

**SYNTHESIS OF SILICONE CONTAINING POLYBISMALEIMIDE
OLIGOMERS WITH DIFFERENT MOLECULAR WEIGHT AND THE
TOUGHNESS OF THEIR CURED RESINS**

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Abstract

A series of new polybismaleimide oligomers with different molecular weight have been synthesized via Diels-Alder(DA) reaction of 4,4'-(bismaleimidodiphenyl) methane and bis(2-furylmethoxy)diphenyl silane at first, then aromatization of above corresponding DA products. The prepared oligomers were characterized by FTIR, ¹HNMR, and the aromatization conditions were determined by FTIR and DSC. The solubility of the aromatized oligomers was tested. The relationship between aromatization time of the oligomers and the thermal stability of their cured resins was investigated, and the influences of the oligomer molecular weight on the thermal stability as well as the toughness of cured resins were also elucidated, respectively. The results indicated that introducing silicone into polybismaleimides can improve the toughness of their cured resins, and the toughness is subjected to the variation of oligomer molecular weight. Also the results revealed that both aromatization degree and molecular weight have influence on the thermal stability of cured resins.

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INTRODUCTION

Many efforts[1~3] have been spent on modifying bismaleimides by introducing silicone linkages into the backbone in order to improve their toughness. A well available way[4~5] of extending bismaleimides by silicone monomer, i.e., diphenylsilandiol, has been investigated in detail. Recently, it has been reported[6~7] that poly(siloxane-imide)s with unique properties could be prepared by Diels-Alder intermolecular polymerization of bismaleimides and bisfurans. Such polymers possess either the outstanding thermal stability assigned to the forming of imide ring after aromatization, or the enhanced processability attributed to the introduction of silicone linkages in the polymer backbone and the formation of unsymmetrical structure in such polyimides. Hence it should be valuable to synthesize polybismaleimide oligomers by this method for improving their processability and the toughness of their cured resins, moreover without sacrificing the thermal stability. Because the molecular weight of polybismaleimide oligomers may have influence on the properties of their cured resins, it merits synthesizing such oligomers with different molecular weight and investigating the influence of molecular weight on the properties of their cured resins, especially on the toughness of them. Furthermore, the aromatization degree of such oligomers may also have influence on the properties of cured resins. This paper described the investigation of synthesis of different molecular weight polybismaleimide oligomers bearing diphenyl silane linkages and the properties of their cured resins.

RESULTS AND DISCUSSION

Synthesis and Characterization of Polybismaleimide Oligomers

Polybismaleimide oligomers were prepared via Diels-Alder intermolecular reaction of bismaleimide and bisfuran at a moderate conditions, namely 72°C and normal pressure. Neither of the reactants could undergo self-polymerization under such conditions. Prepared oligomers were then aromatized in acetic anhydride for 4h to eliminate HO₂, polybismaleimide oligomers(1)-(6) were then prepared. Scheme 1 is the synthesis procedure.

Polybismaleimide oligomers(1)-(6) were characterized by FTIR and ¹HNMR. Fig.1 represents the typical one of IR spectra of them, Fig.2 is the corresponding ¹HNMR spectra. As considered the IR spectra, it was found that all the oligomers showed absorbance at 1770,1710,720cm⁻¹ assigned to imide structure and absorbance at 1000cm⁻¹ due to Si-O-C stretching. It was also observed that all oligomers exhibited absorption around 1660cm⁻¹ attributed to olefinic bond in maleimide ring and absorption around 1123cm⁻¹ derived from Si-Ph stretching. Comparison of the IR spectra before and after aromatization revealed that absorption intensity of 1600cm⁻¹ assigned to olefinic bond decreased after aromatization, while the absorption band around 1283cm⁻¹ due to C-O-C stretching disappeared. This demonstrates that the aromatization reaction has been completed. The ¹HNMR spectra of the corresponding oligomers were in accordance with their molecular structure, and the assignment of every absorption was marked in Fig.2. It could be observed that the absorption at the chemical shifts around 5.0~5.2ppm and 3.4~3.8ppm disappeared after the oligomers were aromatized. This evidence further demonstrates the completion of aromatization reaction.

Aromatization Time and Its influence on Thermal Stability of Cured Resins

Fig.3 is the IR spectra of oligomers after different aromatization time. It could be observed that the absorption band in 1283cm⁻¹ derived from C-O-C stretching decreased gradually when the aromatization time increased. It finally disappeared when the aromatization time reached 4h. In addition, the absorption band of 1600cm⁻¹ due to the olefinic bond in maleimide bridge ring structure reduced with the increasement of aromatization time. This was attributed to the disappearance of olefinic bond in bridge

ring during aromatization reaction.

Fig. 4 shows the DSC traces of the oligomers treated under different aromatization time. It could be found that the curing peak shifted to higher temperature. This may be due to the formation of the charge transfer complex between maleimide ring and bridge ring which could increase the reaction activity and lower the curing temperature. The olefinic bond in maleimide ring is electron-poor double bond, while it is electron-rich double bond in bridge ring due to the $p-\pi$ conjugated effect of bridge oxygen and olefinic bond. The $p-\pi$ conjugated structure in the bridge ring bestows more shared electrons on the olefinic bond and leads to the properties of olefinic bond being similar with that of vinyl ether compounds. It was well documented [8] that maleimide ring and vinyl ether could form weak charge transfer complex and could copolymerize in the control of charge transfer copolymerization. The formation of charge transfer complex in bismaleimide/vinyl ether compound resins could lower their curing temperature [9,10]. This phenomenon may also occur for the cure of non-aromatized polybismaleimide oligomers. With the increasement of aromatization time, the bridge rings gradually decreased, thus such complex concentration decreased, until disappeared when the aromatization time reached 4h. This resulted in the DSC traces shifted to higher temperature. The curing enthalpies of oligomers are -218.8J/g, -173.3J/g, -156.6J/g, -156.2J/g corresponding to different aromatization time of 0, 2, 4, 6h, respectively, thus the aromatization degree can be calculated as 0%, 72.7%, 99.4% and 100% accordingly.

Table 1 lists the TGA data of cured resins derived from the oligomers with different aromatization time. The results indicated that the thermal stability of cured resins increased with increasement of aromatization time, and it tended to become constant when the aromatization time surpassed 4h. The thermal stability of cured resins after aromatization was higher than that before aromatization. This demonstrates that increasement of aromatic imide structure can elevate the thermal stability of the cured resins.

Solubility of Polybismaleimide with Different Molecular Weight

Six solvents were selected to test the solubility of oligomers with different molecular weight. Table 2 is the determining results. It was found that the oligomers could dissolve in low boiling point solvent, such as acetone or tetrahydrofuran. This demonstrates that introduction of silicone linkage and unsymmetrical imide structure can

improve the solubility of oligomers. It could also be observed that the solubility of oligomer(2) and (3) is the best out of six oligomers. This was perhaps due to the combined effects of silicone content and molecular weight in these oligomers. The increasement of molecular weight would decrease the solubility of the oligomers in low boiling point solvents, while the increasement of silicone content would do in an opposite way. In addition, all the oligomers showed better solubility than 4,4'-(bismaleimidodiphenyl)methane, this further demonstrates that introduction of silicone linkage and unsymmetrical imide structure can elevate solubility of oligomers.

Thermal Stability of Cured Resins from Polybismaleimide Oligomers with Different Molecular Weight

Table 3 exhibits the TGA data of different oligomers after curing. The TGA data presented that oligomer(4) cured resin showed the best thermal stability, and the thermal stability from oligomer(1) to (4) cured resins showed the increasing trend, but it dropped from oligomer(4) to (6) cured resins. Because the thermal stability of cured resins is associated with the crosslinking density and the thermal stable structure content, thus with the increasement of molecular weight the crosslinking density abated from oligomer(6) to (1) cured resin, while the aromatic imide structure which is thermal stable unit increased, this combined effect of two factors resulted in above variation of the thermal stability. It is worthy noting that all the cured resins from oligomer(1) to (6) exhibited better thermal stable than that of 4,4'-(bismaleimidodiphenyl)methane. This demonstrates that synthesizing polybismaleimide oligomers via Diels-Alder reaction is a feasible way to obtained outstanding thermal stable resins.

Impact Strength of Cured Resins from Oligomers in Different Molecular Weight

The Charpy impact strength vs. reactant molecular ratio of bismaleimide and bisfuran is illustrated in Fig.5. The results showed that all cured resins possessed higher toughness than that of BMI, and the impact strength of the highest one could attain about 4 times as much as that of BMI cured resin. This elucidated that such molecular design by introducing silicone linkage and increasing aromatic imide structure was a available way to improve the toughness of bismaleimide cured resins. It was also observed from Fig.5 that there existed a maximum for impact strength. This confirmed that the molecular weight of the oligomers had an important role on the toughness of the

cured resins, but increasement of oligomers molecular weight didn't not always elevate the toughness of them.

For further elucidating above toughness variation, the fracture morphology of cured resins from oligomer(1) to (6) was observed by SEM. Fig.6 depicts the SEM observation. The impact fracture of cured resin of oligomer(5) showed conspicuous brittle fracture, while it exhibited partial ductile fracture for that of oligomer(4). However the fracture morphology turned into ductile fracture for the cured resin of oligomer(3) and it presented yielding flow to some extent for that of oligomer(2). The variation of fracture surface for cured resins of the oligomers with different molecular weight matched that of impact strength when the feed molecular ratio of bisfuran and bismaleimide was less than 2:3. It was interesting to observe that there existed many microcravations in the fracture surface when the feed molecular ratio reached to 3:4. These pre-existed microcravations were perhaps derived from the high viscosity of melted oligomers which prevent the air in them from escaping. The pre-existed microcravations may cause stress remained in the matrix , which yielded the drop of the impact strength.

CONCLUSIONS

Based on the view of molecular design, a series of new polybismaleimide oligomers bearing silicone linkage and unsymmetrical aromatic imide structure were synthesized by Diels-Alder intermolecular reaction of bismaleimide and bisfuran. Such synthesis procedure introduced both silicone linkage and aromatic imide structure into polybismaleimide oligomers and could either improve the solubility of them or modify the toughness of their cured resins. The oligomer cured resins exhibited outstanding thermal stability as compared with pure BMI cured resin. The molecular weights of the oligomers have great influence in their properties of their corresponding cured resins.

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Table 1 The TGA data of the cured resins derived from the oligomer(4) at different aromatization time

Aromatization time (hr)	TGA(°C) in air		
	T _i	T ₅	T ₃₀
0	316.4	376.2	448.3
2	376.7	386.7	502.2
4	386.7	406.7	540.0
6	380.0	405.0	540.3

T_i: temperature of initial weight loss; T₅: temperature of 5% weight loss; T₃₀: temperature of 30% weight loss

Table 2 The solubility of polybismaleimide oligomers at 25°C

Solvents	Oligomers					
	(1)	(2)	(3)	(4)	(5)	(6)
NMP	Sol	Sol	Sol	Sol	Sol	Sol
DMF	Sol	Sol	Sol	Sol	Sol	Sol
THF	Sol	Sol	Sol	Sol	Sol	Sol
Acctone	Sol	Sol	Sol	Sol	Sol	PS
GME	PS	Sol	Sol	PS	PS	IS
Ethyl acetate	IS	IS	IS	IS	IS	IS

NMP: N-methyl-2-pyrrolidone; DMF: N,N'-dimethyl formamide; THF: tetrahydronfuran; GMF: glycol monomethyl ether

Sol: soluble; PS: partial soluble; IS: insoluble

Table 3 The TGA data of cured resins derived from the
polybismaleimide oligomers with different molecular weight

Oligomers	TGA(°C) in air		
	T _i	T ₅	T ₃₀
(1)	352.3	366.8	496.5
(2)	364.5	374.9	503.8
(3)	376.7	393.4	541.6
(4)	400.1	413.6	580.2
(5)	393.9	409.1	557.9
(6)	391.6	403.7	535.8
(7)*	337.9	360.5	527.9

T_i: temperature of initial weight loss; T₅: temperature of 5% weight loss; T₃₀:
temperature of 30% weight loss

* the cured resin of 4,4'-bismaleimidodiphenylmethane

Figures legend:

Fig.1 The IR spectra of polybismaleimide oligomer(4)

Where: (a) before aromatization; (b) after aromatization

Fig.2 The ¹HNMR spectra of polybismaleimide oligomer(4)

Where: (a) before aromatization; (b) after aromatization

Fig.3 The IR spectra of polybismaleimide oligomer(4) in different aromatization time

Where the aromatization time is: (a) 0 hr; (b) 2 hr; (c) 4 hr; (d)6 hr

Fig.4 The DSC traces of polybismaleimide oligomer(4) in different aromatization time

Where the aromatization time is: (a) 0 hr; (b) 2 hr; (c) 4 hr; (d)6 hr

Fig.5 The impact strength vs. the feed molecular ratio of bisfuran and bismaleimide

Fig.6 The fracture morphology of cured resins

Where the cured resins are derived from: (a) oligomer(5); (b) oligomer(4); (c)oligomer(3); (d) oligomer(2)

Scheme 1 The synthesis procedure of polybismaleimide oligomers

Where the feed molecular ratios of bismaleimide and bisfuran are: (1) 1:1; (2) 4:3; (3) 3:2; (4) 2:1; (5) 3:1; (6) 4:1, the molecular weight decreases from oligomer(1) to (6)

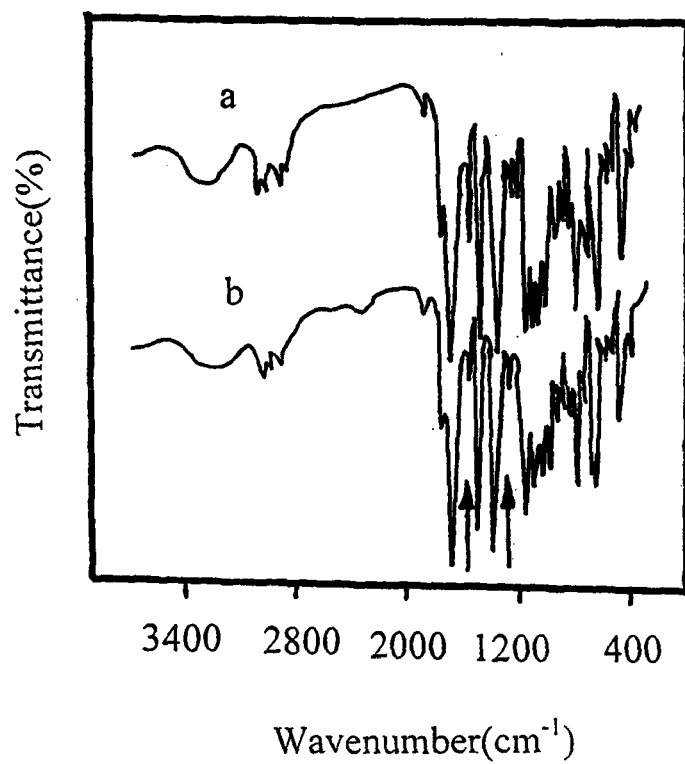


Fig.1

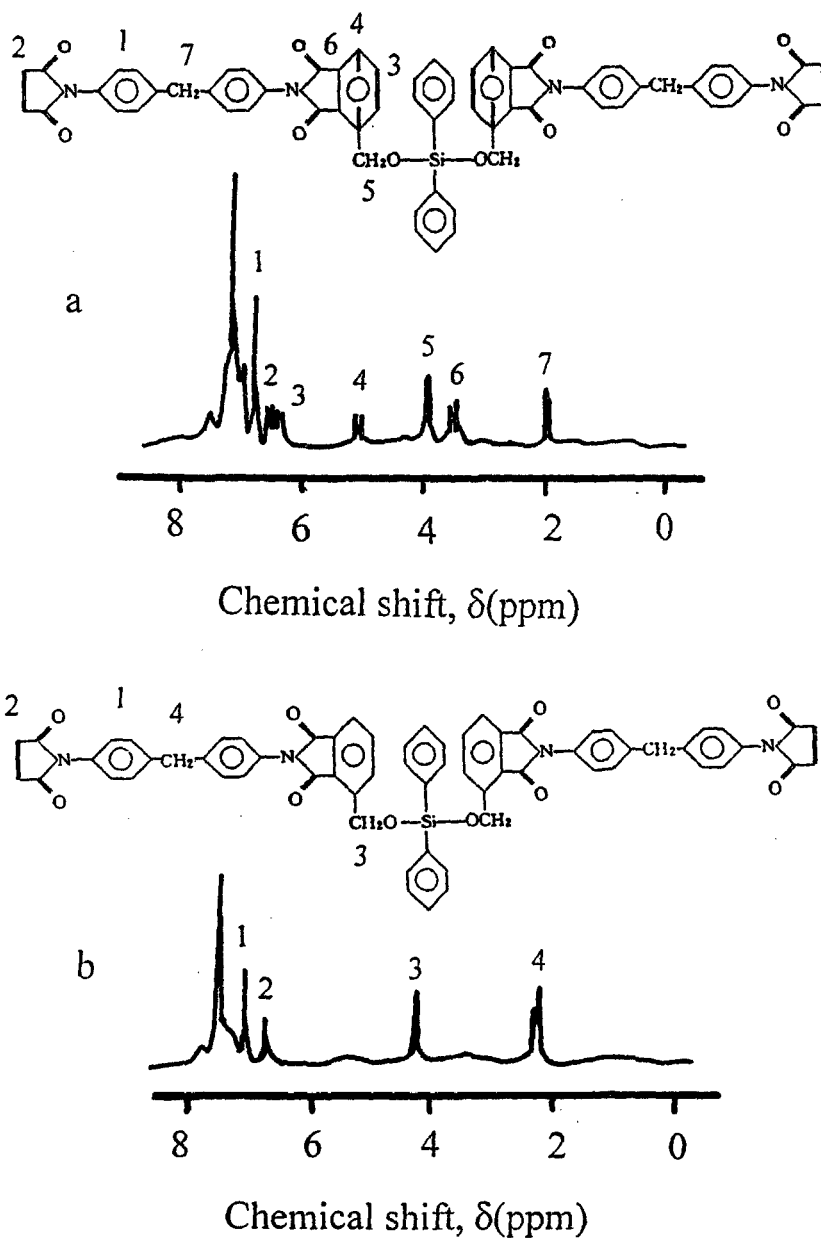


Fig.2

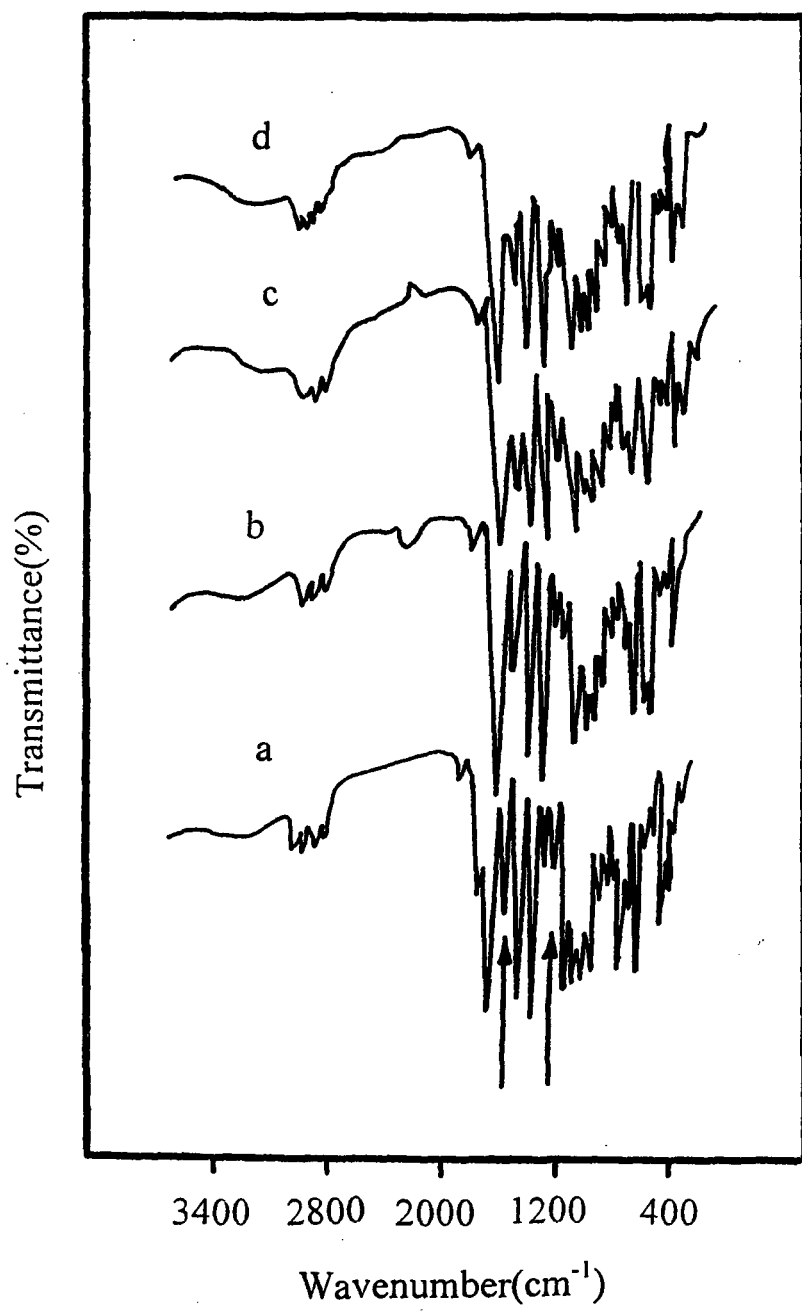


Fig.3

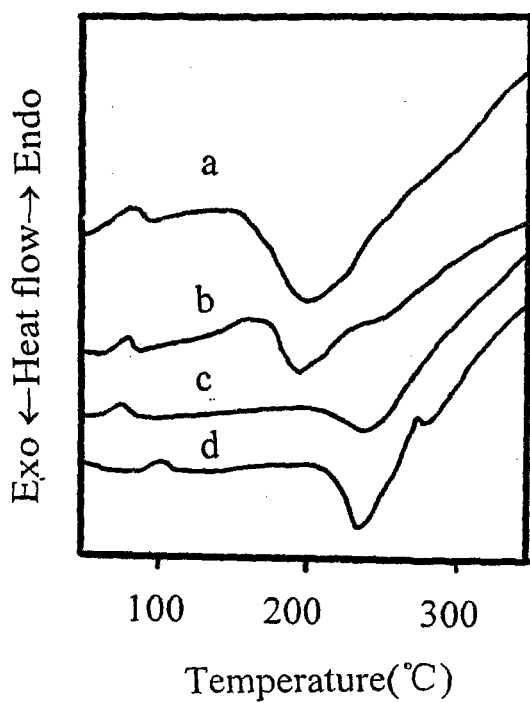


Fig.4

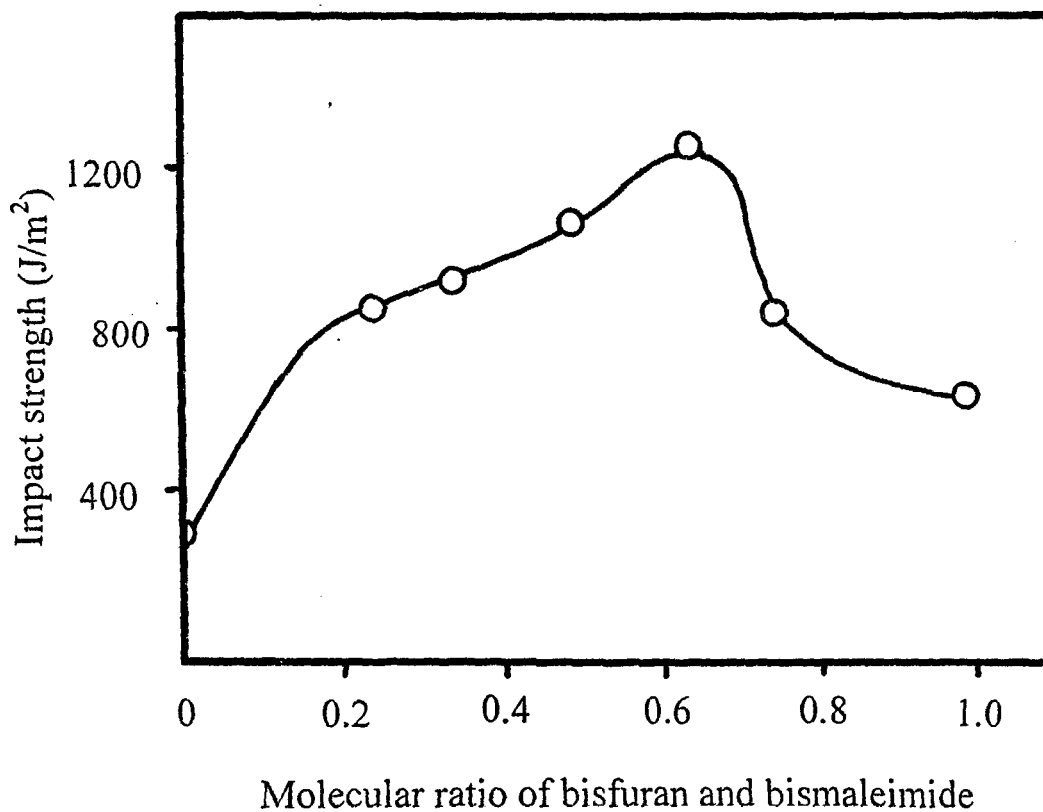


Fig.5

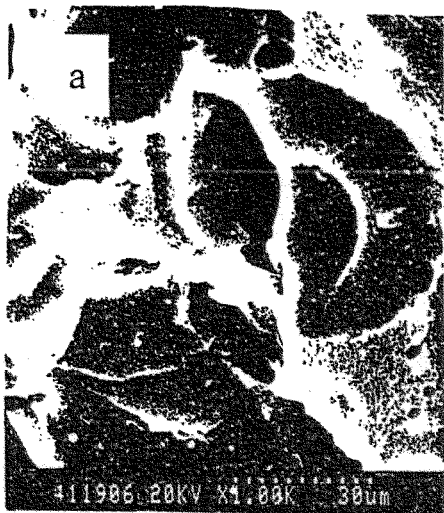
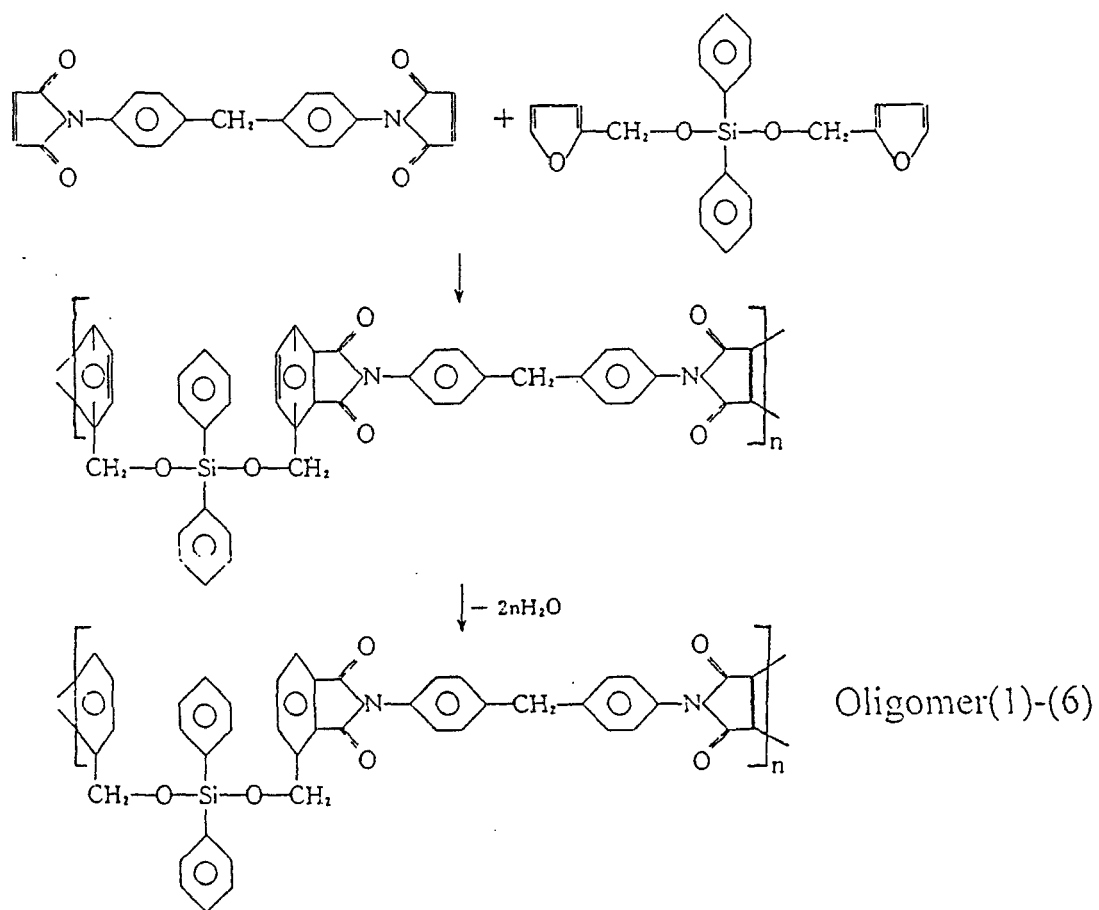


Fig.6



Scheme 1