Fluorenyl Cardo Bismaleimides Ⅰ: Synthesis, Characterization

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Abstract

Three novel fluorenyl Cardo Bismaleimides containing imide structure were synthesized by reacting maleic anhydride with fluorenyl Cardo diamine and different dianhydride. These bismaleimides were characterized by IR spectra (FT-IR), ^{1}H-NMR and elemental analysis. Thermal cure of these fluorenyl Cardo bismaleimides was studied. The thermal properties of these polymers were characterized by differential scanning calorimentry (DSC) and thermogravimetry analysis (TGA). The results show that the bismaleimides containing imide structure improve the solubility of cardo bismaleimides in organic solvents without sacrificing thermal properties.

Keywords: Fluorenyl Cardo bismaleimides; imide structure; thermal stability

Introduction

In recent years, bismaleimide (BMI) resins as high-performance thermosetting resins have been widely used as matrices for advanced composites. They possess many desirable properties, such as high tensile strength and modulus, excellent chemical , corrosion resistance, and hot/wet performance [1-4]. The introduction of fluorenyl "Cardo" groups into polymers such as polyimides[5-11], polyamides[12,13], polyquinolines[14]can endow with the specific properties: (1)excellent heat resistance; (2)excellent solubility. The fluorenyl Cardo polymers were widely used as matrices for advanced composites, microelectronic materials and processable polyimides.

The fluorenyl Cardo Bismaleimides have excellent heat-resistance, high char yield, high the limited oxygen index(LOI) and good flameproofing[15]. But the bismaleimide prepared by 9,9-bis(4-amino phenyl)fluorene(BAFL) has poor solubility in a majority of polar solvents such as chloroform, tetrahydrofuran (THF),N-methyl-2-pyrrolidinone(NMP), N,N-dimethylacetamide (DMAc) etc and this bismaleimide has a high melting point (>300 °C).therefore, it has a poor processabiliy. In the previous study [16], the bismaleimides containing imide structure have less brittle compared with those original bismaleimides because of extended polymer chain without sacrificing thermal properties.

In the present research, a series of novel fluorenyl cardo bismaleimides with imide structure were synthesized and characterized by IR, ^{1}H-NMR, elemental analysis. These bismaleimide monomers have an excellent solubility in various organic solvents. The thermal properties of the cured products of these bismaleimides were characterized by differential scanning calorimentry(DSC) and thermogravimetry analysis (TGA).

Experimental section

Regents and Solvents

9,9-bis (4-aminophenyl)fluorine (BAFL), 4,4'-oxydiphthalic anhydride (Shanghai Research Institute of Synthetic Resins), 3,3',4,4'-benzophenonetetracarboxylic dianhydride (obtained from Daicel), maleic anhydride (Shanghai Shiyi Chemicals reagent Co., Ltd., recrystallized in acetic anhydride before use), DMAc were dried in CaH_2 for 2 days and distilled before use.

Bismaleimides synthesis

In a 250 ml four-necked flask with a nitrogen inlet, a thermometer, a condenser and a mechanical stirrer, 17.4g (0.05mol) of 9,9-bis(4-aminophenyl)fluorene was dissolved in N,N-dimethylacetamide (DMAc), the solution of 10g (0.05mol) maleic anhydride in DMAc was added dropwise with an ice bath and constant stirring. The solution was stirred for about 3hrs, then 0.05mol dianhydride was added directly and carried out for about 3hr.then, a mixture of acetic anhydride and potassium acetate was added at ambient temperature and carried out for 1hr and 60°C for 4 hrs. And the reaction solution was precipitated in a large of waters. Bismaleimide powder was obtained. (Fig.1)

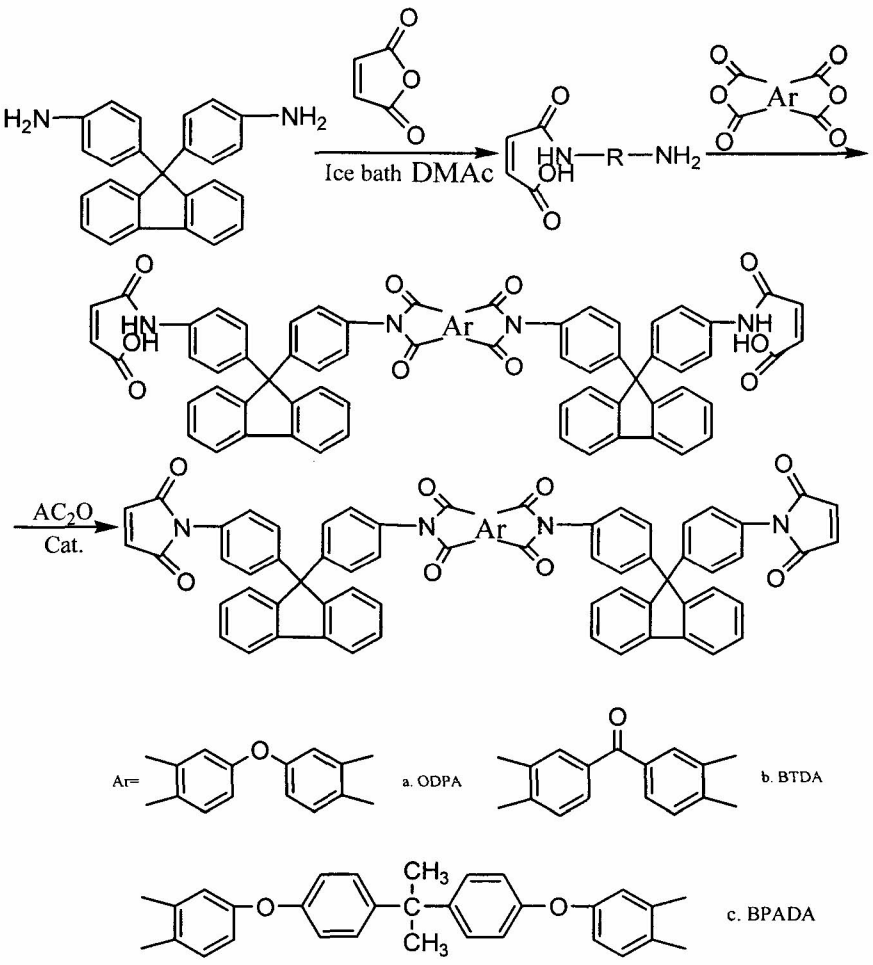
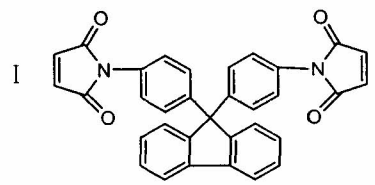
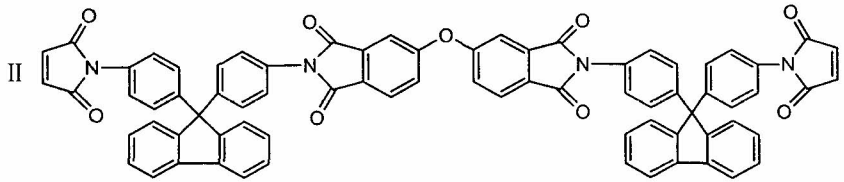


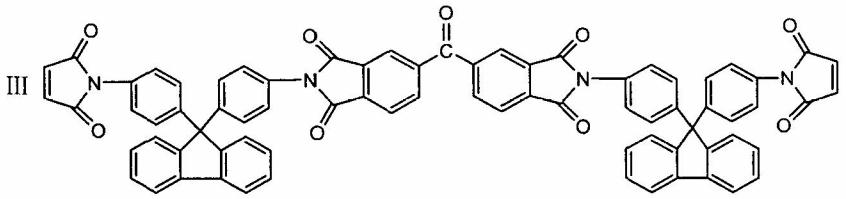
Fig. 1 Synthetic route of fluorenyl cardo bismaleimides

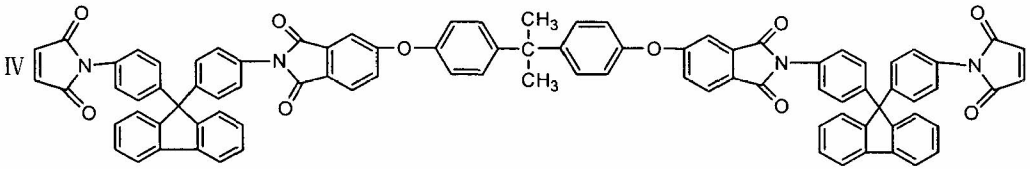
Table 1 Characterization of bismaleimides

Number	Formula	FTIR (KBr)	^{1}H-NMR (DMSO-d6)	Elemental analysis	Appearance
I	$C_{33}H_{20}N_2O_4$	1770,1707,1378（imide structure）cm^{-1}, 1605(Olefinic bond) cm^{-1}	7.16(4H, Olefinic protoms) 7.24-7.98(16H, Aromatic protons)	Anal. Calcd:C, 77.94; H, 3.96; N, 5.51 Found: C, 76.83; H, 4.15; N, 5.42	Light Yellow
II	$C_{74}H_{42}N_4O_9$	1777,1716,1371（imide structure）cm^{-1}, 1605(Olefinic bond) cm^{-1}	7.16(4H, Olefinic protoms) 7.25-7.98(38H, Aromatic protons)	Anal. Calcd:C, 78.57; H, 3.74; N, 4.95; Found: C, 77.08; H, 3.74; N, 4.65;	yellow
III	$C_{75}H_{42}N_4O_9$	1778,1716,1372（imide structure）cm^{-1}, 1618(Olefinic bond) cm^{-1}	7.16(4H, Olefinic protoms) 7.24-8.16(38H, Aromatic protons)	Anal. Calcd:C, 78.80; H, 3.70; N, 4.90; Found:C, 74.38; H, 3.65; N, 4.35;	yellow
IV	$C_{89}H_{56}N_4O_{10}$	1777,1716,1370（imide structure）cm^{-1}, 1612(Olefinic bond) cm^{-1}	1.69(6H,CH3) 7.10(4H, Olefinic protoms) 7.11-7.98(38H, Aromatic protons)	Anal. Calcd:C, 79.69; H, 4.21; N, 4.18; Found:C, 78.01; H, 3.74; N, 4.18;	yellow









Thermal cure of bismaleimides

Four fluorenyl bismaleimides were cured by thermal: Bismaleimides II-IV were heated at 250 °C for 2hrs and then at 300°C for 1.5hr (bismaleimide I: at 350 °C for 3hrs again).

Measurements

IR spectra were recorded on a Nicolet 460, ^{1}H-NMR spectra were obtained at 500MHz using a Bruker Vance DSX-500 in DMSO-d6 with tetramethylsilane as an internal standard. Elemental analysis was performed on a Vario EL III. The thermogravimetriy analysis (TGA) were made with TA TGA Q50 under N_2 atmosphere at a heating rate of 20 °C /min. Differential scanning calorimentry (DSC) was carried out using TA DSC Q10 under N_2 atmosphere at a heating rate of 10 °C /min.

Result and discussion

Synthesis and Characterization of Bismaleimides

Four fluorenyl Bismaleimides were prepared according to the reaction sequences shown in Fig.1. These novel biamaleimides were characterized by FTIR, ^{1}H-NMR, elemental analysis (Table 1).

The solubility of these biamaleimides was studied in various organic solvents. The results show that the incorporation of imide structure into bismaleimide can improve their solubility in organic solvents (Table 2).

Table 2 Solubility[a] of Bismaleimides in organic solvents

Number	NMP	DMAc	CHCl3	CH2Cl2	DMSO	THF	Acetone
I	Ins	Ins	Ins	Ins	S	Ins	Ins
II	S	S	S	S	S	S	Ins
III	S	S	S	S	S	S	Ins
IV	S	S	S	S	S	S	Ins

a. Solubility: S, soluble at room temperature; Ins, insoluble;

Thermal cure of bismaleimides

The same as usual bismaleimide, these novel bismaleimides can be cured by addition-type self-polymerization of maleyl double bonds while they were heated to desirable temperature. The curing behavior of bismaleimides was investigated by DSC. In all bismaleimides, it was found that there is multi-peaks of exotherm and endotherm, and that there exist more than one type of reaction. Broad exothermic peaks were observed in the temperature range of 203-435 °C.

Table3 DSC results of fluorenyl Cardo bismaleimide monomers

Number	T1	T2	T3
I	340	343	381
II	212	335	417
III	213	309,380	435
IV	203	333	408

T1=Temperature of which first energy release could be detected;

T2=Temperature of exothermic peak position;

T3= Temperature of exothermic peak position

Thermal stability of curing resins

Curing of bismaleimides I-Ⅳ according to the procedure described in the experimental section afforded the respective crosslinked resins PI-PⅣ. To discuss thermal stability of curing resins, the initial decomposition temperature(Tid), the maximum decomposition temperature(T_{max}), the char yield (Yc) at 800 °C and the onset temperature corresponding to 5% (T5) weight loss of the system were measured by TGA under nitrogen atmosphere (Table 4). The initial decomposition temperature (Tid) obtained by extrapolation. All cured samples showed stable up to 400 °C(the initial decomposition temperature: 439 °C to 478 °C) , undergoing 5% weight loss in the temperature range of 453°C and 500°C and char yields of 57%-65% at 800 °C under nitrogen atmosphere.

Table 4 TGA results of bismaleimide polymers

Polymer	Tid (°C)	T5 (°C)	T_{max} (°C)	Yc (%)
PI	439	453	574	60
PII	455	484	596	58
PIII	478	500	598	65
PIV	477	485	541	57

Tid= The initial decomposition temperature obtained by extrapolation;

T5= The temperature corresponding to 5%weight loss;

T_{max}= The maximum decomposition temperature;

Yc=The char yield at 800 °C.

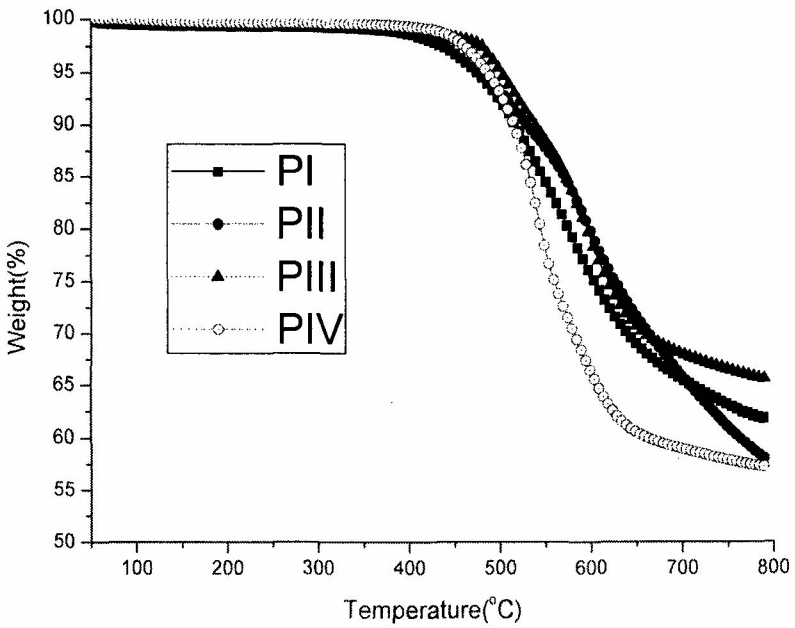


Fig.2 TGA curves of polymer PI—PIV under nitrogen atmosphere

Conclusion

A series of novel fluorenyl cardo bismaleimides with imide structure were synthesized and characterized by IR, ^{1}H-NMR, elemental analysis. DSC observed broad exothermic peaks in the temperature range of 203-435 °C. All cured samples showed stable up to 400 °C. The results show that these bismaleimides containing imide structure improves the solubility of cardo bismaleimides in organic solvents without sacrificing thermal properties.

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