

Synthesis and Characterization of New Bismaleimides Bearing Silicone Linkages

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SYNOPSIS

A series of new bismaleimides bearing silicone linkages have been prepared via Diels – Alder reaction of silicone containing bismaleimides and silicone containing bisfuran compounds. The prepared bismaleimides were characterized by FTIR, NMR as well as elemental analysis, the curing behavior of the bismaleimides and thermal – oxidative stability of their cured resins were investigated by DSC and TGA. The solubility of the bismaleimides were also investigated. The results reveals that prepared bismaleimides can dissolve in low boiling point solvents, and their curing temperatures are in range of 206.4 ~ 285.2°C. The DSC and TGA traces of cured resins demonstrated that the cured resins possess the glass transition temperature in range of 286.7 ~ 331.0°C, and they are stable up to 353.3 ~ 384.1°C.

Keywords: Bismaleimide * Silicone linkages * Diels – Alder reaction * synthesis * Characterization.

INTRODUCTION

Many efforts ^[1~3] had been spend on modifying bismaleimide by introducing silicone linkage into the backbone of polybismaleimide in order to improve its

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brittleness at break. A well available way ^[4-5] of extending bismaleimide by silicone monomer, diphenylsilanediol, had 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 enhancable processability attributed to the introducing of silicone linkages and the forming of unsymmetrical structure in such polyimides. Hence it should be valuable to utilize this method in synthesizing chain - extending bismaleimides for improving processability and toughness without sacrificing thermal stability. However, so far it has not been paid sufficient attention. Especially synthesizing bismaleimide bearing silicone linkages from Diels - Alder reaction of silicone containing bismaleimide and silicone containing bisfuran has not yet been reported. Present paper is the investigation on synthesis and characterization of such new bismaleimides bearing silicone linkages. The main objective of preparing such bismaleimides is expected to bestow attractive properties like enhanced processability, low water up - take as well as excellent thermal stability on bismaleimides by introducing more flexible Si - O linkages and aromatic rings into molecular backbone.

RESULTS AND DISCUSSION

Synthesis of Bismaleimides Bearing Silicone linkages

Bismaleimides bearing silicone linkages were prepared via Diels - Alder reaction of silicone containing bismaleimides ((1) ~ (4)) and silicone containing bisfurans ((5) ~ (6)). Prepared products were then eliminated H₂O to complete aromatization, and aromatized bismaleimides bearing silicone linkages (ABBS₁₋₆) were obtained in high yields. Scheme 1 is the procedure of synthesis.

Solubility of ABBS₁₋₆

Six solvents were selected to test the solubility of ABBS₁₋₆. The test way was that 0.5g ABBS₁₋₆ added into 5ml solvent. Table 1 is the determining results for

solubility of ABBS₁₋₆. It is found that ABBS₁₋₆ can dissolved either in high boiling point and polarized solvents or in low boiling point solvents, such as acetone. As compared with 4, 4' - bismaleimidodiphenylmethane which does not have good solubility in low boiling point solvents, ABBS₁₋₆ owned enhacable solubility in low boiling point solvent due to lowering solubility parameter by introducing silicone linkages into backbone.

Table 1 The solubility of ABBS₁₋₆ at ambient temperature

Solvents	Compounds					
	ABBS ₁	ABBS ₂	ABBS ₃	ABBS ₄	ABBS ₅	ABBS ₆
NMP	Sol	Sol	Sol	Sol	Sol	Sol
DMF	Sol	Sol	Sol	Sol	Sol	Sol
THF	Sol	Sol	Sol	Sol	Sol	Sol
Acetone	Sol	Sol	Sol	Sol	Sol	Sol
GME	Sol	Sol	Sol	Sol	Sol	Sol
Ethyl acetate	Sol	PS	Sol	PS	Sol	PS

NMP, N - methyl - 2 - pyrrolidone; DMF, N, N' - dimethyl formamide; THF, tetrahydronfuran; GMF, glycol monomethyl ether; Sol, Soluble; PS, Partial soluble

Curing Behavior of ABBS₁₋₆ and Glass Transition Temperatures of Their Cured Resins

Table 2 is DSC determining data of ABBS₁₋₆ and their cured resins. It is obvious that all prepared bismaleimides don't have melting point which is indictive of no crystal existed. Bismaleimides were cured by addition - type reaction of the maleimide olefinic bonds to form crosslinked resins. The DSC data of all bismaleimides showed an exotherm in the temperature region of 206.4 ~ 285.2°C assigned to the thermally induced polymerization reactions. Comparison of curing

temperatures of ABBS₁₋₄ revealed that the polymerization of bismaleimides was shifted to high temperatures as side groups of aromatic ring joined to silicon atom increased. The same comparison for ABBS₅₋₆ elucidated that introducing of meso aromatic ring in molecular backbone could low curing temperature, while introducing of diphenyl stiff structure would bring opposite result. It is note that ABBS₁₋₄ show lower curing temperatures as compared with ABBS₅₋₆. This may be due to introducing of meso aromatic ring or diphenyl structure can increase the backbone length of bismaleimides and reduce the concentration of the maleimide olefinic bonds. In respect to the T_{exo} values, the relative reactivity of ABBS₁₋₆ for curing reactions decreased in the following order:

Table 2 DSC data of ABBS₁₋₆ and their cured resins

Compounds	DSC(°C) N ₂			
	T _i	T _{exo}	T _t	T _g
ABBS ₁	215.0	246.7	269.4	315.7
ABBS ₂	215.0	253.3	271.2	320.6
ABBS ₃	206.4	235.3	262.7	286.7
ABBS ₄	210.8	237.2	266.9	291.7
ABBS ₅	220.7	258.5	281.5	299.0
ABBS ₆	225.3	260.2	285.2	331.0

T_i—initial polymerizing temperature; T_{exo}—exothermic peak temperature; T_t—polymerizing termination temperature; T_g—glass transition temperature.

$$6 > 5 > 2 > 1 > 4 > 3$$

The glass transition temperatures of cured ABBS₁₋₆ listed in table 2 showed that increasing in side groups of aromatic ring joined to silicon atom would increase the stiffness of polymer and result in increasing of glass transition temperatures. So did introducing stiff diphenyl structure to backbone of bismaleimide cured resins,

while it would result in opposite effect for introducing meso aromatic ring to backbone of bismaleimide cured resins. This demonstrated that dimethyl silane linkages behaved more flexibility than diphenyl silane linkages because of the small side methyl groups enable the dimethyl silane linkages to rotate easy. It also elucidated that meso aromatic ring in main chain could lowered the stiffness of molecular backbone which resulted in the drop of glass transition temperature.

Thermal – Oxidative Stability of Cured ABBS₁₋₆

Table 3. TGA data of cured ABBS₁₋₆

Cured resins	TGA (°C)			
	Air			
	T _i	T ₅	T ₃₀	T ₅₀
ABBS ₁ *	371.7	393.3	541.7	672.9
ABBS ₂ *	353.3	381.3	543.8	690.2
ABBS ₃ *	384.1	403.2	553.3	602.8
ABBS ₄ *	380.0	400.0	525.8	621.5
ABBS ₅ *	371.3	390.3	540.2	605.3
ABBS ₆ *	374.5	392.1	541.1	604.2

T_i—Temperature of initial weight loss

T₅—Temperature of 5% wt weight loss

T₃₀—Temperature of 30% wt weight loss

T₅₀—Temperature of 50% wt weight loss

The crosslinked resins were obtained after thermal curing of ABBS₁₋₆ at 250°C for 10h, and they are referred to by the notations ABBS₁₋₆*, respectively. Their thermal – oxidative stability was determined by TGA in air atmosphere. The temperatures at different weight loss were tabulated in table 3. Comparison of initial weight loss temperatures for ABBS₁₋₄* reveals that the cured resins bearing

more Si - CH₃ linkages exhibit higher thermal - oxidative stability. This may be due to the appearance of Si - CH₂· radical resulting from long time heating at 250°C lead to further crosslinking and increase the crosslinking density of cured resins^[2]. As compares 50% wt weight loss temperatures for ABBS₁₋₄^{*}, the cured resins bearing more Si - Ph linkages show more thermal - oxidative stability. This demonstrates that introducing Si - Ph can elevate the thermal - oxidative stability of cured resins at the later stage of weight loss. On the other hand, the initial weight loss temperatures of ABBS₅₋₆ is close to ABBS₁^{*} and lower than ABBS₃₋₄^{*}, meanwhile the 50% weight loss temperatures of them is close to ABBS₃^{*}. Because the backbone length of ABBS₅₋₆^{*} is longer than that of ABBS₁₋₄^{*}, ABBS₅₋₆^{*} can obtain lower crosslinking density which results in the lower initial weight loss temperature; while the linkages of ABBS₅₋₆^{*} is mainly consist of Si - CH₃, so the 50% weight loss temperature of them is more close to ABBS₃^{*}. Finally, it can be elucidated that the initial decomposition temperature for these resins is mainly affected by crosslinking density, while the thermal - oxidative stability of them at the later stage of weight loss is mainly affected by the content of Si - Ph linkages.

CONCLUSIONS

Based on molecular design, new bismaleimides bearing silicone linkages (ABBS₁₋₆) were prepared via Diels - Alder reaction. Prepared bismaleimides possess either enhanced solubility in low boiling point solvents or good thermal - oxidative stability. The properties of prepared bismaleimides and their cured resins were dependent on the type of silicone linkages. It was demonstrated that increasing in content of Si - CH₃ linkages could enhance the solubility of prepared bismaleimides in low boiling point solvents, increase curing reaction activity of them and thermal - oxidative stability of their cured resins at initial decomposition stage. It was also elucidated that increasing in Si - Ph linkages can enable the cured resins more thermal - oxidative stability at the later stage of weight loss.

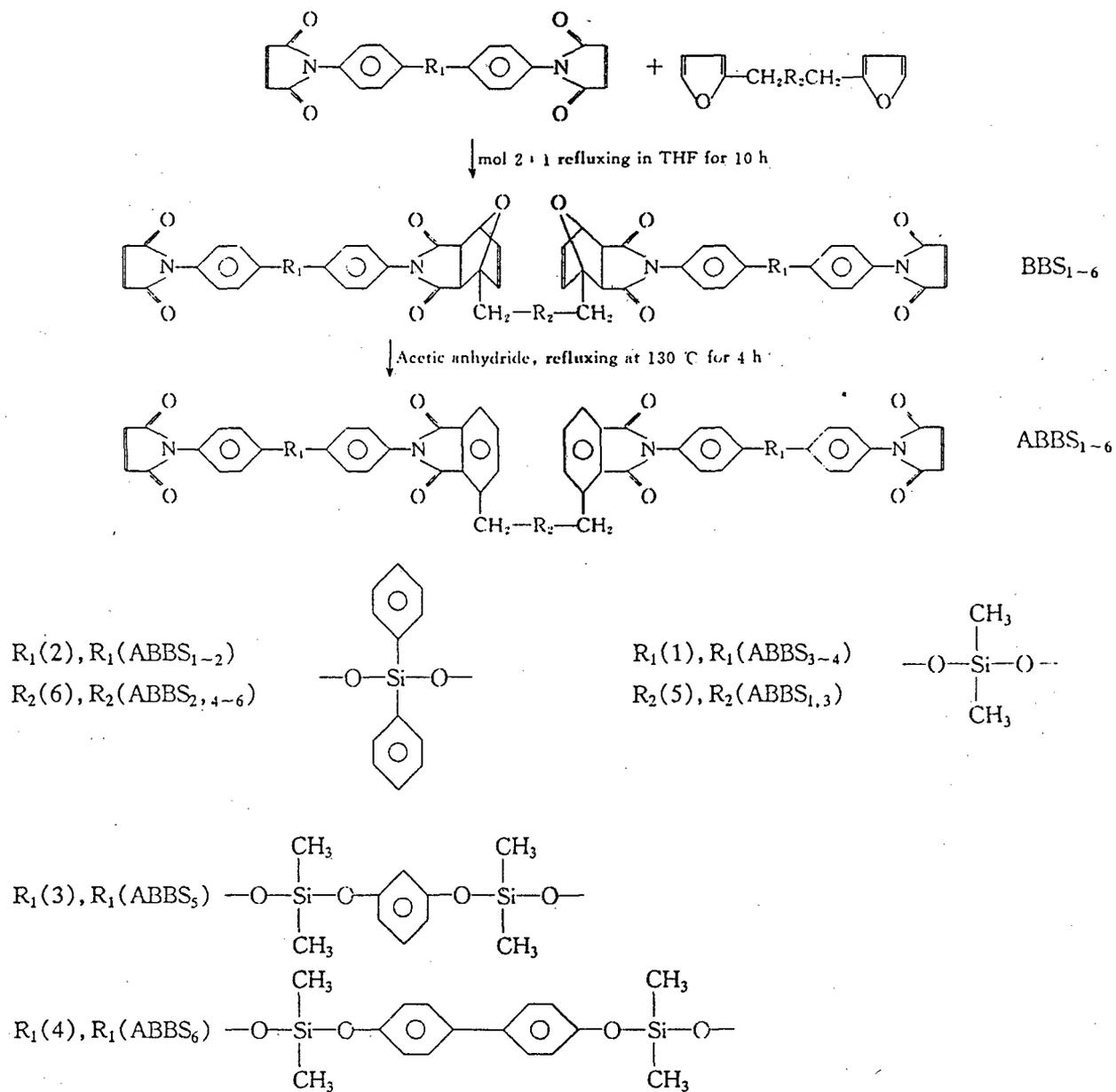
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Scheme 1 Synthesis of bismaleimides bearing silicone linkages (ABBS₁₋₆)