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Studies on the Odd-Even Effect of Methylene Spacers in Bismaleimides

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Abstract: The synthesis of a series of bismaleimides based on diamines containing flexible units of variable length is presented. These structures were characterized by FTIR and NMR. The changes in spectra are dominated by the CH_2 stretching and deformation vibrational bands. The wavenumber of methylene provides a sensitive measure for the chain packing geometry. An attempt has been made to explain the odd-even effects at the molecular level on the basis of the article results. DSC was used to monitor the thermal properties of the samples. The melting points of the bismaleamic acids and bismaleimides are affected by odd-even effect. The reactivity of maleimide group was analyzed. Positions of signals in FTIR and NMR spectra show that BMI should be more stable as the chain length increase.

Introduction

Bismaleimides possess a high degree of thermal stability and chemical resistance, as well as good mechanical properties. However, this family of polymers lacks sufficient flexibility and poor processibility [1, 2]. Since BMI contains two reactive double bonds, the cured network is very brittle due to the high cross-linking density and aromatic nature. One approach to improve its toughness is to introduce the flexible and longer backbone main chain between two maleimide rings. Incorporation of ether, carbonate, ester, or urethane linkages into the polyimide backbone generally provides sufficient flexibility to improve toughness [1-4]. With a repeating unit of alternating methylene backbone structure, the modified bismaleimides was speculated to improve the toughness. Most investigations were focus on aromatic BMIs with two phenyl groups. The bismaleimides containing oxyalkylene linkages has been reported [4], BMI in this paper contain benzene ring between maleimide groups. Because benzene ring is rigid group, the benzene ring is not introduced into the modified BMI in this study. In our study, the BMI includes only -CH_2- repeating unit which is a non-polar and flexible group. Bismaleimides with methylene chains were synthesized. The bismaleimides can be crosslinked directly through their maleimide double bonds. The bismaleimides homo-polymerize readily without catalyst at temperatures between 150 and 300°C. The high reactivity of the maleimide group is attributable to the inductive (polar) effect of the aromatic groups [5]. But the aromatic group is not introduced into the modified BMI in this study. This paper is concerned with the effect on the reactivity of the bridging group between the maleimide end groups.

Although the odd-even effect has been known for a very long time, mostly, packing effects are given as an explanation. The present FTIR and NMR spectral investigation was undertaken to understand the influence of methylene on molecular vibrations, packing density and reactivity. The thermal property was also evaluated.

Results and discussion

FTIR analyses

The outstanding property 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 nucleophilies is activated compared with a classical ethylene C=C bond. But for aliphatic 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, the IR vibration bands of the maleimide ring of the different BMIs are summarized in Table 1.

Tab. 1. The effect of CH_2 on the frequency shift of C=C and C=O.

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

FTIR spectroscopy showed that there was significant odd even effect of methylene groups on the wave number of double bond as shown in Figure 1. When the CH_2 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. It was noticed that 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 2 and Figure 3. 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, BMI should be more stable as the chain length increase.

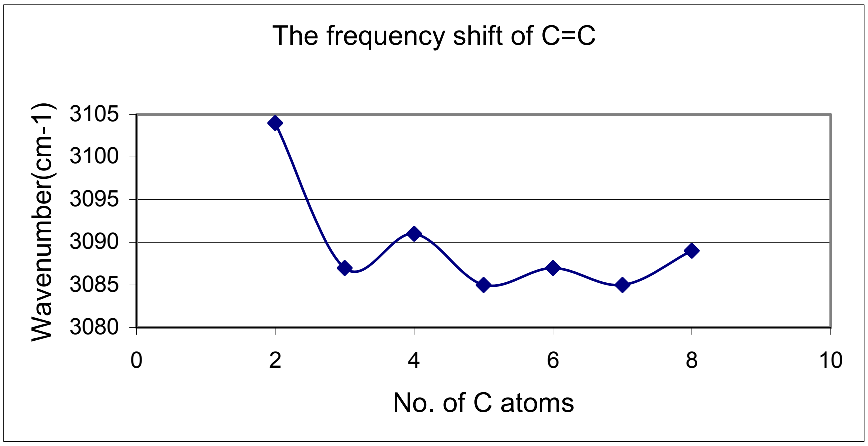


Fig. 1. Effect of the main chain length on the frequency shift of C=C in BMI.

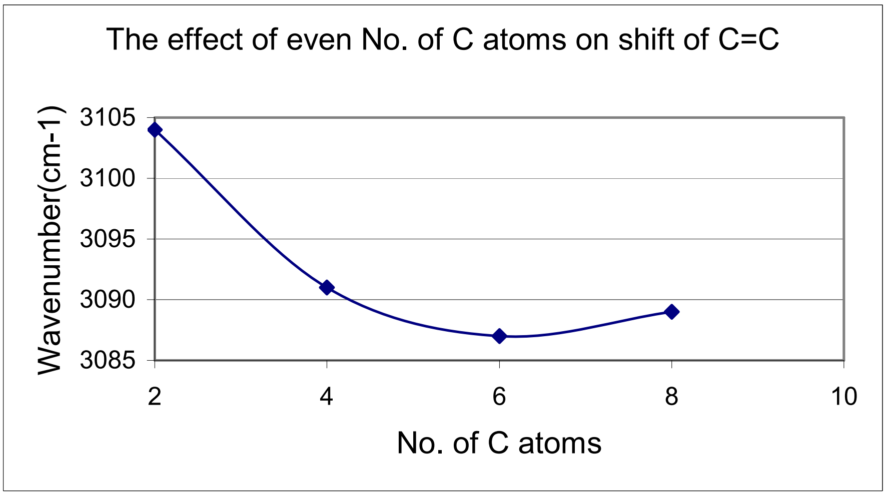


Fig. 2. Effect of the even number of C on the frequency shift of C=C in BMI.

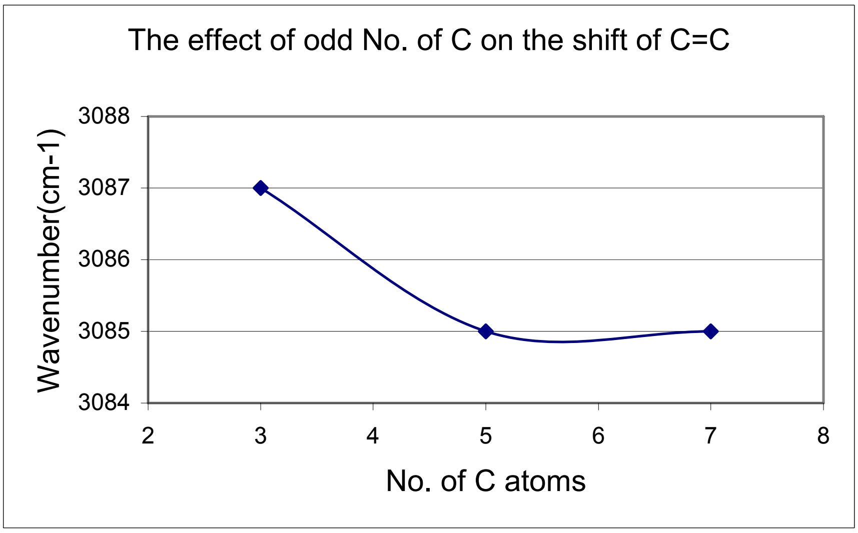


Fig. 3. Effect of the odd number of C on the frequency shift of C=C in BMI.

The effect of the number of carbon on the wave number of carbonyl groups of BMIs is as shown in Figure 4, 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 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 BMI chains. Hans Binder [11] 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 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. BMI molecules with even number of carbon atoms are tightly packed.

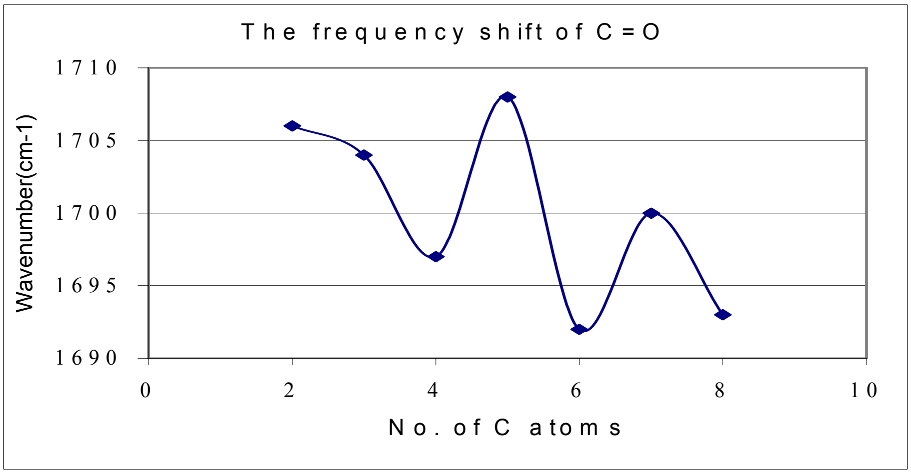


Fig. 4. Effect of the CH_2 on the frequency shift of C=O in BMI.

Figure 5 and Figure 6 show the effect of the odd or even number of carbon atoms on the frequency shift of C=O in 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 leaves a partial positive charge "$\delta+$" on the carbon and a matching partial negative charge "$\delta-$" 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 of 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-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 6 suggesting that the stability had reached a plateau for C >=6.

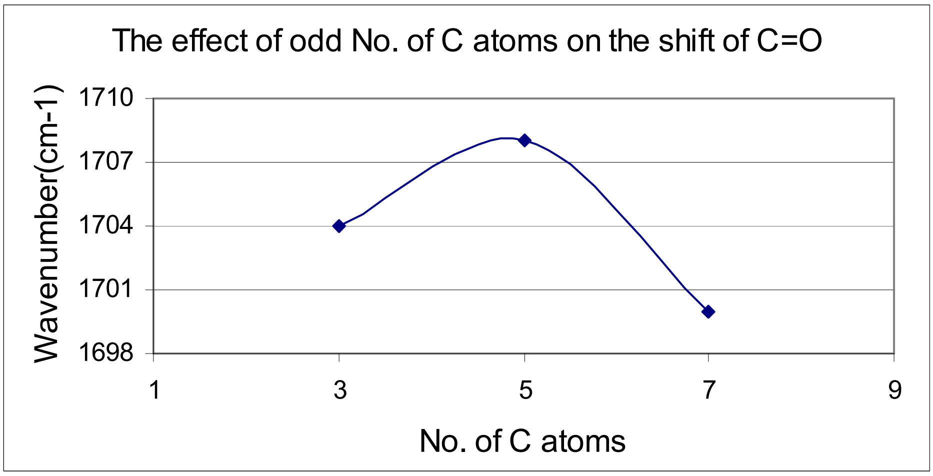


Fig. 5. Effect of the odd number of C on the frequency shift of C=O in BMI.

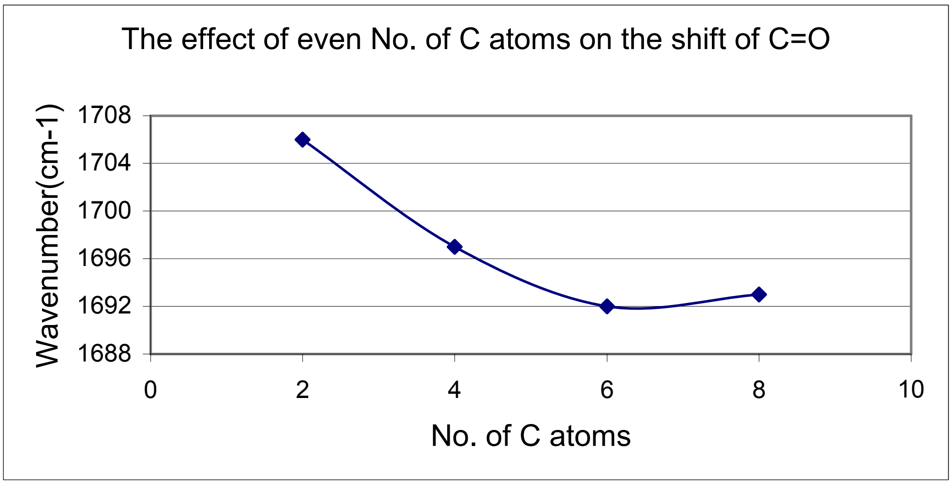


Fig. 6. Effect of the even number of C on the frequency shift of C=O in BMI

NMR analyses

The structures of 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 in line with work reported elsewhere [7]. The region of aliphatic carbons is around 25~40 ppm. The ^{1}H NMR ($CDCl_3$) showed a sharp singlet for BMIs at 6.7 ppm (4H, CH=CH) due to the proton of the double bond. ^{1}H NMR spectra are shown in Table 2.

Tab. 2. ^{1}H NMR chemical shift of the BMI functional group.

BMI	2	3	4	5	6	7	8
Double bond HC=CH (ppm)	6.7014	6.7223	6.6896	6.6834	6.6820	6.6832	6.6845

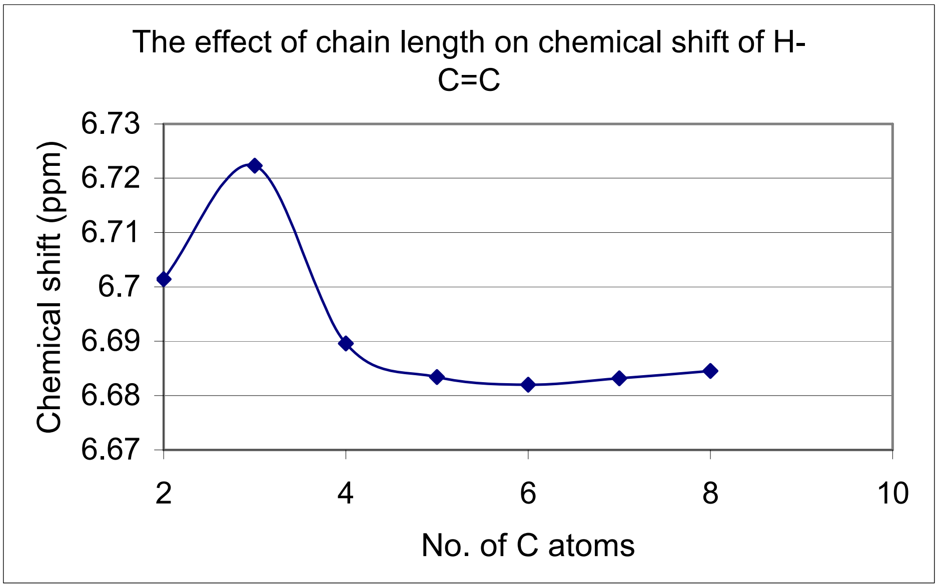


Fig. 7. Effect of the CH_2 on the chemical shift of H-C=C in BMI.

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 BMIs are shown in Table 2. It can be seen from Figure 7 that the aliphatic groups had a slight but noticeable effect on the chemical shifts of maleimide protons.

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, BMI should be more stable as the chain length increase. The chemical shift of BMI-3 is higher than that of other BMI suggesting that BMI-3 is more reactive.

DSC analyses of bismaleamic acids (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 BMAs were observed between 170°C & 191°C as shown in Figure 8. The effect of diamine chain lengths on the melting point of the corresponding bismaleamic acid is shown in Figure 9. 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. BMAs with even CH_2 sequences have higher Tm whilst those with odd sequences have lower Tm. Compounds with an even number of methylene spacers possess planar zigzag packing of the methylene chain while compounds with an odd number of methylene spacers possess non-planar zigzag packing which leads to a lower standard of packing [12]. The packing density tends to decrease for bismaleamic acid which has an odd number of flexible -CH_2- groups resulting in lower melting points. FTIR analysis shows that when CH_2 length is odd, the packing density is lower.

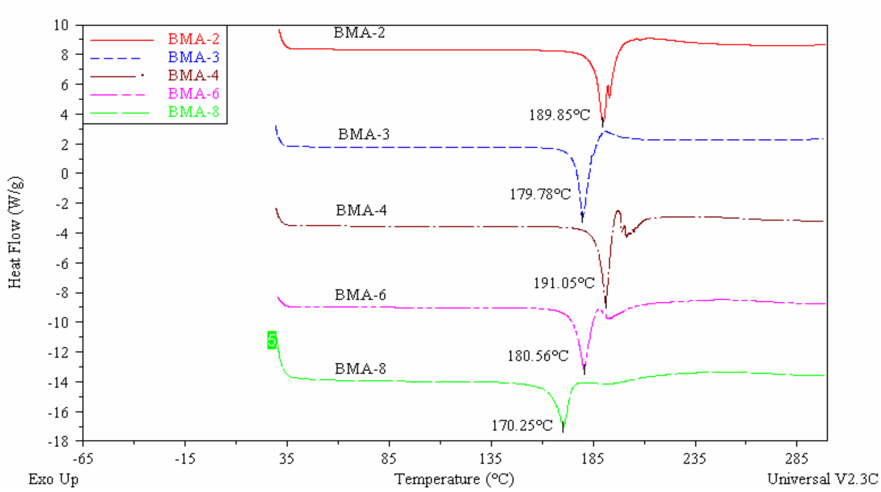


Fig. 8. DSC analysis of BMAs.

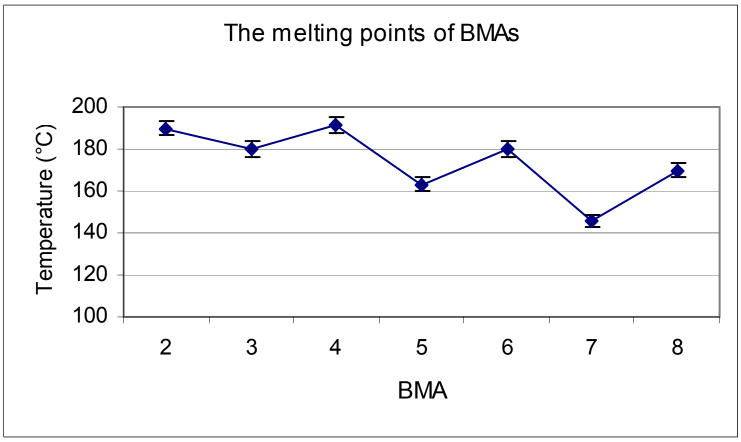


Fig. 9. The effect of chain length on melting points of BMAs.

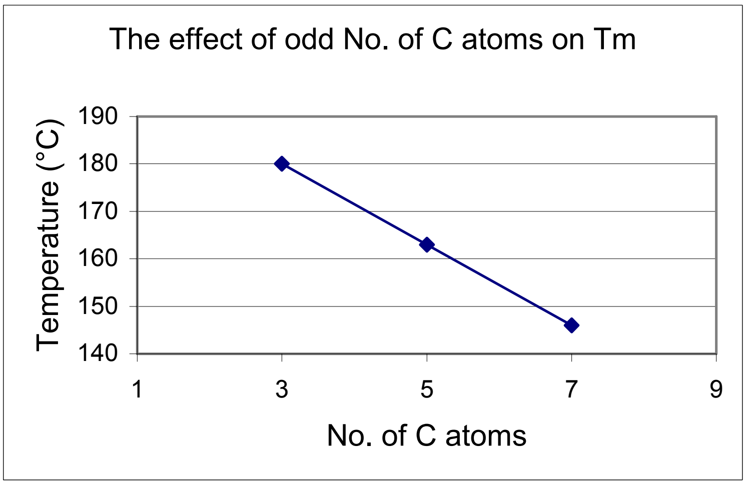


Fig. 10. Effect of the odd number of C on the melting point of BMAs.

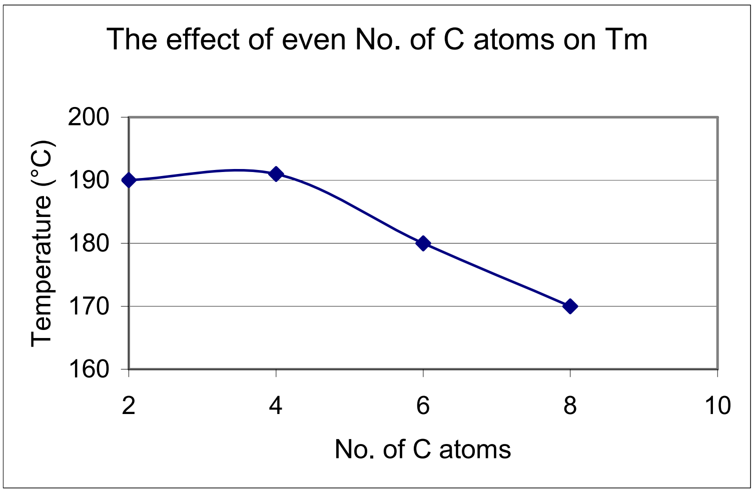


Fig. 11. Effect of the even number of C on the melting point of BMAs.

Figure 10 and 11 show the effect of odd even number of carbon atoms on melting points of BMAs. It is observed that the melting points of BMAs with both the odd and even numbers of methylene units decrease with the chain length increase. The Tm 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 BMAs decrease with the chain length increase.

The magnitude of decrease for the odd BMA is 34ºC (BMA-7~BMA-3), but the magnitude of decrease for the even BMA is 21ºC (BMA-8~BMA-4). Because even-numbered chains pack together in a uniform fashion more compactly than do odd-numbered chains, the change for even BMA is small. Figure 11 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 CH_2 sequence, but the forces tending to displace the heavy group must depend on the motions in the CH_2 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 11. Figure 11 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 points. 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.

DSC analyses of bismaleimides (BMIs)

The thermal and cure behaviour of all the BMI samples were investigated by DSC. The DSC profile of BMIs is shown in Figure 12. Figure 12 showed the endothermic behaviour due to melting of the solid BMI was observed in the lower temperature region and exthothermic peak in the higher temperature region. The obtained products exhibited one endothermic peak (T_m) due to the melting and one exothermic peak (Tp) due to the curing reaction. The initial thermal curing temperature is the onset temperature (To) of the exothermic peak. The melting, curing temperatures and reaction enthalpy of BMI are tabulated in Table 3.

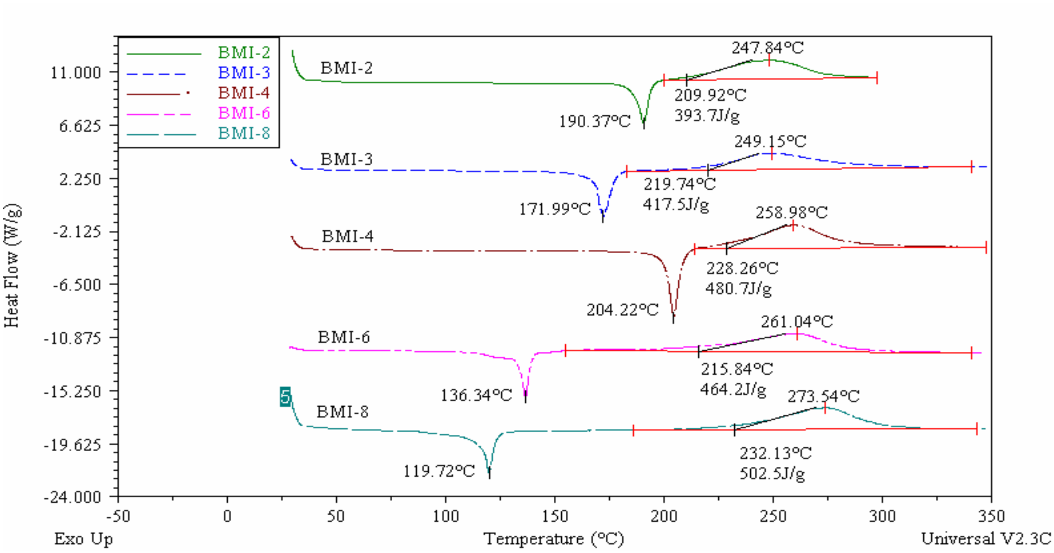


Fig. 12. The melting point and heat curing of BMI monomer.

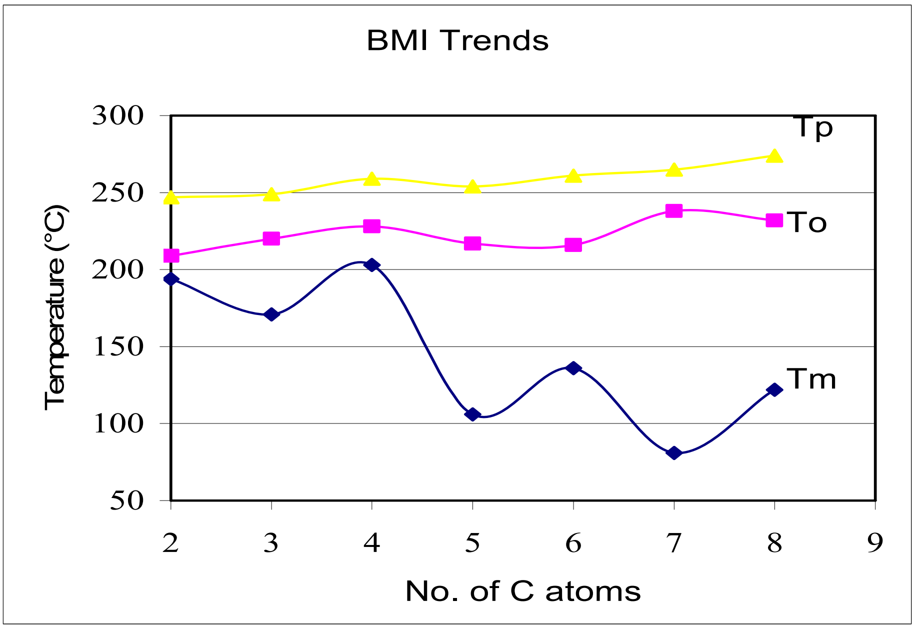


Fig. 13. The effect of chain length on melting points and curing temperatures.

The varying trends of melting point, curing temperature of BMI systems are displayed in Figure 13. It can be seen from Figure 13 that, in general, BMI systems having longer flexible -CH_2- groups have lower melting points. This is because the 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. 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 Tm in polypyromellitmides [12] and in BMI [4] individually. The odd or even number of 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 [12].

Tab. 3. Melting, curing temperatures and curing heat of 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

FTIR analysis found when CH_2 length 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 [4].

It is observed from Figure 13 that the polymerization onset temperatures (To) and the peak temperatures (Tp) of these BMIs increases with chain length increase. That is to say that the exotherm peak is shifted to a higher temperature as the backbone chain length increases. From FTIR and NMR analysis, this is because BMI should be more stable as the chain length increase.

Three structural features of the bismaleimide are known to affect the reactivity of bismaleimide oligomer [5]: (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. The FTIR and NMR analyses in this study have shown that the inductive effect has effect on the reactivity of BMI. BMI should be more stable as the chain length increase. 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 [3]. DSC analyses show the reverse phenomenon. BMI with long flexible chain has high reaction enthalpy and the activation energy. Based on this, it can be deduced that the mobility of the BMI oligomer is not the main factor that affect the reactivity of BMI oligomer. The third factor of steric effect can not be responsible for the differences in the reactivity of the BMI monomers because these are linear aliphatic chain.

Conclusions

In summary, the odd even effect and chain length affect the frequency shift of FTIR and NMR. It was found that when CH_2 length is odd, the packing density is lower. BMI-3,5,7 have odd number of carbons so that their melting points reduced most significantly. BMI should be more stable (less reactive) as the chain length increase.

Experimental part

Materials

Maleic Anhydride, 1,6-Hexanediamine, 1,8-Diaminooctane, Sodium Acetate, Acetic anhydride, Dimethylformamide, (all from Merck^{TM}, Germany), Ethylenediamine, (Fluka^{TM}) 1,3-Diaminaopropane, 1,4-Diaminobutane, 1,7-Diaminoheptane, (all from Aldrich^{TM}, Sigma-Aldrich) and 1,5-Diaminopentane, (TCI^{TM}, Japan) were used as received.

FTIR

FTIR analysis was carried out using a Nicolet 560 FTIR spectrometer. The bismaleimide groups were monitored by FTIR. The typical FTIR spectrum was shown in Figure 14: the vibrations of carbonyl (C=O) absorption at 1705cm^{-1}, ($-CH_2-$) bands between 2880 cm^{-1} and 2980 cm^{-1}, C=C-H of maleimide ring at 3100 cm^{-1}, 825 cm^{-1}, 691 cm^{-1} [6].

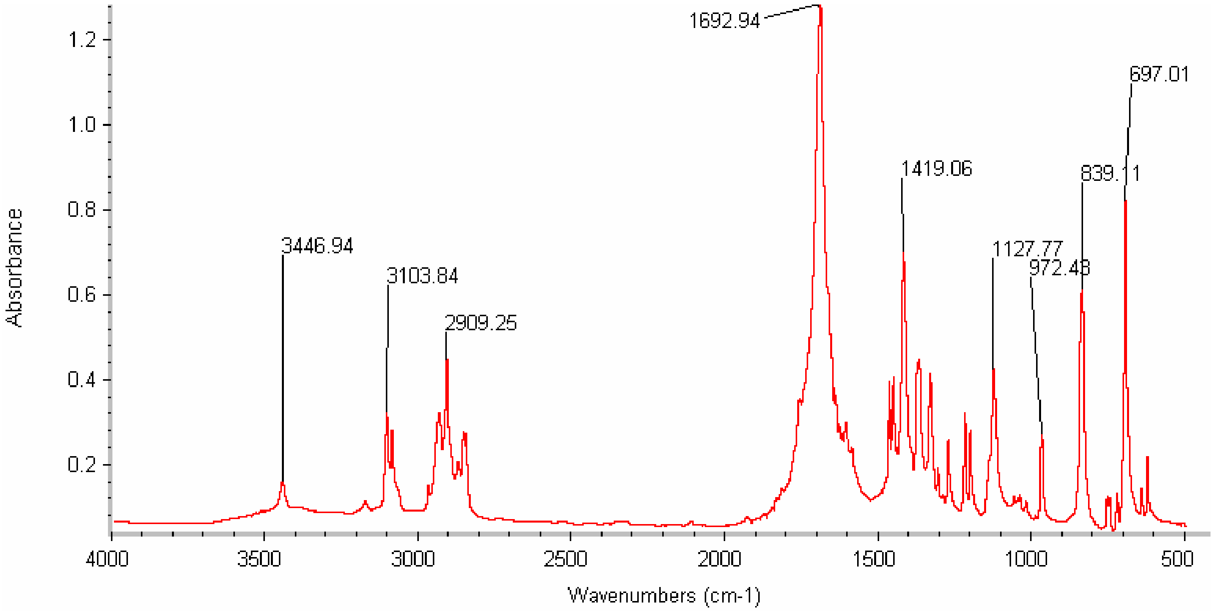


Fig. 14. FTIR spectrum of BMI-8.

Nuclear Magnetic Resonance (NMR) Spectroscopy

^{1}H and ^{13}C NMR were used to obtain 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 were obtained on a Bruker Spectrometer operating at 500 MHz. ^{1}H 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. The region of aliphatic carbons is around 0~60 ppm [7]. In the ^{1}H NMR spectra of BMI, a sharp singlet due to the proton of the double bond appeared at 6.7 ppm (4H, CH=CH) [4, 8].

Differential Scanning Calorimeter (DSC)

Differential Scanning Calorimeter (DSC) TA 2920 was used to monitor the properties of the samples. About 5 mg of sample was heated from room temperature (25°C) to 350°C at a heating rate of 10°C/min in nitrogen gas at a flow rate of 50 cm^3/min.

Synthesis of the BMI systems

The bismaleimides (BMI) were prepared by a two stage method [3, 9-10] shown in Scheme 1. 0.0795 mol of the diamine was dissolved in 150 ml of N,N-dimethylformamide (DMF) and added in a five-necked 500ml reaction flask equipped with a stirrer, a dropping funnel, a temperature controller, nitrogen inlet and a reflux condenser.

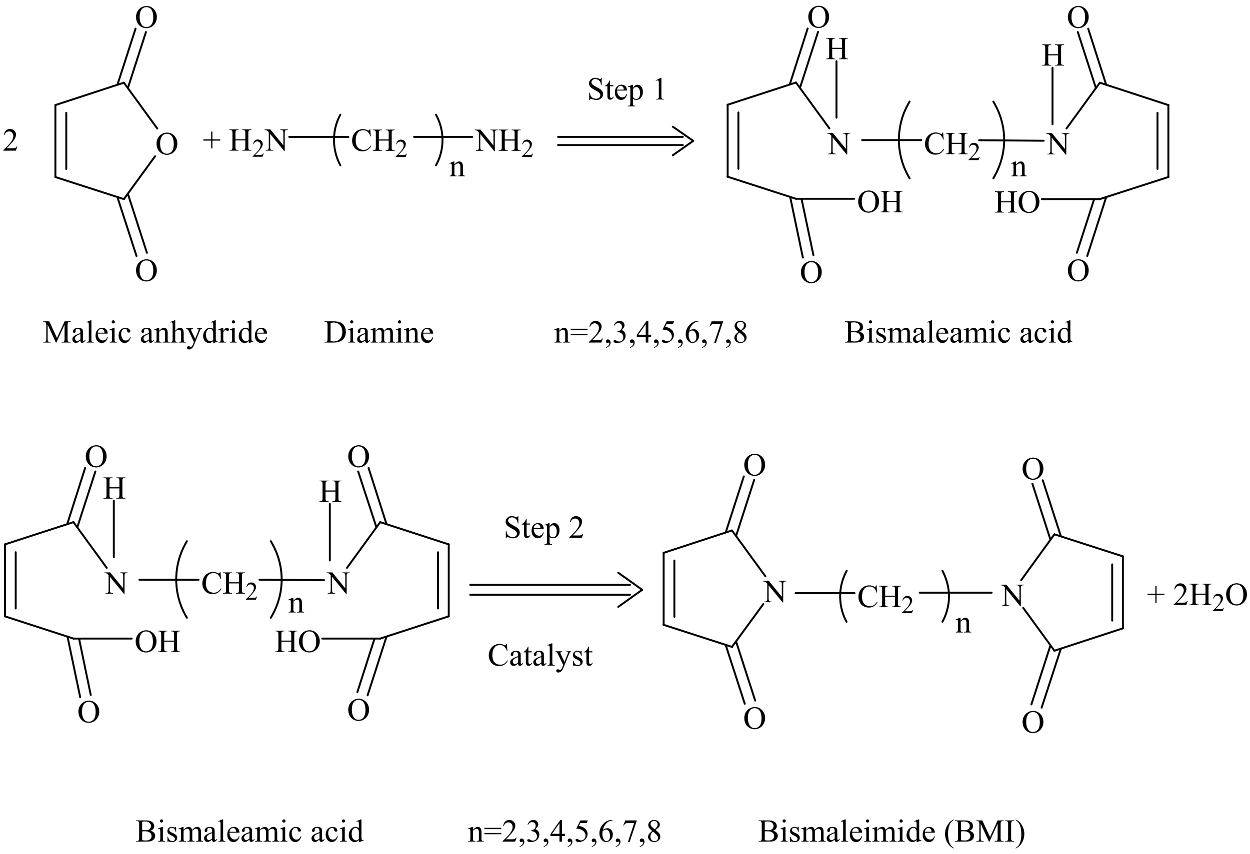
Tab. 4. BMA and BMI code and its main chain.

Bismaleamic acids (BMA)	Bismaleimides (BMI)	Main chain
BMA-2	BMI-2	$-(CH_2)_2-$
BMA-3	BMI-3	$-(CH_2)_3-$
BMA-4	BMI-4	$-(CH_2)_4-$
BMA-5	BMI-5	$-(CH_2)_5-$
BMA-6	BMI-6	$-(CH_2)_6-$
BMA-7	BMI-7	$-(CH_2)_7-$
BMA-8	BMI-8	$-(CH_2)_8-$

Tab. 5. ^{1}H NMR spectra and yield of BMI.

BMI	Yield (%)	^{1}H NMR spectra δ
BMI-2	47	3.75 (4H, 2CH_2)
BMI-3	46	3.5 (4H, 2CH2), 1.9 (2H, CH2)
BMI-4	53	3.5 (4H, 2CH2), 1.5 (4H, 2CH2);
BMI-5	43	3.5 (4H, 2CH2), 1.6 (4H, 2CH2), 1.3 (2H, CH2)
BMI-6	57	3.5 (4H, 2CH2), 1.5 (4H, 2CH2), 1.3 (4H, 2CH2)
BMI-7	56	3.5 (4H, 2CH2), 1.5 (4H, 2CH2), 1.3 (6H, 3CH2)
BMI-8	58	3.5 (4H, 2CH2), 1.5 (4H, 2CH2), 1.3 (8H, 4CH2)

The solution containing 0.159 mol of maleic anhydride in 150 ml of N,N-dimethylformamide(DMF) was added gradually by a dropping funnel over 5 minutes at room temperature. The solution was stirred at 50 °C for 2 h without catalyst and then lasted at 50 °C for 6 h under catalysts of sodium acetate (3.2g) and acetic anhydride (40ml). The solution was cooled to room temperature, removed most of DMF by the rotary evaporator and then added into the distilled water. The precipitate was collected, washed with $NaHCO_3$ and with distilled water for several times and dried by vacuum oven at 50°C for 48 hours. An off-white solid was obtained. According to the relative diamines, the synthesized bismaleimides were called BMI-2, 3, 4, 5, 6, 7, 8 and tabulated in Table 4. ^{1}H NMR spectra and yield are shown in Table 5.



Scheme 1. The formation of bismaleimides by two stage reaction.

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