

Synthesis and Characterization of Novel Chain-Extended Bismaleimides Containing Fluorenyl Cardo Structure

Zhiqiang Hu,^{1,2,3} Shanjun Li,^{1,2} Chunhua Zhang³

¹The Key Laboratory of Molecular Engineering of Polymer, Ministry of Education of China, Shanghai 200433, China

²Department of Macromolecular Science, Fudan University, Shanghai 200433, China

³Shanghai Research Institute of Synthetic Resins, Shanghai 200235, China

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ABSTRACT: Novel fluorenyl cardo chain-extended bismaleimides (FCCEBMIs) were synthesized by reacting maleic anhydride with fluorenyl cardo diamine and different dianhydrides. FCCEBMIs were characterized by FT-IR spectra (FT-IR), ¹H NMR, and elemental analysis. All FCCEBMI monomers were readily soluble in a variety of organic solvents, such as *N*-methyl-2-pyrrolidinone, *N,N*-dimethyl acetamide, chloroform (CHCl₃), methylene chloride (CH₂Cl₂), dimethyl sulfoxide, and tetrahydrofuran when compared with 9,9-bis(4-maleimidophenyl) fluorene. Curing process was investigated by differential scanning

calorimetry. Thermal properties of the cured FCCEBMIs were characterized by thermogravimetry analysis, the cured products are stable up to 430°C. The results show that the FCCEBMIs with imide structure improve significantly the solubility of bismaleimide (BMI) in organic solvents without sacrificing thermal properties of cured BMIs. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 1288–1293, 2008

Key words: chain-extended bismaleimide; cardo; solubility; thermal stability

INTRODUCTION

Bismaleimide (BMI) resins possess many desirable properties, such as high tensile strength and modulus, excellent chemical and corrosion resistance, and hot/wet performance. So they have been widely used as matrices for advanced composites as high-performance thermosetting resins.^{1–4}

These polymers containing fluorenyl structure in the backbone were termed fluorenyl cardo polymer. The introduction of fluorenyl “Cardo” groups into polymers, such as polyimides,^{5–10} polyamides,^{11,12} and polyquinolines,¹³ can endow with the specific properties: (1) excellent heat resistance; (2) excellent solubility. In the previous study, fluorenyl cardo bismaleimide [9,9-bis(4-maleimidophenyl)fluorene] has been synthesized and showed many excellent properties, such as good heat-resistance, high char yield, high limited oxygen index, and good flameproofing.¹⁴ But the processability of this BMI monomer is very difficult because of its poor solubility in a majority of polar solvents such as chloroform (CHCl₃), tetrahydrofuran (THF), *N*-methyl-2-pyrrolidinone (NMP), and *N,N*-dimethyl acetamide (DMAc) and high melting point (>300°C). The research works of Mikroyannidis and Anastasios^{15,16} have suggested

that chain-extended BMIs with imide structure can improve the processability of BMI because of extended polymer chain without sacrificing thermal properties. Varma et al.¹⁷ have also applied chain extension on the BMI derived from tris(*m*-aminophenyl)phosphine oxide. Moreover, Mahesh and Alagar¹⁸ prepared chain-extended BMI-modified polyurethane-epoxy matrices. Mizori and Dershem¹⁹ reported a series of imide-extended BMI compounds prepared by the condensation of appropriate anhydrides with appropriate diamines to give amine-terminated compounds and then condensed with excess maleic anhydride.

In the present research, our objective is to investigate the effect of incorporation of different chain-extended imide structure into 9,9-bis(4-maleimidophenyl)fluorene on the solubility of BMI monomer and thermal stability of their cured products. Novel fluorenyl cardo chain-extended bismaleimides (FCCEBMIs) were synthesized by reacting maleic anhydride with fluorenyl cardo diamine and different dianhydrides and were characterized by FT-IR, ¹H NMR, and elemental analysis. The solubility of all FCCEBMI monomers in various organic solvents, such as NMP, DMAc, CHCl₃, methylene chloride (CH₂Cl₂), dimethyl sulfoxide (DMSO), THF, and acetone were evaluated and compared with the solubility of 9,9-bis(4-maleimidophenyl)fluorene prepared by directly reacting maleic anhydride with 9,9-bis(4-aminophenyl)fluorene (BAFL). Curing process was

Correspondence to: S. Li (sjli@fudan.edu.cn).

investigated by differential scanning calorimetry (DSC). Thermal properties of the cured products were characterized by thermogravimetry analysis (TGA).

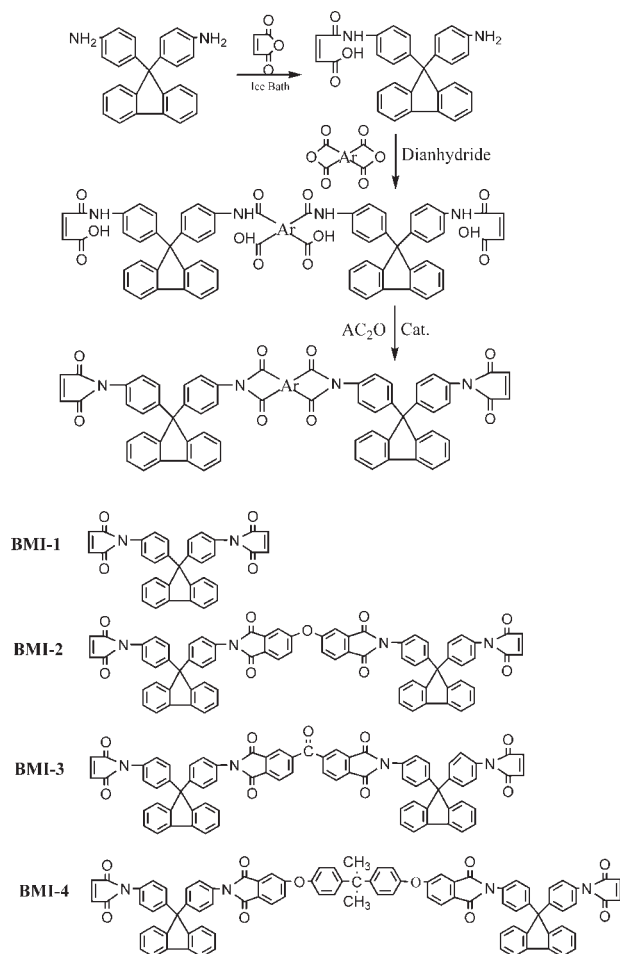
EXPERIMENTAL

Reagents and solvents

BAFL, 4,4'-oxydiphthalic anhydride (ODPA), 2,2-bis[4-(3,4-dicarboxyphenoxy)phenyl]propane dianhydride (BPADA; Shanghai Research Institute of Synthetic Resins, Shanghai, China), 3,3',4,4'-benzophenone-tetracarboxylic dianhydride (BTDA; obtained from Daicel, Japan), maleic anhydride (Shanghai Shiyi Chemicals Reagent Co., Shanghai, China; recrystallized in acetic anhydride before use), and DMAc were dried in CaH₂ for 2 days and distilled before use.

Monomer synthesis

All monomers in this work were synthesized by synthetic route shown in Scheme 1.



Scheme 1 Synthetic route and structure of fluorenyl cardo bismaleimides.

9,9-Bis(4-maleimidophenyl)fluorene (BMI-1)

In a 250-mL four-necked flask with a nitrogen inlet, a thermometer, a condenser, and a mechanical stirrer, 17.4 g (0.05 mol) BAFL was dissolved in DMAc, and then the solution of 9.8 g (0.1 mol) maleic anhydride in DMAc was added dropwise in an ice bath with constant stirring. After the solution was reacted for 3 h, a mixture of acetic anhydride and potassium acetate was added at an ambient temperature and carried out for 1 h, and at 60°C for 4 h to ensure the completion of imidization. And, the reaction solution was precipitated in a large amount of water. The product was filtered and dried in vacuo, and then yellow BMI powder was obtained.

FCCEBMI monomer with ODPA (BMI-2)

In a 250-mL four-necked flask with a nitrogen inlet, a thermometer, a condenser, and a mechanical stirrer, 17.4 g (0.05 mol) of BAFL was dissolved in DMAc, and then the solution of 4.9 g (0.05 mol) maleic anhydride in DMAc was added dropwise in an ice bath with constant stirring. The solution was reacted for 3 h, and then 0.05-mol ODPA was added directly and carried out for 3 h, a mixture of acetic anhydride and potassium acetate was added at ambient temperature and carried out for 1 h, and at 60°C for 4 h to ensure the completion of imidization. And, the reaction solution was precipitated in a large amount of water. Yellow BMI powder was obtained.

FCCEBMI monomer with BTDA (BMI-3)

According to aforementioned method, except 0.05-mol BTDA was added. The product is yellow powder.

FCCEBMI monomer with BPADA (BMI-4)

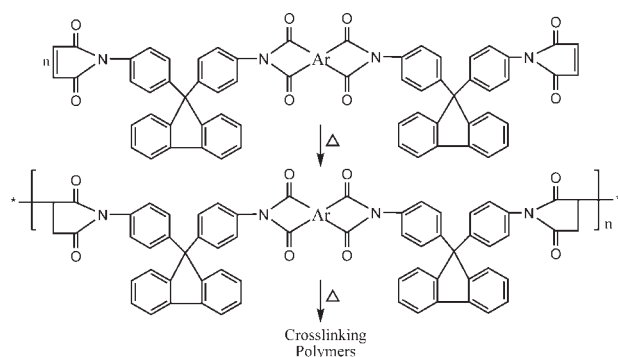
According to aforementioned method, except 0.05-mol BPADA was added. The product is yellow powder.

Thermal cure of fluorenyl cardo BMIs

Fluorenyl BMI monomers were cured by thermal self-polymerization (Scheme 2). The fluorenyl cardo BMI powders were placed into a die, which was then heated from room temperature to the desired temperature in oven. BMI-1 was cured at 250°C for 2 h, at 300°C for 1.5 h, and then at 350°C for 1 h again. Other fluorenyl chain-extended BMIs (BMI-2–BMI-4) were cured at 250°C for 2 h and then at 300°C for 1.5 h.

Co-curing of BMI-2/DBA

Prepolymerization of BMI-2 and *O,O'*-diallyl bisphenol A (DBA) (mole ratio 1 : 1) was carried out for 1 h



Scheme 2 Thermal cure of fluorenyl cardo bismaleimides.

at 135°C, and then curing behavior of the prepolymer was investigated by DSC.

Measurements

IR spectra were recorded on a Nicolet 460, ^1H NMR spectra were obtained at 500 MHz using a Bruker Vance DSX-500 in $\text{DMSO-}d_6$ with tetramethylsilane as an internal standard. Elemental analysis was performed on a Vario EL III. The TGA were made with TA TGA Q50 under N_2 atmosphere at a heating rate of 20°C/min. DSC was carried out using TA DSC Q10 under N_2 atmosphere at a heating rate of 10°C/min. Computer simulation used Chem3D Ultra molecular modeling from Cambridgesoft Corporation (Version 9.0).

RESULTS AND DISCUSSION

Synthesis and characterization of fluorenyl cardo BMIs

Fluorenyl cardo BMIs were prepared according to the reaction sequences shown in Scheme 1, and were characterized by FT-IR, ^1H NMR, and elemental analysis. The structure of BMIs was confirmed by IR, and the typical FT-IR spectra of chain-extended BMI, BMI-4 as an example, are presented in Figure 1. As shown in Figure 1, BMI-4 exhibited the characteristic absorptions: 3095 cm^{-1} ($=\text{C}-\text{H}$), 1777, 1716 cm^{-1} ($\text{C}=\text{O}$, imide carbonyl group), 1370 cm^{-1} ($\text{C}-\text{N}$, imide group), 1618 cm^{-1} ($\text{C}=\text{C}$, olefinic bond), 2966 cm^{-1} (CH_3 , $\text{C}-\text{H}$), 1271, 1237 cm^{-1} (CH_3), 1119 cm^{-1} (ether bond). IR spectra of all BMIs revealed that the characteristic absorptions of imide groups appeared around 1770–1778, 1707–1716, and 1370–1378 cm^{-1} , and those of the olefinic bond appeared around 1605–1618 cm^{-1} . Meanwhile, the characteristic IR absorptions of FCCEBMIs related with its chemical structure are also listed in Table I.

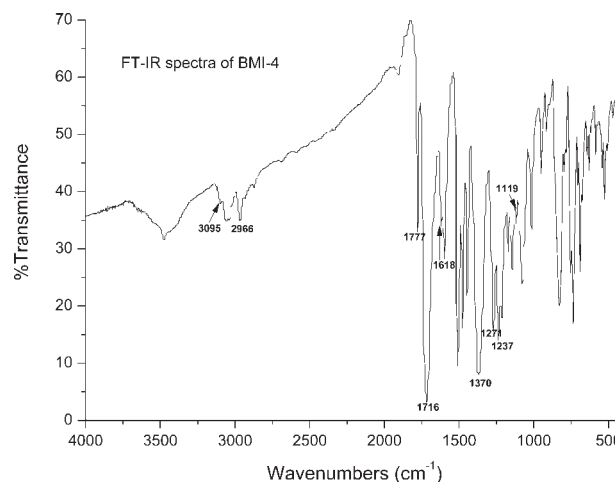


Figure 1 FT-IR spectra of BMI-4.

The ^1H NMR spectral data and elemental analysis data of all BMI monomers are listed in Tables II and III, respectively. As shown in Table II, signals of maleimido double bonds appeared at 7.10–7.16 ppm, and signals of aromatic protons appeared at 7.11–8.16 ppm. For BMI-4, the signal at 1.69 ppm was attributed to the protons of methyl (CH_3) of BPADA.

The solubility of FCCEBMIs

The solubility of fluorenyl cardo BMIs was evaluated in various organic solvents. As shown in Table IV, all FCCEBMIs have better solubility in a variety of organic solvents, such as NMP, DMAc, chloroform (CHCl_3), methylene chloride (CH_2Cl_2), DMSO, and THF than 9,9-bis(4-maleimidophenyl)fluorene. The results show that the incorporation of imide structure into BMI can obviously improve their solubility in organic solvents.

Several facts might be attributed to the improvement of the solubility of chain-extended BMI monomers. By computer modeling, the stereochemical

TABLE I
FT-IR Spectral Data of Fluorenyl Cardo Bismaleimides

Monomer	FT-IR (KBr, cm^{-1})			
	Imide structure	$=\text{C}-\text{H}$	Olefinic bond	Particular structure
BMI-1	1770, 1707, 1378	3100	1606	
BMI-2	1777, 1716, 1371	3095	1605	1120 ($-\text{O}-$)
BMI-3	1778, 1716, 1372	3096	1618	1669 ($\text{C}=\text{O}$) 2966 (CH_3 , $\text{C}-\text{H}$)
BMI-4	1777, 1716, 1370	3095	1618	1271, 1237 (CH_3), 1119 ($-\text{O}-$)

TABLE II
¹H NMR Spectral Data of Fluorenyl Cardo Bismaleimides

Monomer	Chemical shifts (δ , ppm) and assignments (DMSO- <i>d</i> ₆)
BMI-1	7.16 (4H, olefinic protons), 7.24–7.98 (16H, aromatic protons)
BMI-2	7.16 (4H, olefinic protons), 7.25–7.98 (38H, aromatic protons)
BMI-3	7.16 (4H, olefinic protons), 7.24–8.16 (38H, aromatic protons)
BMI-4	1.69 (6H, CH ₃), 7.10 (4H, olefinic protons), 7.11–7.98 (46H, aromatic protons)

configurations of BMI-1 and BMI-2 are shown in Figures 2 and 3, respectively. As shown in the previous report²⁰ and Figure 2, the regular and symmetrical stereo configuration might be the reason leading to the poor solubility of BMI-1 in organic solvents. We can also find that the chain-extended BMI-2 reveals a random stereo configuration as shown in Figure 3, because the introduction of imide structure causes breaking of regular and symmetrical structure; therefore, the introduction of imide structure on BMI can improve the solubility of these monomers. Moreover, the flexible linkages of dianhydride such as ether (—O—), carbonyl, and isopropyl bonds (—C(CH₃)₂—) can also improve the solubility of chain-extended BMIs, and as a result weakens the conjugation of main chain, increases the conformational entropy of molecule, and decreases the free energy of solution.

Thermal cure of FCCEBMIs

As the conventional BMIs [e.g., bis(4-maleimido-phenyl) methane] FCCEBMIs can be cured by addition-type self-polymerization of maleyl double bonds by heating at desirable temperature. The curing

TABLE III
Elemental Analysis Results of Fluorenyl Cardo Bismaleimides

Monomer	Formula	Anal. Calcd	Found
BMI-1	C ₃₃ H ₂₀ N ₂ O ₄	C, 77.94; H, 3.96; N, 5.51	C, 76.83; H, 4.15; N, 5.42
BMI-2	C ₇₄ H ₄₂ N ₄ O ₉	C, 78.57; H, 3.74; N, 4.95	C, 77.08; H, 3.74; N, 4.65
BMI-3	C ₇₅ H ₄₂ N ₄ O ₉	C, 78.80; H, 3.70; N, 4.90	C, 74.38; H, 3.65; N, 4.35
BMI-4	C ₈₉ H ₅₆ N ₄ O ₁₀	C, 79.69; H, 4.21; N, 4.18	C, 78.01; H, 3.74; N, 4.18

TABLE IV
Solubility of FCCEBMIs in Organic Solvents

Monomer	NMP	DMAc	CHCl ₃	CH ₂ Cl ₂	DMSO	THF	Acetone
BMI-1	Ins	Ins	Ins	Ins	S	Ins	Ins
BMI-2	S	S	S	S	S	S	Ins
BMI-3	S	S	S	S	S	S	Ins
BMI-4	S	S	S	S	S	S	Ins

S, soluble at room temperature; Ins, insoluble.

behavior of FCCEBMIs was investigated by DSC. It was found that the curing behavior of BMI-1 is relatively simple because of its molecular structure without the extended imide unit (Fig. 4). As shown in DSC curing curve, BMI-1 can be cured immediately after melting, the endothermic peak (melting) and exothermic peak (thermally induced polymerization reaction) are all very sharp. However, broad endothermic and exothermic peaks were observed for chain-extended BMIs (BMI-2–BMI-4) in the temperature range of 203–435°C (Fig. 5 and Table V), which illustrates that the curing reaction of FCCEBMIs involves more than one type of reaction.¹⁶ FCCEBMIs does not have a determinate melting temperature because of long molecular structures. There might be a collaborative process of melting and self-polymerization of FCCEBMIs at this temperature range.

Co-curing of BMI-2/DBA

Co-curing of BMIs and DBA is a basic toughening way of BMI resins. Most representative BMI modified by DBA is XU292 system reported by Ciba-Geigy Company in 1984. To further investigate the

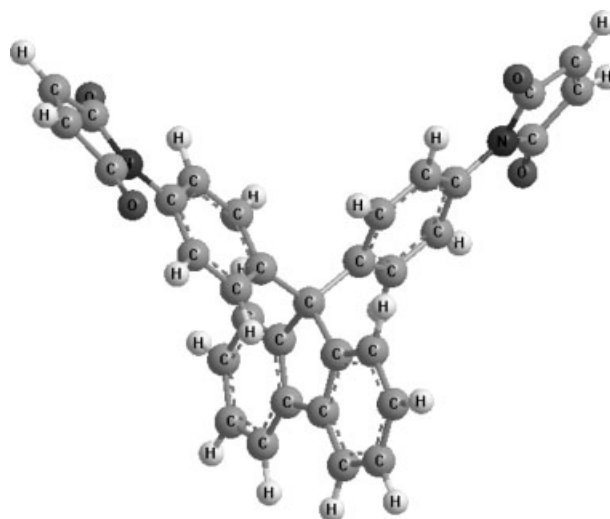


Figure 2 3D structure molding of BMI-1 at lowest energy state by molecular mechanics.

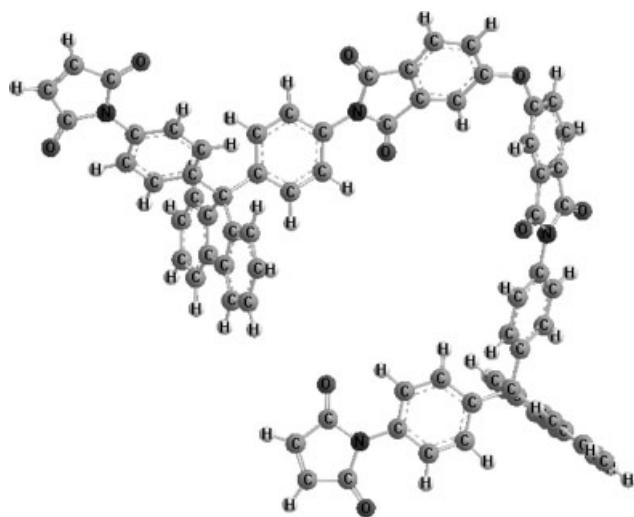


Figure 3 3D structure molding of BMI-2 at lowest energy state by molecular mechanics.

curing behaviors of fluorenyl cardo chain-extended BMI, we first prepared a prepolymer of BMI-2/DBA (mole ratio 1 : 1) and studied its curing process by DSC. In Figure 6, as the similar result of XU292 system [bis(4-maleimidophenyl)methane modified by DBA],²⁰ DSC curing curve of the prepolymer of BMI-2/DBA has two reactive exothermic peaks: the main peak is around 274.9°C, and the secondary peak is around 170.5°C.

According to the previous report,²¹ at the lower reaction temperature ene reaction between maleyl double bond of BMI and allylic double bond of DBA occurred first to yield the intermediate containing styrene structure. With the increase in the temperature, Diels–Alder reaction readily occurred between the intermediate and BMI to yield the crosslink

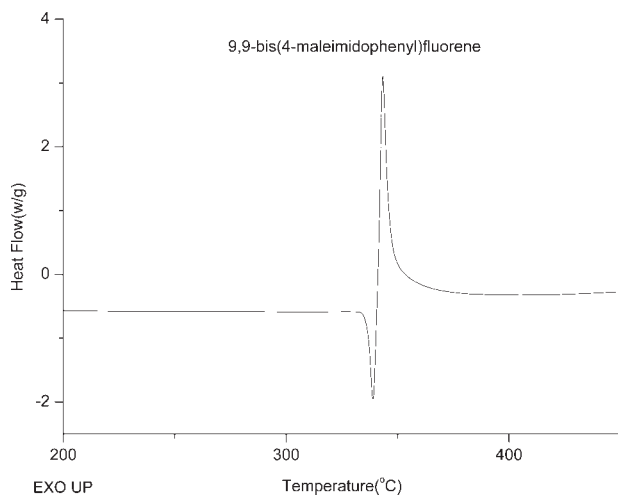


Figure 4 DSC traces of BMI-1 (9,9-bis(4-maleimidophenyl)fluorene).

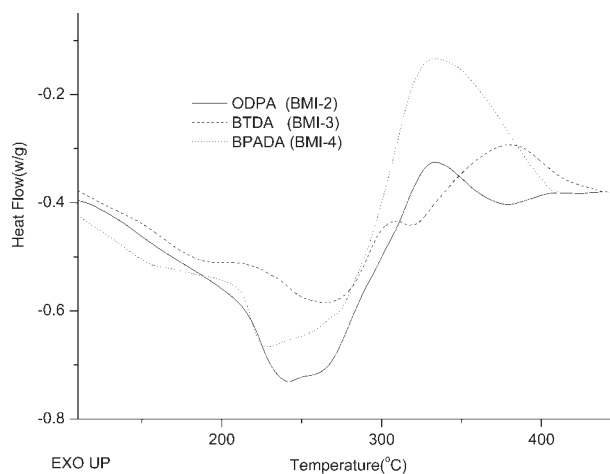


Figure 5 DSC traces of chain-extended bismaleimides FCCEBMIs.

product, and would lead to the emergence of secondary peak in DSC curve.

Thermal stability of cured resins

The resins obtained by curing of all fluorenyl cardo BMIs (BMI-1, BMI-2, BMI-3, and BMI-4) are referred to TP-1, TP-2, TP-3, and TP-4, respectively. To discuss thermal stability of these curing products, the initial decomposition temperature (T_{id}), the temperature of maximum rate of decomposition (T_{max}), the char yield (Y_c) at 800°C, and the onset temperature corresponding to 5% (T_5) weight loss of the system were measured by TGA under nitrogen atmosphere at a heating rate of 20°C/min, the results are given in Table VI and Figure 7.

All cured samples were stable up to 430°C (the initial decomposition temperature at 439–478°C), T_5 in the range of 453–500°C, and Y_c of 57–65% at 800°C under nitrogen atmosphere. Furthermore, thermal-cured samples of all chain-extended BMIs (TP-2–TP-4) have higher T_{id} and T_5 than that of 9,9-bis(4-maleimidophenyl)fluorene (TP-1). Therefore, the results show that the synthesis of chain-extended BMIs with imide structure improves the solubility of

TABLE V
DSC Results of Fluorenyl Cardo Bismaleimides

Monomer	T_1 (°C)	T_2 (°C)	T_3 (°C)
BMI-1	340	343	381
BMI-2	212	335	417
BMI-3	213	309, 380	435
BMI-4	203	333	408

T_1 , temperature of which first energy release could be detected; T_2 , temperature of exothermic peak position; T_3 , temperature indicating end of exotherm.

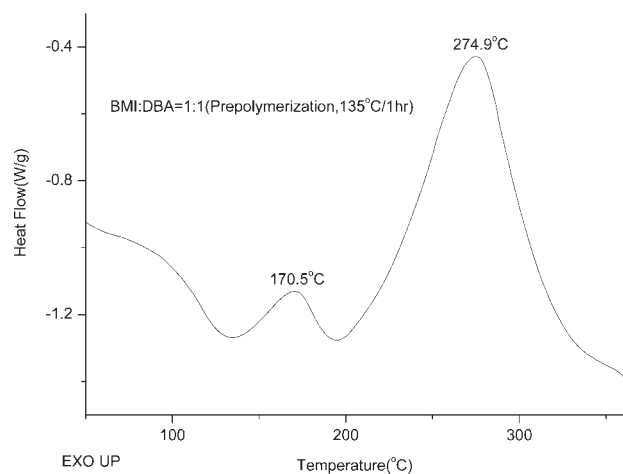


Figure 6 DSC curing curve of BMI-2/DBA (1 : 1).

TABLE VI
TGA Results of Thermal-Cured Resins

Cured products	T_{id} (°C)	T_5 (°C)	T_{max} (°C)	Y_c (%)
TP-1	439	453	574	60
TP-2	455	484	596	58
TP-3	478	500	598	65
TP-4	477	485	541	57

T_{id} , the initial decomposition temperature obtained by extrapolation; T_5 , the temperature corresponding to 5% weight loss; T_{max} , the temperature of maximum rate of decomposition; Y_c , the char yield at 800°C.

BMI in organic solvents without sacrificing thermal properties of cured products.

CONCLUSIONS

Novel FCCEBMIs were synthesized and characterized. All chain-extended BMI monomers were readily soluble in a variety of organic solvents, such as NMP, DMAc, CHCl_3 , CH_2Cl_2 , DMSO, and THF when compared with 9,9-bis(4-maleimidophenyl)fluorene. DSC traces of FCCEBMIs appear broad exothermic peaks in the range of 203–435°C. FCCEBMIs display different behavior of thermal cure with bis(4-maleimidophenyl)methane. The cured FCCEBMIs show thermal stability up to 430°C. The results show that the FCCEBMIs with imide structure improve significantly the solubility of BMI in organic solvents without sacrificing thermal properties of cured BMIs.

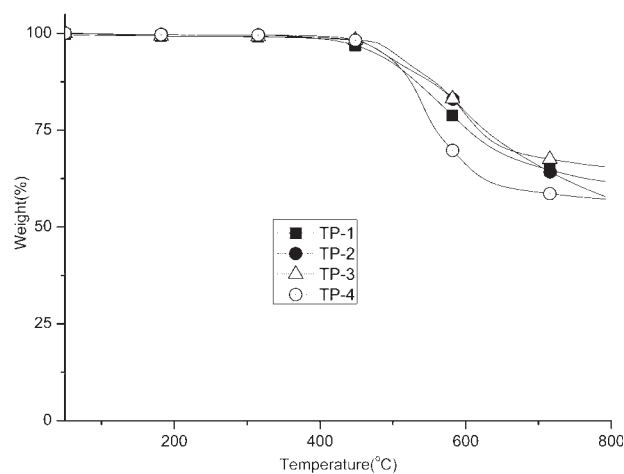


Figure 7 TGA curves of thermal-cured polymers (TP-1-TP-4) under nitrogen atmosphere.

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