

# Bismaleimides and Biscitraconimides: Synthesis and Properties

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**ABSTRACT:** A series of bismaleimide and biscitraconimide compounds with ester units were synthesized by a condensation reaction between 3-maleimido benzoic acid chloride or 4-maleimido benzoic acid chloride and citraconimido benzoyl chloride with 4,4-(hexafluoroisopropylidene)diphenol and 4,4-hydroxyphenylsulfone. The monomers were

characterized by IR,  $^1\text{H-NMR}$ , and elemental analysis. Differential scanning calorimetry, thermogravimetric analysis, and isothermal weight loss were performed to evaluate the thermal properties. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 3806–3812, 2004

## INTRODUCTION

Bismaleimide (BMI) resins are a generation of matrix resins with thermal stabilities and radiation and fire resistances better than epoxy resins.<sup>1–8</sup> They are important members of high-performance polymers because of their attractive combination of chemical, physical, and mechanical properties. They are the material of choice for rigid and lightweight, fiber-reinforced structural composites because of its excellent thermal and oxidation stabilities and because of the fact that no voids are formed in the material because of the evolution of the condensation products.<sup>9–11</sup> The unsaturated end groups of BMI can be thermally polymerized without the formation of volatile byproducts, which provides considerable advantages in processing over the conventional condensation-type polyimides.<sup>12</sup> BMI resins can be easily processed, but most BMIs also have a number of disadvantages, such as brittleness (because of their high crosslink density), a high melting temperature, and curing temperature.<sup>13–15</sup> Further attempts have been made to improve the processability and properties of BMI resins, for example, by the introduction of various substituents into the aromatic rings or flexible bridges in the main chain. In this study, we examined the influence of monomer structure on the solubility, reactivity, and thermal properties of these compounds.

## EXPERIMENTAL

3-Maleimido benzoic acid (3-MBA) and 4-maleimido benzoic acid (4-MBA) were obtained as described elsewhere<sup>16</sup> (3-MBA mp = 238–240°C and 4-MBA mp

= 225–228°C). The melting points from the literature<sup>17</sup> were 239–241 and 225–228°C, respectively.

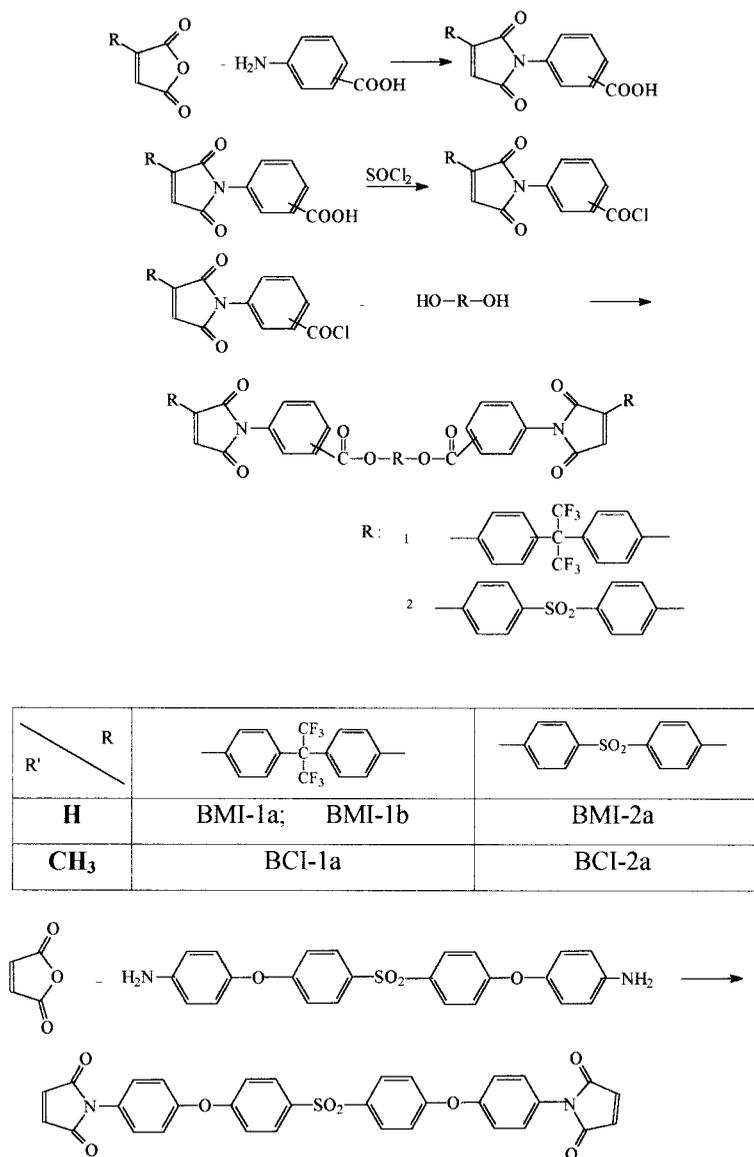
3-Maleimido benzoic acid chloride (3-MBAC) and 4-maleimido benzoic acid chloride (4-MBAC) were prepared as described in the literature<sup>18</sup> (3-MBAC mp = 125–128°C and 4-MBAC mp = 169–171°C). The melting point from the literature<sup>19</sup> for 4-MBAC was 170°C.

### 4-Citraconimido benzoic acid

A solution of 4-aminobenzoic acid (0.1 mol) in acetone (100 mL) was placed in a three-necked flask equipped with a mechanical stirrer and thermometer, and citracon anhydride (0.11 mol) in acetone (80 mL) was added at 25°C over a period of 15 min. Cyclodehydration of the acid intermediate to citraconimide was carried out by treatment with fused magnesium acetate (0.05 g), triethylamine (0.03 mol), and acetic anhydride (0.15 mol). The solution was refluxed for 1.5 h. The mixture was filtered, cooled at room temperature, and poured into water, and the resulting solid was separated by filtration. The product was washed four times with water and dried *in vacuo* at 80°C.

### 4-citraconimido benzoyl chloride (4-CBC)

Acid chlorides of *N*-(*p*-carboxyphenyl) citraconimide were prepared as follows. In a 250-mL, round-bottomed flask, *N*-(*p*-carboxyphenyl) citraconimide (0.05 mol) was suspended in 100 mL of dichloroethane (DCE). Redistilled thionyl chloride (20 mL) was carefully added to this solution. The reaction mixture was then heated slowly at reflux and maintained at this temperature for 4 h.



Scheme 1

The hot solution was filtered and thionyl chloride and DCE excess were distilled off under reduced pressure. The product was washed with DCE and then recrystallized from toluene. A yellow product of the acid chloride was obtained. [4-Citraconimide benzoyl chloride: yield = 74%; mp = 154–158°C (mp from the literature<sup>17</sup> = 155–160°C)].

#### Syntheses of BMIs and biscitraconimides (BCIs)

BMI-1a, BMI-2a, and BMI-1b were synthesized according to the method of Hoyt and Benicewicz.<sup>19</sup>

BCI-1a and BCI-2a were synthesized following the literature.<sup>17</sup> 4-CBC (0.04 mol) in 100 mL of CHCl<sub>3</sub> was cooled in an ice bath. Triethylamine (0.04 mol) as an acid acceptor and a solution of diphenol (0.02 mol) in 60 mL of CHCl<sub>3</sub> were added. After it was stirred for

1.5 h, the mixture was filtered and precipitated in petroleum ether. The product was filtered and then thoroughly washed (three times) with water. The filtered, precipitated product was dried and was then recrystallized.

BMI-3 was obtained by the reaction of maleic anhydride with 4,4-bis(4-aminophenoxy)diphenyl sulfone according to the method reported by Dix et al.<sup>20</sup> The syntheses of these compounds are presented in Scheme 1.

#### BMI-1a

The monomer was recrystallized from DCE/ethanol (yield = 68%; mp = 212–215°C).

IR (KBr) cm<sup>-1</sup>: 1780 and 1730 (C=O imide), 1750 (C=O ester), 1215–1190 (hexafluoroisopropylidene group).

ANAL. Calcd for  $C_{37}H_{20}F_6N_2O_8$  (%): C, 60.49; H, 2.74; F, 15.51; N, 3.81. Found: C, 60.13; H, 2.95; F, 15.31; N, 3.73.

#### BMI-2a

The product was recrystallized from DCE/ethanol (yield = 71%; mp = 235–240°C).

IR (KBr)  $cm^{-1}$ : 1785 and 1725 (C=O imide), 1755 (C=O ester), 1330 and 1160 ( $-SO_2$ ).

ANAL. Calcd for  $C_{37}H_{20}N_2O_{10}S$  (%): C, 62.96; H, 3.10; N, 4.31; S, 4.94. Found: C, 62.31; H, 2.92; N, 3.68; S, 5.21.

#### BMI-1b

The product was recrystallized from ethanol {yield = 70.%; mp = 121°C [thermo-optical analysis (TOA)]}.

IR (KBr)  $cm^{-1}$ : 1790 and 1720 (C=O imide), 1750 (C=O ester), 1225–1180 (hexafluoroisopropylidene group)

ANAL. Calcd for  $C_{37}H_{20}F_6N_2O_8$  (%): C, 60.49; H, 2.93; F, 15.51; N, 3.81. Found: C, 60.08; H, 2.93; F, 15.21; N, 4.03.

#### BCI-1a

The monomer was recrystallized from DCE/ethanol {yield = 67%; mp = 166°C [differential scanning calorimetry (DSC)]}.

IR (KBr)  $cm^{-1}$ : 1790 and 1725 (C=O imide), 1740 (C=O ester), 1230–1180 (hexafluoroisopropylidene group)

ANAL. Calcd for  $C_{39}H_{24}F_6N_2O_8$  (%): C, 61.42; H, 3.17; F, 14.94; N, 3.67. Found: C, 60.97; H, 2.96; F, 15.09; N, 3.28.

#### BCI-2a

The product was recrystallized from DCE/ethanol [yield = 71%; mp = 180°C (TOA)].

IR (KBr)  $cm^{-1}$ : 1790 and 1720 (C=O imide), 1755 (C=O ester), 1330 and 1165 ( $-SO_2$ ).

ANAL. Calcd for  $C_{36}H_{24}N_2O_{10}S$  (%): C, 63.90; H, 3.57; N, 4.13; S, 4.73. Found: C, 63.57; H, 3.82; N, 3.92; S, 4.49.

#### BMI-3

The monomer was recrystallized from benzene (yield = 73%; mp = 190–194°C).

IR (KBr)  $cm^{-1}$ : 1790 and 1715 (C=O imide), 1340 and 1165 ( $-SO_2$ ), 1265 ( $-O-$ ).

ANAL. Calcd for  $C_{32}H_{20}N_2O_8S$  (%): C, 64.86; H, 3.40; N, 4.72; S, 5.41. Found: C, 64.47; H, 3.61; N, 4.36; S, 5.73.

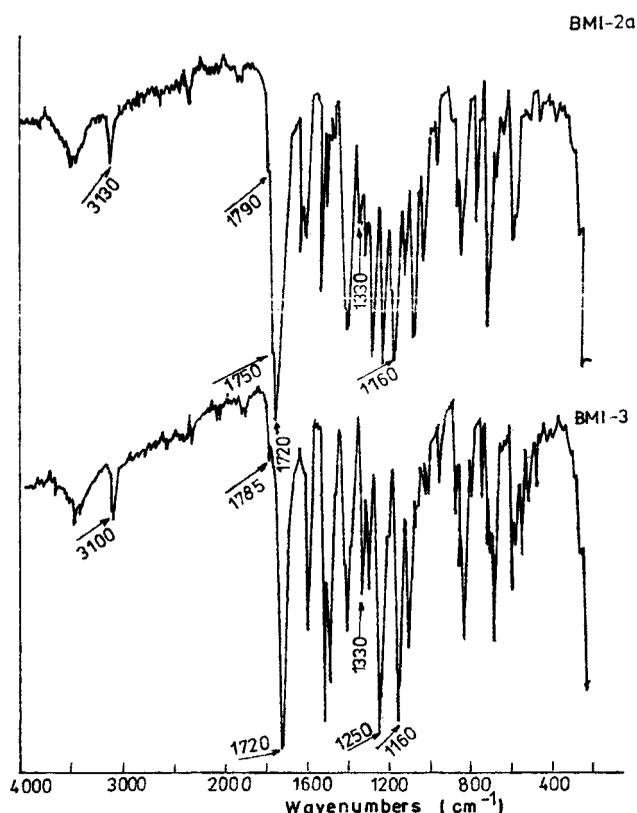


Figure 1 IR spectra of monomers BMI-2a and BMI-3.

#### Measurements

The IR spectra were recorded on a Specord M 90 Carl Zeiss Jena spectrophotometer with the KBr pellet technique.  $^1H$ -NMR spectra were run on a Jeol 60-MHz NMR spectrometer at 60°C in dimethyl sulfoxide ( $DMSO$ )- $d_6$  with tetramethylsilane as an internal reference. DSC measurements were done with a Mettler TA Instruments DSC 12E at a heating rate of 10°C/min in nitrogen. Thermogravimetric analysis (TGA) was carried out in air with an F. Paulik derivatograph at a heating rate of 12°C/min. TOA was carried out in air at a heating rate of 9.6°C/min, as described previously.<sup>21</sup>

Melting points were determined with a Gallenkamp hot-block melting-point apparatus.

#### RESULTS AND DISCUSSION

The IR spectra of the obtained BMIs and BCIs showed a characteristic carbonyl doublet in the range 1790–1715  $cm^{-1}$ . The absorption peaks around 1755–1740  $cm^{-1}$  corresponded to the ester groups. BMI-1a, BMI-1b, and BCI-1a showed an absorption band at 1230–1190  $cm^{-1}$  because of the hexafluoroisopropylidene group. BMI-2a, BMI-3, and BCI-2a showed characteristic absorption bands at 1340–1330 and 1165–1166  $cm^{-1}$  corresponding to the  $-SO_2$  group (assigned to

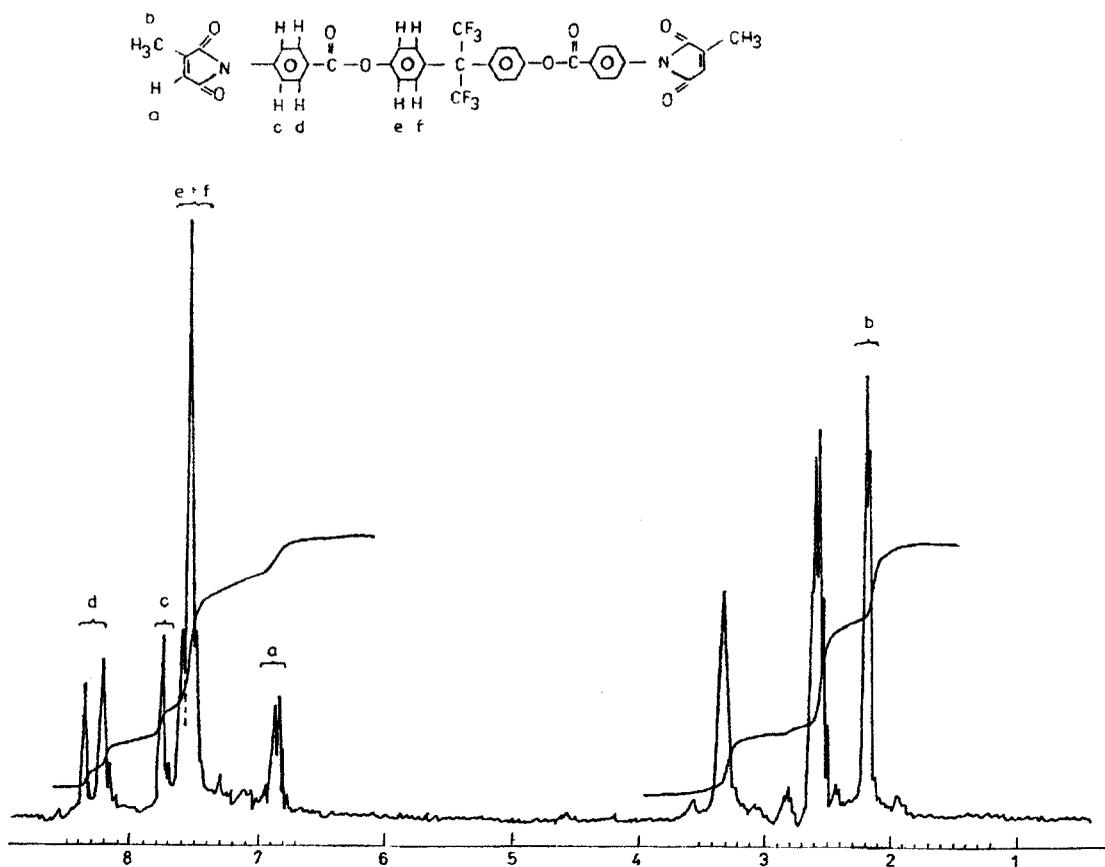


Figure 2  $^1\text{H-NMR}$  spectra of monomer BCI-1a.

the stretching asymmetrical and symmetrical vibrations, respectively). In addition, the characteristic absorption of the ether group of monomer BMI-3 appeared at  $1265\text{ cm}^{-1}$ . Figure 1 presents the IR spectra of BMI-2a and BMI-3.

The  $^1\text{H-NMR}$  spectra of BCI-1a confirmed its chemical structure (Fig. 2). The  $^1\text{H-NMR}$  spectra of BCI-1a exhibited two doublets in the range 8.36–8.22 and 7.76–7.67 ppm associated with aromatic protons (ortho to the ester group and ortho to  $-\text{N}-$ ). Also, the monomer BCI-1a showed a doublet in the range 7.50–7.00 ppm for aromatic protons [ortho to  $-\text{O}-$  ester and ortho to  $-\text{C}(\text{CF}_3)_2$ ]. A multiplet appeared at

6.90–6.77 ppm because of olefinic protons. In addition the monomer showed a doublet in the region 2.20–2.17 ppm associated with the aliphatic protons ( $\text{CH}_3$ ). The solubilities of the monomers were evaluated in various solvents. All of the monomers exhibited high solubility in aprotic dipolar solvents [i.e., *N*-methylpyrrolidone (NMP), dimethylformamide (DMF), DMSO,  $\text{CHCl}_3$ ], except BMI-3 (partially soluble on heating in  $\text{CHCl}_3$ ; see Table I).

The monomers BMI-1a, BMI-2a, BMI-1b, BCI-1a, and BCI-2a had solubility better than BMI-3 (influence of ester group). In addition, monomers with the hexafluoroisopropylidene group had the best solubil-

TABLE I  
Solubility of BMI and BCI Monomers

Monomer	Solvent						
	NMP	DMF	$\text{CHCl}_3$	DMSO	Benzene	Toluene	Acetone
BMI-1a	++	++	++	++	++	++	++
BMI-2a	++	++	++	++	±	±	+
BMI-1b	++	++	++	++	++	+	++
BCI-1a	++	++	++	++	+	++	++
BCI-2a	++	++	++	++	+	±	++
BMI-3	++	++	±	++	-	-	±

Solubility: ++ = soluble at room temperature; + = soluble on heating; ± = partially soluble on heating; - = insoluble.

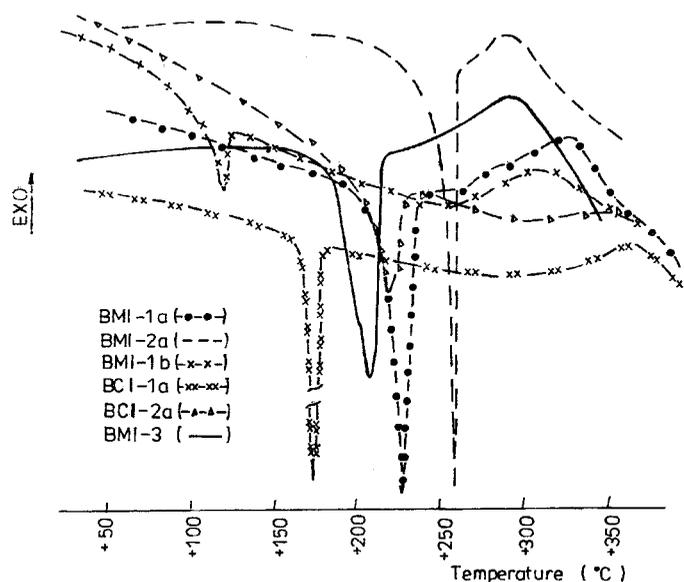


Figure 3 DSC scans of BMI-1a, BMI-2a, BMI-1b, BMI-3, BCI-1a, and BCI-2a.

ity (the introduction of hexafluoroisopropylidene in the monomer backbone enhanced the compound solubility).

The thermal behavior for BMIs and BCIs were investigated by DSC measurements. Figure 3 shows the DSC curves of BMI-1a, BMI-2a, BMI-1b, BCI-1a, BCI-2a, and BMI-3.

The DSC curves for the BMIs and BCIs were characterized by sharp melting endotherms in the temperature range 123–257°C because of the melting of these monomers. The crosslinking reaction was responsible for the exotherm peak in the temperature range 250–256°C with a heat of polymerization of 24–82 KJ/mol. The rate of polymerization of the monomers at a certain temperature was affected by the structure of the bridging units and the substituted position. The electron-withdrawing or the electron-donating capacity of the BMI (or BCI) highly influenced ester reactivity. To establish a structure–reactivity relationship, BMI-3, BMI-2a, and BCI-2a were compared, with the consideration that all of them contained the  $-\text{SO}_2$  group on the main chain. By the point of view of their reactivity, we observed the following order. BMI-3, which contained an ether group, showed the highest reactivity. BMI-2a, which had an ester group, followed, and last was BCI-2a, which contained both an ester group and a methylene group.

Some comparisons performed on BMI-1a, BMI-1b, and BCI-1a (compounds with hexafluoroisopropylidene units) led us to the following conclusion: BMI-1b was the most reactive compound because of substituents in the meta position; it was followed by BMI-1a and then BCI-1a, the latter with one more methylene group. On the basis of the onset of the

curing regime, the BMIs (or BCIs) could be ordered by their double-bond reactivity, as follows: BMI-3 > BMI-1b > BMI-1a > BMI-2a > BCI-2a > BCI-1a. In conclusion, BMI-3 had the highest reactivity (due to the ether group influence) compared to all of the other compounds. As for the BCIs, BCI-1a and BCI-2a had the lowest reactivity (due to methylene group influence).

The thermal stabilities of BMI and BCI compounds were evaluated by TGA and isothermal gravimetric analysis (IGA). The thermogravimetric (TG) curves of the compounds are shown in Figure 4, and the data of the onset of initial decomposition temperature (IDT), temperature at maximum decomposition ( $\text{PDT}_{\text{max}}$ ), and percentage char yield at 600°C are listed in Table II.

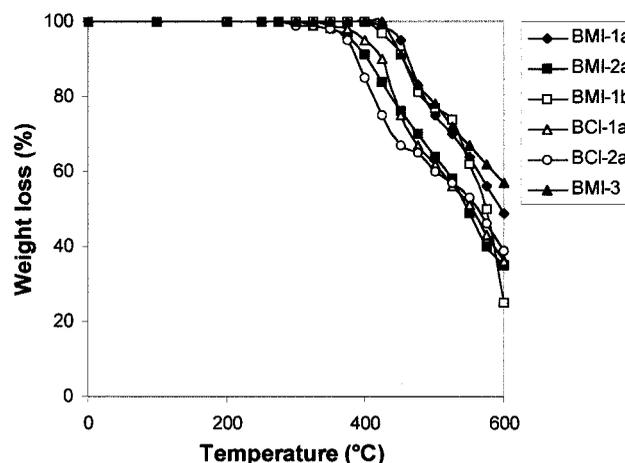


Figure 4 TGA thermograms of BMIs and BCIs in an air atmosphere at a heating rate of 12°C/min.

TABLE II  
Physical and Thermal Properties of the Prepared Compounds

No.	Monomer	mp <sup>a</sup> (°C)	DSC				TG		
			T <sub>end</sub> (°C)	T <sub>exo</sub> (°C)	T <sub>p</sub> <sup>b</sup> (°C)	ΔH (kJ/mol)	IDT (°C)	PDT <sub>max</sub> (°C)	Y (%) <sup>c</sup>
1	BMI-1a	210–215	220	297	245	82.1	443	459	49
2	BMI-2a	235–240	257	289	272	60.0	390	428	35
3	BMI-1b	121 <sup>d</sup>	123	313	235	51.4	422	446	52
4	BCI-1a	166 <sup>e</sup>	175	358	318	24.5	396	452	36
5	BCI-2a	179–180	224	356	298	50.6	357	400	39
6	BMI-3	204–208	207	298	232	79.6	435	458	57

<sup>a</sup> Melting point determined visually in a capillary tube melting-point apparatus.

<sup>b</sup> Start of polymerization as measured by DSC.

<sup>c</sup> char yield at 600°C

<sup>d</sup> Melting point as measured by TOA

<sup>e</sup> Melting point as measured by DSC.

BCI-2a showed the lowest thermostability, whereas BMI-3 had the highest thermostability. So, methylene groups from BCIs had a negative influence on their thermostability. At the same time, ether units between aromatic rings had a beneficial influence on the thermal stability. However, through comparison, we studied BCI-1a and BCI-2a, compounds with hexafluoroisopropylidene groups, and compounds containing —SO<sub>2</sub> groups. A better thermostability was observed for the first compounds because of their hexafluoroisopropylidene moieties, which had a beneficial influence. With IDT considered as thermostability criteria, the following order was established: BMI-3 > BMI-1a > BMI-1b > BCI-1a > BMI-2a > BCI-2a.

This investigation was expanded to include the evaluation of the thermooxidative stability of these compounds by IGA. Figure 5 presents the IGA traces of these resins at 300 and 350°C for monomers BMI-1b and BMI-2a in static air. After isothermal aging at 300°C for 20 h, their weight losses were 7.17, 17.19, 7.88, 45.90, 27.92, and 12.95%, respectively. At 350°C after 20 h, BMI-1b and BMI-2a

showed weight losses of 15.05 and 50%, respectively. The high thermostability at 300°C of BMI, which contained fluorine atoms, was noticeable, as well as very good thermal behavior even at 350°C (BMI-1b). As was expected from a thermostability point of view, BCI-1a and BCI-2a had the lowest values (because of the increasing aliphatic ratio for each monomer unit). Interestingly, by comparison, there was a significant difference between the monomers BMI-2a and BMI-1b at 350°C.

## CONCLUSIONS

Various BMIs and BCIs containing ester units on the main chain and having hexafluoroisopropylidene and SO<sub>2</sub> groups were synthesized. A study of the confirmation of the structure of these compounds (IR, <sup>1</sup>H-NMR, and elemental analysis) and their solubilities and thermal behaviors was performed.

A comparative study established the relationship between the structure and properties of the synthesized compounds.

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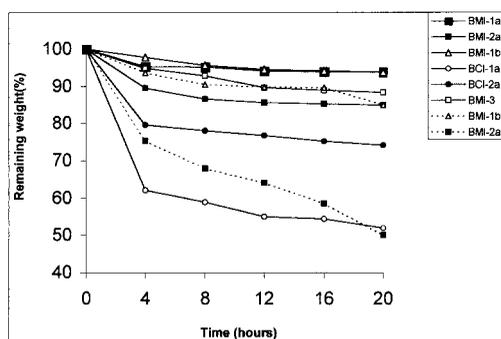


Figure 5 IGA traces of polymers at 300°C in static air for BMI-1a, BMI-2a, BMI-1b, BCI-1a, and BCI-2a and at 350°C for BMI-1b and BMI-2a.

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