. It is well known that the presence of oxygen traces in polymer decomposition has a catalyst or initiator role in thermal or thermo-oxidative decomposition. Therefore, the decomposition temperatures decreased with BMI-230B content increase.

The toughness increased with BMI-230B content as shown in Table 7.1. It means that the blend of BMI-230 and BMI-6 has good blending properties. This improvement in tensile strength resulted from introducing the softer segment of the BMI-230B. Because the

ether bonds between crosslinking points would reduce the brittleness of the polymer, so the toughness increased with BMI-230B incorporated.

The blended material with 50% BMI-230B is better than commercial C-BMI in terms of dielectric constant and toughness (from tensile test). Increase in BMI-230B content from 20% to 90% cause a slightly increase in dielectric constant and toughness. The glass transition temperature and CTE of B50 is moderate. The degradation temperature is high up to 420 °C. The moisture absorption of B50 is close to C-BMI.

7.2 The A-BMI and O-BMI as additives to modify C-BMI

C-BMI has problems with brittleness of the final polymer due to the high crosslinking density in the polymer network and a high dielectric constant. In order to reduce the brittleness, the C-BMI could be blended with another BMI which has high toughness. This was why O-BMIs which have high toughness and which contained ether bridges (-O-) inserted into the molecule were synthesized and characterized. Moreover, the dielectric constant of the C-BMI may be reduced by blending with another BMI which has a lower dielectric constant. This was why A-BMIs with low dielectric constant were also synthesized.

In order to examine their effectiveness in increasing the toughness and decreasing the dielectric constant of the C-BMI, both O-BMI and A-BMI respectively were blended with C-BMI. The properties of the A-BMI/C-BMI blend systems in which C-BMI had

Chapter Seven***The blends of the BMI systems***

been blended with 10 wt% and 20 wt% of each grade of A-BMI that had been synthesized is as shown in Table 7.2. The properties of O-BMI/C-BMI blend systems in which C-BMI was blended with 10 wt% and 20 wt% of each type of O-BMI that had been synthesized is shown in Table 7.3.

Table 7.2 The properties of the blend systems (C-BMI blended with A-BMIs)

		K	T _g (°C)	CTE	T _d (°C)	Moisture (%)
BMI-2	10 wt%	3.47	461	45	486	5.19
	20 wt%	3.33	456	43	483	5.59
BMI-3	10 wt%	3.45	460	46	487	5.20
	20 wt%	3.50	455	45	484	5.59
BMI-4	10 wt%	3.32	459	46	486	5.20
	20 wt%	3.23	453	49	483	5.59
BMI-5	10 wt%	3.30	459	50	487	5.03
	20 wt%	3.20	452	54	485	5.26
BMI-6	10 wt%	3.32	459	50	483	4.98
	20 wt%	3.23	453	55	478	5.16
BMI-7	10 wt%	3.57	457	51.5	485	4.85
	20 wt%	3.73	450	57	481	4.90
BMI-8	10 wt%	3.33	457	50.5	485	4.78
	20 wt%	3.26	450	55	480	4.76
C-BMI		3.4	465	46	491	4.8

Figure 7.3 Effect of the A-BMI content on dielectric constant of the blending

Figure 7.4 Effect of the A-BMI content on Tg of the blending

The dielectric constant of the blending systems changed slightly as the A-BMI content increased as shown in Figure 7.3, because the amount of the A-BMI was added only 10%

and 20% weight as additives. It was observed that the glass transition temperature decreased and CTE increased with the chain length increase as shown in Figure 7.4 and Figure 7.5. Introduction of long chain into two maleimide groups would decrease its crosslink density and increase free volume of the cured sample, thus decrease the T_g and increase the thermal expansion coefficient. A-BMI as additives (10 wt% & 20 wt%) decreases the T_g of the blending systems. Therefore, the glass transition temperatures of the blending systems decrease with the length of main chain of A-BMI increase.

Figure 7.5 Effect of the A-BMI content on CTE of the blending

All the blending systems showed a little decrease in onset temperature of degradation as the chain length of A-BMI increased as shown in Figure 7.6. A-BMI as additives (10 wt% & 20 wt%) decreases the T_d of the blending systems. Thus, increasing the number of aliphatic C atoms on the backbone chain appeared to lower the thermal stability of the blending systems.

Figure 7.6 Effect of the A-BMI content on Td of the blending

Figure 7.7 Effect of the A-BMI content on moisture absorption of the blending

It can be seen from Figure 7.7 that the moisture absorption of the blending systems decreased with the chain length. Because the moisture absorption of A-BMIs decreases

Chapter Seven***The blends of the BMI systems***

with the chain length increase, A-BMI as additives (10 wt% & 20 wt%) also decreases the moisture absorption of the blending systems.

In summary, the glass transition temperatures, decomposition temperatures, CTE and moisture absorption became lower as the A-BMI content increased. Addition of small amounts of A-BMI did not lead to any appreciable improvement in the properties of the blend systems.

Table 7.3 The properties of blend systems (C-BMI blended with different types and amounts of O-BMI)

		Toughness	T _g (°C)	CTE	T _d (°C)	Moisture (%)
BMI-230B	10 wt%	28	397	49	480	4.9
	20 wt%	30	370	52	471	4.9
BMI-400B	10 wt%	28	390	50	477	5.1
	20 wt%	31	356	54	465	5.3
BMI-600	10 wt%	29	388	50	473	8.5
	20 wt%	32	351	55	455	12.2
BMI-900	10 wt%	32	387	53	473	13
	20 wt%	38	349	61	455	21
BMI-2000	10 wt%	40	385	55	475	24
	20 wt%	55	345	64	459	44

Chapter Seven

The blends of the BMI systems

BMI-2000B	10 wt%	43	384	56	474	23
	20 wt%	50	343	66	458	40
BMI-4000B	10 wt%	53	384	57	475	44
	20 wt%	80	342	68	460	84
C-BMI		3.4	465	46	491	4.8

Figure 7.8 Effect of the O-BMI content on toughness of the blending

The toughness increased with O-BMI content as shown in Figure 7.8. This improvement in toughness resulted from introducing the softer segment of the O-BMI. Because the ether bonds between crosslinking points would reduce the brittleness of the polymer, so the toughness increased with O-BMI content.

Figure 7.9 Effect of the O-BMI content on Tg of the blending

Figure 7.10 Effect of the O-BMI content on CTE of the blending

Figure 7.11 Effect of the O-BMI content on Td of the blending

Figure 7.12 Effect of the O-BMI content on moisture absorption of the blending

It was observed that the glass transition temperatures, decomposition temperatures decreased and CTE increased significantly when the O-BMI content was increased as

shown in Figures 7.9, 7.10 and 7.11 respectively. Because the polymer with ether group is able to rotate freely in the network, the glass transition temperatures decreased with O-BMI content increase. The presence of oxygen traces in polymer decomposition plays a catalyst or initiator role in thermal or thermo-oxidative decomposition. Therefore, the decomposition temperatures decreased when the O-BMI content increased.

It can be seen from Figure 7.12 that the moisture absorption of the blending systems increased with the amount of O-BMI content. The moisture absorption depends on the polarity in a polymer to form hydrogen bonds. The ether bridges in the O-BMI polymers and water molecules could readily form hydrogen-bonded complexes. The increase in ether groups of O-BMI polymer with increasing main chain length probably led to the increase of the moisture absorption in Figure 7.12. It is apparent that addition of O-BMI as an additives (10 wt% & 20 wt%) would also increase the moisture absorption of the blending systems.

7.3 The characterization of blending of BMI-6, BMI-230B and C-BMI

BMI-6 is the best A-BMI (See 5.3 section) and BMI-230B is the best O-BMI (See 6.3 section). Next, blending trials were conducted to determine the amounts of A-BMI and O-BMI that have to be added to C-BMI in order to obtain a blend mixture that has a dielectric constant below 3.0 and an increase in toughness of at above 30. It can be seen in Figure 6.16 that BMI-400B has changed to a tough material, which has a low stress and high strain value. If the stress-strain plot for the blend system is like this, indicating

Chapter Seven

The blends of the BMI systems

the material is tough and the toughness value of the material should be at above 30.

Compared with C-BMI, BMI-6 has a lower dielectric constant and BMI-230B has a better toughness. Table 7.4 shows the properties of a blend system with 0%, 10%, 20% and 100% BMI-6. Table 7.5 shows the properties of the blend system with 0%, 10%, 20% 30% and 100% BMI-230B.

Table 7.4 The properties of blend systems (C-BMI blended with different amounts of BMI-6)

		ε	T _g (°C)	CTE	T _d (°C)	Moisture (%)
BMI-6	0 wt%	3.4	465	46	491	4.8
	10 wt%	3.32	459	50	483	4.98
	20 wt%	3.23	453	55	478	5.16
	100 wt%	2.55	404	90	464	6.60

Figure 7.13 Effect of the BMI-6 content on K & moisture absorption of the blending

Figure 7.14 Effect of the BMI-6 content on thermal properties of the blending

The dielectric constant, Tg and Td of the BMI-6 and C-BMI blending systems decreased as the BMI-6 content increased as shown in Figure 7.13 and Figure 7.14. The change in physical properties with % content of A-BMI is linear. C-BMI has problems with a high dielectric constant. The dielectric constant of the C-BMI may be reduced by blending with BMI-6 which has a lower dielectric constant. It can be seen from Figure 7.13 that when the A-BMI content is above 30%, the dielectric constant of the blend mixture would be less than the desired value of 3.0. For this reason, it was decided that the A-BMI content in the tertiary A-BMI/O-BMI/C-BMI blend mixture should be 30%. It can be seen from Figure 7.13 and Figure 7.14 that the moisture absorption and CTE of the blending systems increased with the amount of BMI-6 content. Introduction of long chain into two maleimide groups would decrease its crosslink density and increase free volume of the cured sample, thus increase the thermal expansion coefficient. BMI-6 as additives

Chapter Seven

The blends of the BMI systems

increases the CTE of the blending systems. C-BMI has lower moisture absorption than BMI-6. Therefore, the moisture absorption of the blending systems increased with the amount of BMI-6 content.

Table 7.5 The properties of blend systems (C-BMI blended with different amounts of BMI-230B)

		Toughness (MPa)	T _g (°C)	CTE	T _d (°C)	Moisture (%)
BMI-230B	0 wt%	25	465	46	491	4.8
	10 wt%	28	397	49	480	4.9
	20 wt%	30	370	52	471	4.9
	100 wt%	50	148	82	393	4.9

Figure 7.15 Effect of the BMI-230B content on the properties of the blending

Figure 7.16 Effect of the BMI-230B content on the Tg & Td of the blending

The toughness and CTE increased as the BMI-230B content grew as shown in Figure 7.15. C-BMI has problems with brittleness of the final polymer. It can be deduced from Figure 7.15 that the toughness of the O-BMI/C-BMI blend mixture can probably be increased at least 30% from 25 to 30 when the BMI-230B content is above 30%. Therefore, it was decided that the A-BMI content in the tertiary A-BMI/O-BMI/C-BMI blend mixture should be 30%.

It was observed that the glass transition temperatures and decomposition temperatures decreased when the BMI-230B content was increased as shown in Figure 7.16. Introduction of ether group and long chain into two maleimide groups would decrease its crosslink density and increase free volume of the cured sample, thus decrease the Tg of the blend system. BMI-230B polymer with longer chain is easier for oxygen to diffuse.

Chapter Seven***The blends of the BMI systems***

Therefore, the decomposition temperatures decreased with the BMI-230B content.

From the above considerations & observations, it can be seen that the brittleness and dielectric constant can be reduced to the desired level by blending the C-BMI with BMI-6 and BMI-230B. In order to confirm that this can indeed be achieved and that there are no negative effects in a ternary blend system comprising A-BMI/O-BMI/C-BMI, a blend system comprising 30% A-BMI, 30% O-BMI and 40% C-BMI was prepared. The physical property of such a ternary blend system was determined and is summarized in Table 7.6. It can be seen from Table 7.6 that no negative effects which would lead to adverse unexpected trends in the dielectric constant and toughness were obtained in the ternary A-BMI/O-BMI/C-BMI system as compared to the binary A-BMI/C-BMI and O-BMI/C-BMI blend systems.

Table 7.6 The properties of the blended BMI-6, BMI-230B and C-BMI systems

	The blending systems			C-BMI
	BMI-6 30 wt %	BMI-230B 30 wt %	C-BMI 40 wt %	
Dielectric constant (50°C, 100 kHz)	2.9			3.4
Toughness (MPa)	34			25
T _g (°C)	336			465
CTE	69			46
T _d (°C)	448			491
Moisture absorption (%)	5.3			4.8

Chapter Seven

The blends of the BMI systems

The blended system is better than C-BMI in terms of dielectric constant and toughness (from tensile test). The glass transition temperature and CTE of the blended system is moderate. The degradation temperature is high up to 450 °C. The moisture absorption of the blended system is close to C-BMI.

Chapter 8 Conclusions

The purpose of this work is to synthesize a series of bismaleimides and study the effect of varying aliphatic or aliphatic-ether chain length on the properties of bismaleimide systems. In order to achieve a polymer structure with a low dielectric constant, repeating units with less polar groups (CH_2 and OCH_2) were selected as the main chain to obtain BMIs with low dielectric constants. The flexible ether group also improved the toughness of BMI polymer. The fourteen bismaleimides prepared by the reactions of diamines with maleic anhydride, gave corresponding bismaleamic acids. Results from analysis showed bismaleamic acid were formed very rapidly and modification in the main chain had little effect on the rate of formation. The formation of bismaleimide from bismaleamic acid, on the other hand, required longer reaction time.

8.1 A-BMI systems

The thermal, dielectric and tensile properties are all influenced by the chain length of A-BMI and the odd-even effect. FTIR and NMR find when CH_2 length is odd, the packing density is lower. A-BMI should be more stable as the chain length increase. As the chain length increased, the peak curing temperature and gel temperature of A-BMI both increased due to the thermodynamic effect, but the melting point and glass transition decreased. For bismaleamic acid and bismaleimide, the odd-even chain-length effect had an impact on the melt temperatures, i.e. an even number of carbons on the main chain had higher melting temperatures. BMI-3, BMI-5, BMI-7 which have odd number of carbons in

the main chain had significantly lower melting points. In general, an increase in length of the backbone chain resulted in lower melting points of the A-BMIs, leading to larger processing temperature ranges.

The cured A-BMIs had high T_g values of approximately 400°C and excellent stability even at high temperatures of approximately 450°C in dry air and in pure nitrogen. The TGA results indicated that the uncured BMIs had a tendency to vaporize rapidly during processing.

The CTE values for bismaleimides increased with chain length. The incorporation of non-polar methylene ($-\text{CH}_2-$) group into the A-BMI systems lead to BMIs with lower dielectric constants ranging from 2.0 to 2.6 at 100kHz. The tensile properties of the A-BMIs were affected significantly by the odd even effect. BMI-3, BMI-5, BMI-7 which had odd number of carbons atoms had lower failure stresses and failure strains than those of the even ones. The A-BMIs have a higher tensile strength than the aromatic C-BMI. The processing window (T_o - T_m) of C-BMI is 34°C, except for BMI-2 and BMI-4, A-BMIs have larger processing ranges (49-134°C) than that of C-BMI.

8.2 O-BMI systems

For O-BMI systems, their thermal, dielectric and tensile properties are also affected by the chain length of O-BMI. As the chain length increased, the peak curing temperature, gel temperatures and gel times of BMI all decreased. This is because there are three factors that

make O-BMI monomer more reactive as the length of chain was increased. The presence of methylene ($-\text{CH}_2-$) and ether ($-\text{O}-$) groups in the BMI affect the reactivity of the double bonds in maleimide ring. For A-BMI system, the thermodynamic effect plays an important role; but for O-BMI systems, the inductive effect, chain mobility and thermodynamic effect all affect the reactivity of double bonds. O-BMI polymers containing longer chain have lower degradation temperature, but O-BMI polymers also show good stability with degradation temperature at approximately 300°C in dry air and in pure nitrogen. The magnitude of the dielectric constant ($\epsilon = 3\sim 6$ at 100kHz) increases with the increasing chain length. Introduction of methylene ($-\text{CH}_2-$) and ether ($-\text{O}-$) groups effectively increased the toughness of the cured O-BMI. BMI-230B has a low dielectric constant and the improved toughness.

8.3 A-BMI & O-BMI as additives to modify C- BMI

BMI-6 was blended with various level of BMI-230B. The dielectric constant and toughness increased as the BMI-230B content increased. The glass transition temperatures and decomposition temperatures decreased and CTE changed less with BMI-230B content increase. A-BMI (except BMI-3 and BMI-7) blending with C-BMI can decrease the dielectric constant of copolymer. Blending O-BMI with C-BMI enhanced toughness of copolymer. Blending the C-BMI with BMI-6 and BMI-230B can achieve the decreased dielectric constant and enhanced toughness (from tensile test) compared with C-BMI.

Chapter 9 Future Work

The objective of this research work was to develop, characterize a series of BMI and evaluate the effects of varying the chain length of the aliphatic and aliphatic-ether diamines on the resultant bismaleimide systems. The A-BMI & O-BMI as additives to modify C-BMI was evaluated. The future work is to study the blending of A-BMI & O-BMI systems as described below:

9.1 Thermal properties

Thermal properties such as T_g, CTE and thermal decomposition of A-BMIs and O-BMIs have been evaluated. Although T_g and thermal stability of A-BMIs appeared to be relatively insensitive to the number of aliphatic carbon atoms in the chain, CTE values for A-BMIs increased significantly as chain length increased. Because CTEs of most synthetic polymers may be ten times greater than those of common metals or silicon, severe thermal distortions can arise when polymers are bonded to metals or silicon [61]. T_g, CTE and thermal decomposition of A-BMIs and O-BMIs blending system should be evaluated.

9.2 Cure Study on the A-BMI and O-BMIs blending systems

The cure behaviour of the A-BMIs and O-BMIs blends will be evaluated using DSC and DEA. The purpose is to establish two important cure parameters for this current system, namely, the rate of cure and end point of cure. DSC will be used to determine the rate of the reaction [111] while DEA will be used to determine the end point. It is known that the

extent of cure directly affects the thermal, mechanical and physical properties of the curing system and the end point parameter is used to determine the point at which these properties are optimized. One parameter commonly used in monitoring the extent of cure is the T_g and generally T_g increases with the extent of cure [112, 113].

9.3 Rheological property

The rheological properties of the melting state and curing period of the BMI blending systems will be evaluated. The processability of a resin is determined by its solubility in solvents, melt viscosity (flowability), and processing window. Typically, a sample with low viscosity makes processing easy. However, the presence and high content of aromatic or heterocyclic segments in a thermosetting resin drastically reduces solubility, and increases the melting point and melt viscosity of the monomer. The aliphatic segments in BMI decrease the melting point and melt viscosity of the monomer. Gel time and gel temperature should be tested.

9.4 Mechanical properties

Mechanical properties of the blending BMIs will be evaluated for their flexural modulus, yield stress, yield strain and toughness. Stress-strain experiments and flexural strength tests will be carried out. The property of most interest is the fracture toughness. This measures the cohesive strength of the material and is given by the area under the stress-strain curve. Elongation-at-break values will be obtained by stress-strain measurements at various strain rates carried out at room temperature. Other mechanical properties that will be obtained

from stress-strain experiments are the Young's modulus, tensile strength, yield point, yield strength, and ultimate tensile strength. Young's modulus will be used in calculation of thermal mismatch. The brittleness of BMI can be attributed to chain stiffness as a result of highly cross-linked structure and the steric effects of aromatic phenylene groups. The main concern of this research is therefore to correlate chain flexibility to material toughness.

9.5 Dielectric properties

A knowledge of the dielectric constant is important if the material is to be used either as an insulator or as the dielectric material in microelectronics. The dielectric constant (ϵ) and the dielectric loss ($\tan\delta$) will be determined in this project. The ϵ and $\tan\delta$ depend chiefly on the behavior of the molecular chains and their super-molecular structures. Dielectric measurements will be made using parallel plate capacitance methods at frequencies between 0.1kHz-1MHz and over a range of temperatures. Generally, the conductivity of a polymer increases with increasing ϵ . The dielectric constant (ϵ) and the dielectric loss ($\tan\delta$) will be done for the blending systems.

9.6 Adhesion properties

It was believed that good adhesion between the polymer encapsulants and silicon chip would reduce the possibility of package cracks due to delamination during curing shrinkage and thermal cycling. Adhesion depends on both materials in contact and on the way the bond is fabricated. Interaction of permanent dipoles results in strong bonds, especial the hydrogen bond. The most important of the adhesive bonds are hydrogen bonds

and Van der Waals' forces, that give rise to attraction between molecules but will suffer from exposure to humidity. Another important adhesive bond is the London or dispersion force. Molecules must be in close proximity for London forces to be effective. This explains why a very flexible molecule is a better adhesive than a moderately flexible molecule [52]. The quality of a bond is usually measured by "practical adhesion" tests, such as the peel test.

9.7 Moisture absorption

Films of hydrophilic polymers are often permeable to water vapor, whereas hydrophobic polymers form films that are impervious to water. Such considerations must be taken into account when choosing a polymer for packaging [30]. Polyimides that exhibit high water uptake are relatively easily attacked by aqueous and non-aqueous caustic solutions. And this major concern, typically, moisture absorption increases the dielectric constant and can lead to adhesion loss, corrosion, increased stress changes in the mechanical behavior, molecular weight breakdown by hydrolysis and blistering during heating. Maximum amount and kinetics of water uptake can be measured by thermogravimetric analysis. Generally, aliphatic polyimides exhibit a relatively low water uptake.

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Appendix I Synthesis

Table 1. The molar mass and properties of compounds

	Molar mass (g/mol)	T _m (°C)	T _p (°C)	T _g (°C)	T _d (°C)	Moisture absorp. (%)
Sodium Acetate	82.03					
Acetic Anhydride	102.09					
Dimethylformamide	73.10					
BMA-2	256.22					
BMA-3	270.25					
BMA-4	284.27					
BMA-5	298.29					
BMA-6	312.33					
BMA-7	326.35					
BMA-8	340.38					
BMI-2	220.18	194	247	-	451	8.7±0.5
BMI-3	234.21	171	249	413	456	8.8±0.5
BMI-4	248.23	203	259	405	458	7.1±0.5
BMI-5	262.26	108	253	402	458	6.6±0.4
BMI-6	276.29	136	261	404	461	6.6±0.4
BMI-7	290.32	85	258	388	448	5.3±0.3
BMI-8	304.34	122	274	392	445	4.6±0.2
C-BMI (4,4'-Bismaleimido- diphenylmethane)	358.36	159	219	465	492	4.8±0.2

Appendix

Figure 1 The plots of A-BMA formation

Appendix

Appendix

Appendix

Appendix II FTIR analyses

Figure 1 FTIR spectra of BMA-2,3,4,6

Appendix

Figure 2 FTIR spectra of BMA-8 and BMI-2,3,4

Appendix

Figure 3 FTIR spectra of BMI-5,6,7,8

Appendix

Figure 4 FTIR spectra of BMI-230B,400B,600,900

Figure 5 FTIR spectra of BMI-2000,2000B,4000B

Appendix III NMR analyses

Figure 1 ^1H NMR spectrum of BMI-3

Appendix

Figure 2 ^1H NMR spectrum of BMI-5

Appendix

Figure 3 ^1H NMR spectrum of BMI-7

Appendix

Figure 4 ^1H NMR spectrum of BMI-2,4

Appendix

Figure 5 ^1H NMR spectrum of BMI-6,8

Appendix IV DSC analyses

Appendix

Appendix

Appendix

Appendix V DEA analyses

Figure 1 The dielectric constants of A-BMI polymers

Figure 2 The dielectric constant of C-BMI

Appendix

Figure 3 The dielectric loss of BMI-3,4,5,6,7,8 polymers

Appendix

Figure 4 The dielectric loss of BMI-2,230B,400B,600,900,2000B polymers

Appendix

Figure 5 The dielectric loss of BMI-2000,4000B polymers

Figure 6 The dielectric constants of O-BMI polymers

Appendix VI TGA & TMA analyses

Appendix

Figure 1 TGA analyses of the A-BMI, O-BMI and C-BMI polymers

Figure 2 TMA analyses of the A-BMI, O-BMI and C-BMI polymers

Appendix VII

Gel points

Figure 1 The gelation of O-BMI monomers

Figure 2 The gelation of O-BMI monomers

Figure 3 The gelation of O-BMI monomers

Appendix

Figure 4 The gelation of A-BMI monomers

Figure 5 The gelation of A-BMI monomers

Appendix

Figure 6 The gelation of A-BMI monomers

Figure 7 The gelation of BMI-8 & C-BMI monomers

Appendix VIII Data analyses

Table 5.5 The effect of CH₂ on the frequency shift of double bond and C=O

A-BMI		2	3	4	5	6	7	8
Double bond C=C (cm ⁻¹)		3104	3087	3091	3085	3087	3085	3089
	D*	1552	1029	773	617	515	441	386
Carbonyl group C=O (cm ⁻¹)		1706	1704	1697	1708	1692	1700	1693
	D*	853	568	424	342	282	243	212

D*: To be divided by No. of CH₂

Table 5.7 Melting, curing temperatures and curing heat of A-BMI systems

	T _m (°C)		T _o (°C)		ΔT= T _o - T _m		T _p (°C)		-ΔH	
		D*		D*		D*		D*	J/g	kJ/mol
BMI-2	194	97	209	105	15	8	247	124	393	87
BMI-3	171	57	220	73	49	16	249	83	417	98
BMI-4	203	51	228	57	25	6	259	65	480	119
BMI-5	108	22	212	42	103	21	253	51	469	123
BMI-6	136	23	216	36	80	13	261	44	464	128
BMI-7	85	12	215	31	130	19	258	37	413	120
BMI-8	122	15	232	29	110	14	274	34	502	153
C-BMI	159	159	193	193	34	34	219	219	185	66

D*: To be divided by No. of CH₂

*Appendix***Table 5.8 Effect of chain length on curing time of A-BMI**

A-BMI		2	3	4	5	6	7	8	C-BMI
Time (min)		75	75	90	270	300	330	270	20
	D*	38	25	23	54	50	47	34	20

D*: To be divided by No. of CH₂**Table 5.9 Gel Temperature and Gel Time of A-BMI**

	Gel time (s) isotherm at 230°C		Gel temperature (°C)	
		D*		D*
BMI-2	100	50	210	105
BMI-3	200	67	210	70
BMI-4	210	53	218	55
BMI-5	210	42	215	43
BMI-6	275	46	222	37
BMI-7	360	51	220	31
BMI-8	370	46	230	29
C-BMI	150	150	215	215

D*: To be divided by No. of CH₂

Table 5. 12 A-BMI polymers: Tg and CTE

	T _g (°C)	CTE (α1) (μm/m°C)		CTE (α2) (μm/m°C)	
			D*		D*
BMI-2	–	31.5	15.8	31.5	15.8
BMI-3	413	43.2	14.4	152	50.7
BMI-4	405	60.2	15.1	232	58.0
BMI-5	402	85	17.0	242	48.4
BMI-6	404	89.7	15.0	213	35.5
BMI-7	388	101	14.4	230	32.9
BMI-8	392	90.9	11.4	239	29.9
C-BMI	465	46	46.0	173	173.0

D*: To be divided by No. of CH₂**Table 5.14 Dielectric loss peak of A-BMI polymer**

A-BMI	Dielectric loss peaks					
	β °C (1 Hz)		γ °C (1 Hz)		γ °C (100 kHz)	
		D*		D*		D*
BMI-2	18	9.0	-113	-56.5	2.5	1.3
BMI-3	15	5.0	-108	-36.0	5.4	1.8
BMI-4	8.3	2.1	-102	-25.5	-8	-2.0
BMI-5	6.8	1.4	-95	-19.0	-9.8	-2.0
BMI-6	5.8	1.0	-92	-15.3	-10.4	-1.7
BMI-7	6.3	0.9	-81	-11.6	7.3	1.0
BMI-8	-0.6	-0.1	-78	-9.8	7.3	0.9

D*: To be divided by No. of CH₂