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Synthesis And Properties Of New Bismaleimides With Mesogen Groups And Flexible Spacers

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ABSTRACT

This paper deals with the synthesis and thermal properties of seven new high temperature liquid-crystalline thermosets based on maleimide functional group and flexible segments. The melting temperatures are generally lower than 200⁰C. The crosslinking directly obtained from the liquid crystal state could be achieved only with two bismaleimides. However, crosslinking obtained from the isotropic state systematically gives an orderly state. It gives at the end of the reaction a smectic C order. The obtained materials show degradation temperatures higher 400⁰C and high T_δ that can reach 280⁰C.   © 2007 Trade Science Inc. - INDIA

INTRODUCTION

Bismaleimides (BMIs) constitute a well-studied group of compounds not only for scientific reasons but also for their many applications. Many scientific works have been carried out to obtain new molecules that lead to research on property-structure correlations[1] and on the mechanisms of thermal, ionic or radiations crosslinking[2-7]. Technologically, these crosslinked molecules yield interesting materials in optics[8], adhesives[9] and competitive composite materials[10-14]. Thermal stability and easy processing make then really interesting.

These molecules are crosslinked in an amorphous state. But Hoyt, Benicewicz and Huang obtained the first liquid crystalline BMIs that crosslink in an orderly state of nematic type[15-17]. These liquid crystalline BMIs are strongly rigid molecules. They are made up mainly of aromatic groups. They have very high melting temperatures and they crosslink quickly after melting. Afterwards, other liquid crystalline BMIs were synthesized. These BMIs are oligomers[18-20] and BMIs presenting a flexible group inserted among strongly rigid imide[21], arylidine cycloalkanone or cardo type groups[22].

In 1999, a patent was registered. It described the carrying out of liquid crystalline BMIs presenting a mesogenic group in the center and flexible groups at the extremity of the molecules[23]. Other works show that it is possible to obtain an orderly material from non-liquid crystalline BMIs when associated with liquid crystalline compounds. An orderly state was obtained

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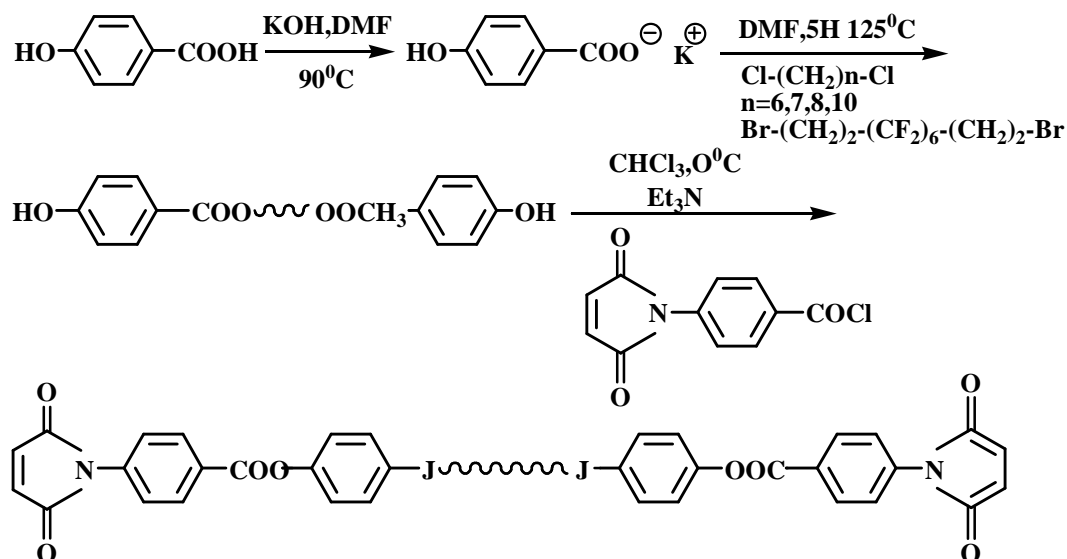
SCHEME 1 : Synthesis of BMI series II and III (BMI fluorinated)
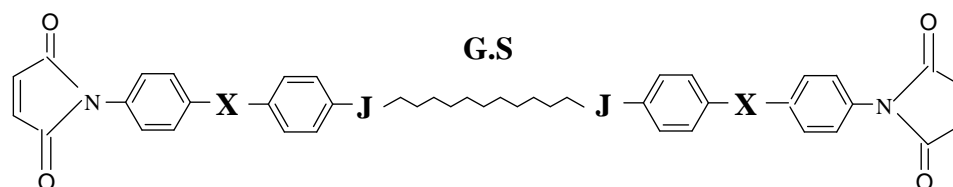
	Serie I	Serie II	Serie III	
			EO	**F**
X	-OOC-	-COO-	-CONH-	-COO-
J	-O-	-COO-	-O-	-COO-
G.S.	$-(CH_2)_n-$	$-(CH_2)_n-$	$-(OCH_2CH_2)_n-$	F*
n	5, 7, 8, 10	6, 7, 8, 10	5	F*

Figure 1 Bismaleimides studied. EO: ethylene oxidizes, F: fluorinated, J: Junction, G.S.: flexible group, X: function inside the mesogenic group, F*: $-(CH_2)_2-(CF_2)_6-(CH_2)_2-$

by crosslinking usual BMIs with chemically inert liquid crystalline compounds[24,25]. It was also obtained by copolymerization of a non-liquid crystalline BMIs and a mesogenic thermoset like the liquid crystalline epoxy[26]. Many works were carried out. Indeed, thermoset liquid crystalline has a strong potential for development[27,28]. The liquid crystalline state has already improved glass transition temperatures or mechanical properties of polyepoxydes[29-37] and polydiacrylates, polymethacrylates[6,37]. From these compounds it is possible to carry out high modulus materials.

We carried out specific liquid crystalline BMIs by incorporating flexible groups of polymethylenic, poly-ethylene oxides and fluorinated type among "arylates" and "aramides" mesogenic groups[38-40]. These flexible groups made it possible to lower melting point temperatures. Degradation temperatures are not catastrophic. These works follow preceding works[38, 39] and made it possible to carry out three series of BMIs and study their thermal properties(Figure 1).

EXPERIMENTAL

Reagents, solvents and analyses

All the reagents and the solvents are pure products from Aldrich and were used without further purification. The ^{1}H NMR spectra were recorded on a Bruker spectrometer (400 MHz) with deutered chloroform as solvent. The FTIR spectra were recorded on an Infrared

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Fourier Transform spectrophotometer Nicolet (Impact 410). The IR spectra were obtained with KBr pellets. Calorimetric studies were carried out with a DSC-92 Setaram thermal analyzer with a scan rate of 10^0C min^{-1} and 20^0C min^{-1}. Thermogravimetric analyses (TGA) were performed under an air atmosphere at a heating rate of 10^0C min^{-1} up to 800^0C with a TG-DTA-92 Setaram thermogravimetric analyser. The degradation tempe ratures (Td_1 and Td_2) are determined at the inflexion points of the TGA curves. Transition temperatures and textures were observed in polarized light with an olympus microscope equipped with a Mettler FP 90 plate heating system(PLM). Dynamic Mechanical Analysis(DMA) was performed with a solid visco analyser 2980 from T.A. Instruments. The 'dynamic compression' method is used. A pike press the sample. This method makes it possible to work with small crosslinked products. The sample is cylinder-shaped (diameter: about 15mm and height: about 5mm). Vibration frequency was fixed at 1Hz. Pre-tension load and amplitude of deformation were optimised respectively to 1N and 2µm. Samples were heated from 35^0C to 300^0C(or 350^0C) at $3^0C min^{-1}$ to avoid all artefacts. Tan δ(tan δ=E''/E') is precisely determined by the device.

Synthesis

The syntheses of 4-maleimidobenzoyl chloride (SCHEME 1), of the N-(4-hydroxyphenyl) maleimide (SCHEME 2), the α,ω-bis(4-carboxyphenoxy) alkane (SCHEME 2) and of BMI «amide-aromatic» (Figure 1) were carried out using published protocols[38-49].

The last stage of the synthesis of bismaleimides of series II and III fluorinated was carried out using the same protocol (SCHEME 1). Two solutions were carried out: A and B. Solution A consisted in 0.0182mol of triethylamine, 0.0091mol of derivative diphenolic and 20 ml of anhydrous chloroform. Solution B consisted in 0.0191mol of 4-maleimidobenzoyl chloride in 20ml of anhydrous chloroform. Solution A was added drop by drop to solution B. The mixture was maintained at 0^0C. After two hours of reaction at 0^0C, the mixture was filtered. Then, the liquid part was evaporated. The solid was dissolved in dimethylformamide(DMF) and was precipitated in water, filtered, and dried. The solid was dissolved in a minimum of DMF. This solution was purified on a silica column with chloroform as eluent. The solvent

was evaporated and the solid that was obtained was dissolved in a minimum of DMF, then precipitated in water, filtered, and dried. The BMIs were characterized (structure and purity) by ^1H NMR, FTIR, DSC and elemental analyses[40].

The last stage of the synthesis of series I was carried out by pouring drop by drop 0.15mol of triethylamine in a solution of 20ml of anhydrous chloroform and 20ml

| BMI II n=6	Yield:	60%
$C_{42}H_{32}O_{12}N_2$:	Calc.	C 66.67, H 4.23, N 3.70, O 25.40
(M=756g mol^{-1})	Found	C 67.27, H 4.48, N 3.78,O 25.30
BMI II n=7	Yield:	65%
$C_{43}H_{34}O_{12}N_2$:	Calc.	C 67.01, H 4.42, N 3.64, O 24.93
(M=770g mol^{-1})	Found	C 66.52, H 4.50, N 3.70, O 25.08
BMI II n=8	Yield:	64%
$C_{44}H_{36}O_{12}N_2$:	Calc.	C 67.34, H 4.62, N 3.57,O 24.46
(M=784g mol^{-1})	Found	C 66.87 H 4.66 N 3.56, O 24.13
BMI II n=10	Yield:	52%
$C_{46}H_{40}O_{12}N_2$:	Calc.	C 67.98, H 4.93, N 3.45, O 23.64
(M=812g mol^{-1})	Found	C 66.93, H 5.01, N 3.50,O 23.72
BMI III fluorinated	Yield:	51%
$C_{46}H_{28}O_{12}N_2F_{12}$:	Calc.	C 53.70, H 2.72, N 2.72, O 18.68, F 22.18
(M=1028g mol^{-1})	Found	C 51.53, H 2.60, N 2.87, O 19.79, F 23.01

of anhydrous tetrahydrofurane containing 0.157mol of N-(4-hydroxyphenyl) maleimide and 0.0787mol of dichloride acyl. The mixture was maintained under agitation at 0^0C for 1 hour. Then, the precipitate was filtered, then washed with water. The solid was washed with a solution of potassium hydroxide, then dried at room temperature under reduced pressure. The solid was then dissolved in DMSO and precipitated in methanol. The product was dissolved in a minimum of DMF and purified by chromatography on silica gel with chloroform as solvent. Two purifications on column are enough to obtain a good purity.

Crosslinking

BMIs were thermally crosslinked before the DMA study. Conditions of crosslinking were: 15min at 275^0C

| BMI I n=5	Yield:	35%
$C_{39}H_{30}O_{10}N_2$:	Calc.	C 68.22, H 4.37, N 4.08, O 23.32
(M=686g mol^{-1})	Found	C 67.51, H 4.42, N 4.19, O 23.38
BMI I n=7	Yield:	35%
$C_{41}H_{34}O_{10}N_2$:	Calc.	C 68.91, H 4.76, N 3.92, O 22.41
(M=714g mol^{-1})	Found	C 69.35, H 5.36, N 3.60, O 22.76
BMI I n=8	Yield:	32%
$C_{42}H_{36}O_{10}N_2$:	Calc.	C 69.23, H 4.95, N 3.85, O 21.98
(M=728g mol^{-1})	Found	C 67.54, H 5.21, N 3.82, O 21.64
BMI I n=10	Yield:	38%
$C_{44}H_{40}O_{10}N_2$:	Calc.	C 69.84, H 5.29, N 3.70, O 21.16
(M=756g mol^{-1})	Found	C 68.24, H 5.42, N 3.84, O 20.55
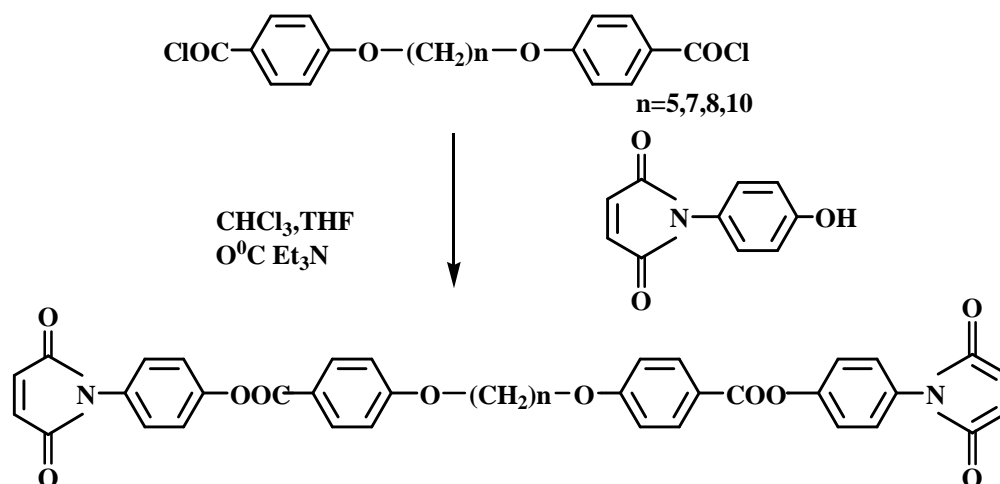
SCHEME 2 : Synthesis of BMI serie I

and 30min at 300⁰C for BMI I n=5; BMI I n=7; BMI I n=8; BMI I n=10; BMI II n=7; BMI II n=10; BMI III (EO); BMI III (fluorinated)-15min at 290⁰C and 15min at 310⁰C for BMI II n=6-15min at 250⁰C and 15min at 300⁰C for BMI II n=8. These cure conditions make it possible to obtain rates of advance τ close to 1. These τ rates were evaluated with DSC by studying the evolution of the crosslinking exotherm($\tau = \Delta H_t / \Delta H_{t=0}$). ΔH_t represents the enthalpy of reticulation at time t, $\Delta H_{t=0}$ the enthalpy at time 0. These crosslinking conditions are not optimal but enable a comparison of BMIs.

RESULTS AND DISCUSSION

Synthesis

The BMI series II(n=6 and 8) and III (EO) were synthesized using protocols already developed in laboratory[38,39,41]. The other BMIs are original. Diphenolic and diacyl derivatives were carried out under good conditions(atmospheric pressure and low reactions temperatures) with interesting yields using previously published protocols. The last steps of the BMI syntheses with maleimidobenzoyl chloride (SCHEME 1) were carried out with yields ranging from 51% to 65% while the last stages of the BMI syntheses with N-hydroxyphenylmaleimide(SCHEME 2) were carried out with yields reaching 32% to 38%. The reaction yields that lead to the production of the BMI serie I are the lowest ones. This can be explained by problems of reagent solubility. The acyl dichlorides (SCHEME 2) are very little soluble in the chloroform
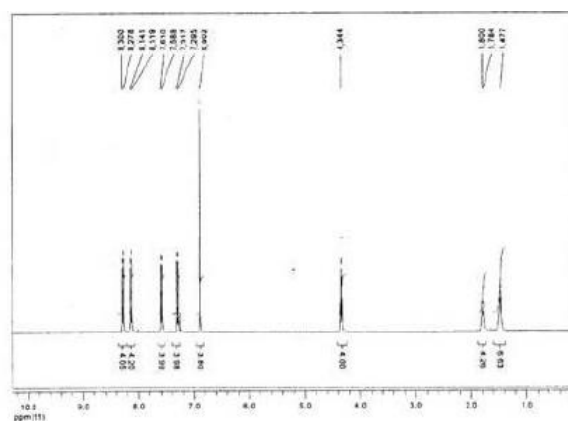
Figure 2 : ¹H NMR spectrum (example) of BMI Serie II n=7

used during the last stage. The solubility is better by mixing chloroform with THF. The mixture chloroform-THF makes it possible to obtain better yields. The yields of BMI serie II near 65%, are interesting for esterifications which are carried out on two sites of the molecule. The good quality of the BMI purity was systematically confirmed by elemental analyses, DSC, ¹H NMR and FTIR (examples: Figure 2 and 3).

The spectra (Figure 2 and 3) given as examples show a good purity of the products. The spectra ¹H NMR show schematically three groups of signals: the aromatic and ethylenic protons appear between 6,6ppm and 8,4ppm. Then, around 4ppm, the protons located on the carbon atoms the nearest of the junctions appear, and finally the other protons making the flexible group show a resonance between 1 and 3ppm. For the BMI series I and II, the most important modifications concern the aromatic protons. For the ester junction, the deblin
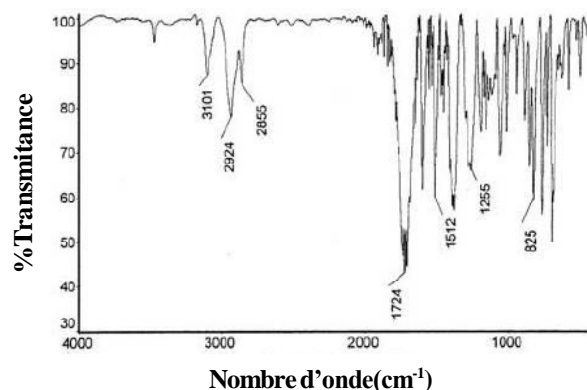
Nombre d'onde(cm⁻¹)

Figure 3 : FTIR spectrum(example) of BMI Serie II n=7

(A)

Temperature(⁰C)
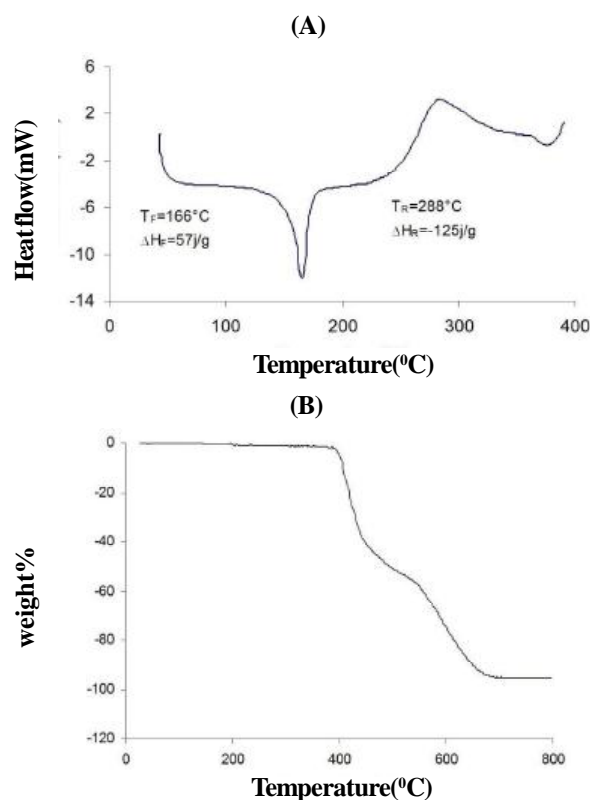
(B)

Temperature(⁰C)

Figure 4 : DSC (A) and TGA (B) thermograms of BMI II n=7 (example: air)

dage of the protons located on the carbon at the point α of the junction is higher. This deblindage becomes more important in the presence of fluorinated groups(BMI serie III fluorinated). Then the general appearance of the spectrum between 1 and 3ppm depends on the length of the flexible group. For the longest BMIs, an extra signal appears(near 1,45ppm). It corresponds to the protons which are situated on the carbon located at the point β of the junction. The influence of the inductive effects on the protons placed at the centre of the flexible group is less

important. The FTIR spectra of the BMIs of the three series are little different (Figure 3). Like the ^{1}H NMR spectra, they show a good purity of the products. They all bring up the absorption bands of aromatics and of esters and methylenic groups. The absorption bands, phenolic and acid intermediates used for the BMI synthesis, are not present[40]. Some typical bands could be specified. At 3100cm⁻¹, we find the absorption band of the vibrations (H-C=) of the maleimide rings. This signal is very fine when the compound is amorphous[50]. The obtained spectra show relatively wide signals (often with a shoulder), which characterize products showing good crystallinity[50]. The BMI III (fluorinated) shows a doublet typical of the strongly crystallyne compounds[40]. This result is confirmed by microscopical examination which brings up a strong reflection of polarized light. The absorption bands measuring 2850cm⁻¹ and about 2925cm⁻¹ correspond to the vibrations of the bonds C-H of methylenic groups present in the flexible group. The absorption bands measuring 2848cm⁻¹ and 2923cm⁻¹ are, as foreseen, much less intense with fluorinated BMI. At 1700cm⁻¹, we find the absorption bands of carbonyl groups: esters and imides. At about 1500cm⁻¹, we find the bands due to the vibrations of the aromatic C=C bonds. At about 1270 cm⁻¹, the C-O vibrations of ethers occur. They are important for the BMI serie I. At 820cm⁻¹ the bands typical of the C-H bonds of aromatic cycles are present.

Thermal behaviours

Temperatures and melting enthalpy were determined by DSC (Figure 4-example). Temperatures were given at the peak of melting endotherm. Enthalpies change according to BMIs from 43kJmol⁻¹ to 87kJmol⁻¹. They present a parity effect. The enthalpies of odd BMIs are lower than those of the even BMIs (TABLE 1, Figure 5-A). This parity effect could be partly explained by a higher density of crystallites, a larger crystallinity, for the molecules showing even numbers of methylenic groups. The molecules with even groups are better aligned[38-40]. They could crystallize more easily. The BMI serie III (fluorinated) is a good example for this observation (ΔHm is high).

The same parity effect was highlighted with the melting temperatures. The melting temperatures of synthesized BMIs vary depending on flexible group

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TABLE 1 : Thermal properties of BMI

Series	n	Tm °C	ΔH_m kJmol⁻¹	ΔSm J mol K⁻¹	T_R °C	ΔH_R kJmol⁻¹	Td_1 °C	Td_2 °C	Tanδ (°C)
I	5	226	59	119	307	161	427	571	165
	7	216	78	159	299	139	445	577	230
	8	231	87	172	288	164	446	612	216
	10	211	68	140	279	86	450	596	191
II	6	212	50	103	325	150	416	609	177
	7	166	44	100	288	96	418	573	178
	8	182	50	110	308	139	425	650	280
	10	156	58	134	292	104	404	575	160
III	EO	187	43	94	286	109	422	596	264
	F	143	69	166	297	122	383	588	143

Tm: Melting temperatures(DSC-peak of endothermic); ΔH_m: enthalpy of melting; ΔSm: entropy of melting; T_R: Temperatures of polymerization (top of the exothermic); ΔH_R: enthalpy of polymerization; Td_1: first degradation temperatures; Td_2: second degradation temperatures; Tanδ(DMA)
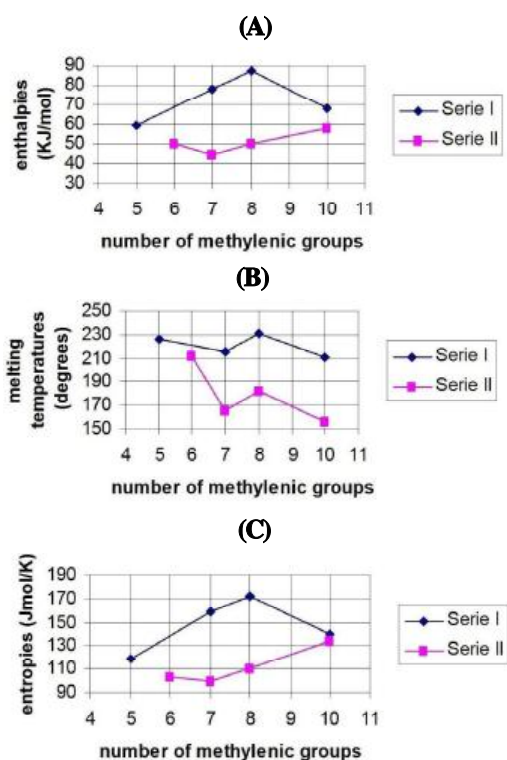
(A)

(B)

(C)

Figure 5 : Parity effect: enthalpies (A), melting temperatures (B) and entropies (C) according to the number of methylenic groups present in the flexible group

length from 143⁰C to 231⁰C(TABLE 1, Figure 5-B). They decrease according to flexible group length. The melting temperatures of odd BMIs are relatively low. The junction plays also an important role in the melting temperatures. The comparison between the melting temperatures of BMI (n=7, 8 and 10) of series I and II shows that the ester junction enables a significant lowering of the melting temperatures (Figure 5). Indeed, the ester junction, in comparison with the ether junction,

brings more flexibility to the molecule. Furthermore we can notice that if we compare the BMI serie II n=10 to BMI serie III (F), we observe that the presence of fluor in the flexible group also enables the lowering of the melting temperature.

The entropy variations computed from melting temperatures and enthalpies also show a parity effect (Figure 5-C). Similar parity effects have been characterized and analyzed with non-reactive dimesogenic compounds with central flexible groups[47,48]. They could come from the aligned structure of even molecules. The melting temperatures of laboratory synthetized BMIs are interesting because they are not very high. Polymethylenic, polyethylene oxides and fluorinated groups bring flexibility to the "arylate" and "aramide" BMIs.

Temperatures and crosslinking enthalpies, as well as melting temperatures, were characterized by DSC (Figure 4(A) and TABLE 1). The exothermic peaks which correspond to the highest crosslinking speeds happen at about 300°C for the whole of the BMIs. For these BMIs, temperatures do not depend on flexible group length(TABLE 1). Crosslinking enthalpies happen between 86kJmol⁻¹ and 164kJ mol⁻¹ for a heating rate of 10°Cmin⁻¹. They decrease slightly with flexible groups length(TABLE 1). They are similar to those of other non liquid crystalline BMIs.

Degradation temperatures were characterized by TGA (Figure 4(B); example). The thermograms show two mass losses (Figure 4(B)). They correspond to two different degradation kinetics. In the air, the first breaking down temperature happens, following n, between 383°C and 450°C (TABLE1). The second happens approximately around 600°C. The first degradation kinetics could mainly correspond to the degradation of the flexible group. The second could correspond to the oxidation of the remainder of the macromolecule after crosslinking. The degradation process could begin with a homolytic breaking from the CH connection located at ester or ether junctions. This assumption seems to be confirmed by the relative weakness of "fluorinated" BMIs to thermal oxidation. Indeed, fluorine atoms exercise their attractive effect on electrons and take part in the CH connection destabilization. These protons fixed on carbons in ethers or esters α junctions, show a strong deblindage in NMR. The BMI with ether junction (serie I) have a better resistance to thermal oxidation
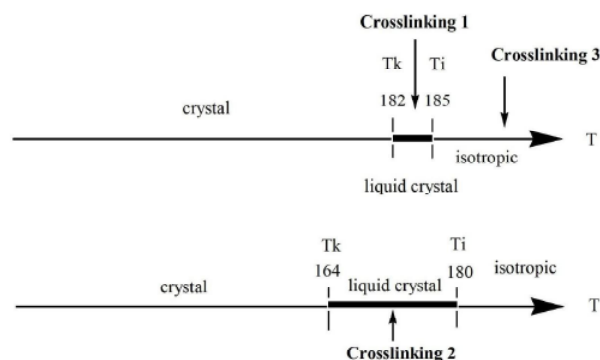
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Figure 6 : BMI II n=8: example of thermotropic behaviour and crosslinking; Tk and Ti were determined at the first and second heating by microscopy (PLM)
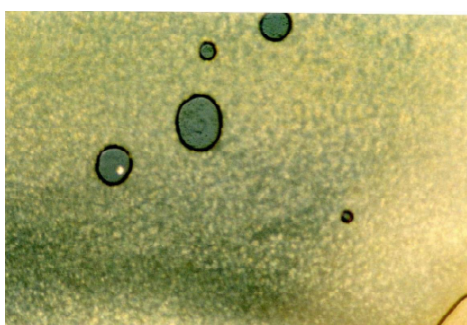

Figure 7 : Microphotography of BMI II n=7 (X 200): liquid crystalline state obtained at 165°C after melting during the first heating

TABLE 2 : Thermotropic properties of BMI. T_k : transition crystalline state-liquid crystalline state(PLM); Ti: tempera ture of isotropisation(PLM); ( ) : rough values; R_1 (between Tk and Ti at the first heating), R_2 (between Tk and Ti at the second heating), R_3 (over Ti) : crosslinking possibilities : NO: no crosslinking, YES: possible crosslinking

Series	n	First heating		Second heating		Crosslinking		
		T_K °C	Ti °C	T_K °C	Ti °C	R_1	R_2	R_3
I	5	223	228	(158)	207	NO	NO	YES
	7	220	225	(189)	206	NO	NO	YES
	8	210	215	(167)	212	NO	YES	YES
	10	197	200	(160)	165	NO	YES	YES
II	6	206	214	163	185	YES	YES	YES
	7	163	166	154	171	NO	NO	YES
	8	182	185	164	180	YES	YES	YES
	10	152	154	(145)	152	NO	NO	YES
III	EO	186	193	(85)	182	NO	NO	YES
	F	148	150	(125)	132	NO	NO	YES

(for medium Td1 at 442°C) than the BMI with ester junction (serie II : for medium Td1 at 416°C). The effect of attraction of electrons is stronger with ester groups. This phenomenon can be observed from the spectra

^{1}H NMR, for instance for the BMIs n=10 of series I and II which show respectively for the protons of carbons located at the point α of the junctions, chemical shifts of 3,99ppm and 4,32ppm. The chemical shifts of the protons of carbons which are near the ester groups are more deblinded.

Liquid crystalline behaviour

The study of these BMIs with Polarized Light Microscopy(PLM) shows that they present a thermotropic behaviour. During the first phase of heating, the liquid crystalline field observed(ΔT=Ti-Tk) is systematically very low (TABLE 2, Figure 6 and 7). But it is with the second heating, after melting and getting back to room temperature, that the liquid crystalline state can be best observed (Figure 6, 8 and TABLE 2).

Observing textures and transitions is often difficult due to the particular character of these liquid crystals. Indeed, during the heating, melting the crystalline part turns into the liquid crystalline state but these BMIs crosslink under the effect of heat. The higher the melt-ing temperature is, the faster the speed of crosslinking is, and the more significant its rate of crosslinking. There-fore, to limit this crosslinking characterizations of tran-sition temperatures and structures were carried out with high heating and cooling rates(10^0Cmin^{-1} and 20^0C min^{-1}). But these high speeds disturb the formation phe-nomena of mesomorphic and crystalline states. Tests were carried out with radical reaction inhibitors. They were negative. They do not completely stop polymer-ization. Moreover, they behave as impurities that modify temperatures transition by plasticization.

These new BMIs with flexible groups present a thermotropic behaviour on several heating-cooling cycles, whereas the rigid liquid crystalline BMIs crosslink immediately after melting in the nematic state.

During the first phase of heating (TABLE 2), the liquid crystalline state occurs immediately after melting (Figure 7). This mesomorphic state is stable only in one very narrow thermal field. But, it is during the new phase of heating that the liquid crystalline state can be best observed (Figure 8). Transitions from crystalline state to liquid crystalline state and from liquid crystalline state to isotropic state are clearer. The field of stability is relatively significant and the texture is characteristic of the smectic state (Figure 8). Several heating – cooling
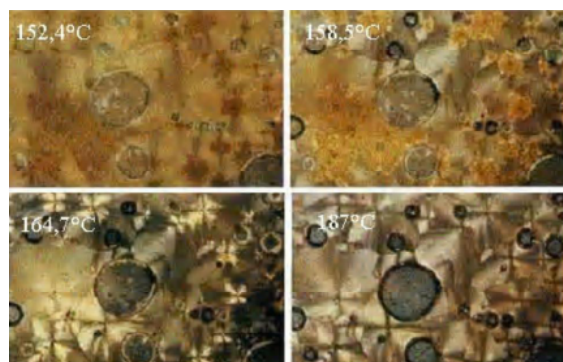
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Figure 8 : Microphotography of BMI II n=8(X 200): transition crystalline state - liquid crystalline state during the second heating

cycles are possible. Thermal behaviour is very close to the thermal behaviour of usual non-reagent liquid crystals. The BMIs of serie II show the clearest liquid crystalline character, the easiest to observe (TABLE 2, Figure 6 and 8). This better result could be due to the presence of the ester junction which enables an increase of the length of the mesogenic group, through its conjugation with the aromatic cycle.

Crosslinking in the smectic order

These BMIs can be crosslinked by providing an orderly smectic C state. Three types of crosslinking were studied(Figure 6): crosslinking in the liquid crystalline state obtained immediately after melting (R_1), in the liquid crystalline state obtained during the phase of re-heating (R_2) and finally from the isotropic phase obtained after the first melting (R_3).

During R_1, BMI II n=6 and II n=8 crosslink in the orderly smectic C state (TABLE 2). Crosslinking in the smectic state had already been characterized for BMI II n=6[38,39]. This smectic C state was also characterized,

using BMI II n=8, by X-ray diffraction (Figure 9a). The spectrum presents a reflection corresponding to a smectic periodicity at narrow angle (d=35.5 ±Å). The comparison between d and the length of the repetitive unit gives an angle of Tilt of $\theta=35^0C(\cos\theta=d/l)$. At wide angles, an additional line is observed. With smectic C, there is another more orderly phase of type SmI or SmJ. Nowadays, we cannot explain the presence of these more ordered phases. During R_1, the BMIs of series I and III, do not crosslink in the orderly state. The ether junction, which brings more rigidity to the molecule, could destabilize the mesophase during crosslinking. BMI II n=7 and II n=10 could not be crosslinked. Their transition temperature are not high enough. The bismaleimides crosslink at higher temperatures. The mechanisms and the kinetics of crosslinking in the liquid crystalline state are not yet known with precision. They have been very much studied especially liquid crystalline diacrylates and diepoxydes [27,51-55]. Reactions are faster in the liquid crystalline state than in the amorphous state. This higher speed is explained by a greater proximity of the reactive groups due to order.

The number of BMIs crosslinking in a orderly state during R_2 is more significant. We showed from the BMI serie II n=8 that this crosslinking is carried out in the smectic C state (SmC1). Indeed, the X-ray spectrum (Figure 9b) presents a reflection corresponding to a smectic periodicity at narrow angles(d=35.5±Å). The Tilt angle is always 35^0C. As previously, an additional line is observed at wide angles that corresponds to smectic orderly SmI or SmJ.

R_3 tests make it possible to obtain a crosslinking revealing the liquid crystalline smectic C state from the amorphous state with all BMIs. This smectic state is characterized by a strong reflection observed with PLM.

Figure 9 : Pinhole camera powder X-ray diagrams of BMI II n=8 a,b,c
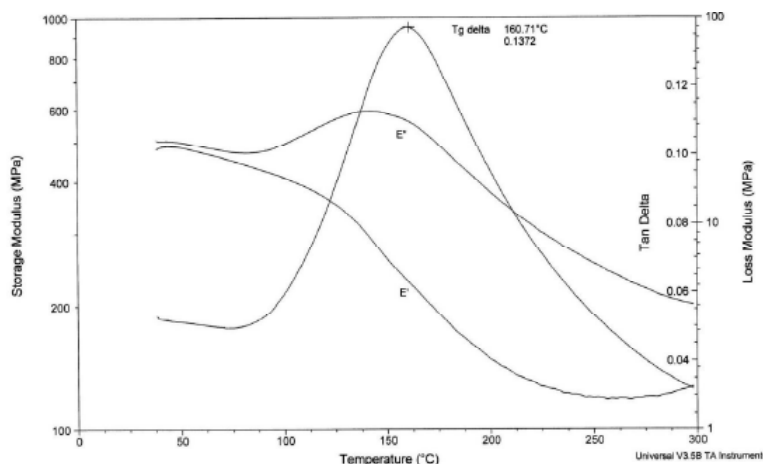
Figure 10 : Example of DMA spectra: BMI II n=10

The most intense reflections in polarized light are obtained for BMI serie II n=8 and serie III(EO). This smectic state was also characterized by X-ray diffraction from serie II n=8(Figure 9c). The orderly structure is of type SmC1. The R_3 results are interesting. The liquid crystalline order occurs by heating after melting. Hoyt and Benicewicz already observed this phenomenon from liquid crystalline bisnadimides. Their explanation can be applied to bismaleimides. The liquid crystalline state occurs at a certain stage of the crosslinking. It could occur when the length of the oligomer formed presents a critical length which would allow the mesophase formation. The rigid liquid crystalline bisnadimides crosslink showing mesomorphic state of nematic type. BMIs with flexible groups, synthesized in laboratory, crosslink showing a liquid crystalline smectic C state. The order obtained with these BMIs with flexible groups is more important. Other authors have shown that the flexible group at the center of the molecule also makes it possible to obtain a smectic state from liquid crystalline epoxydes.

Thermomecanical properties

Tan δ(energy dissipation) were characterized by DMA (TABLE 1, Figure 10). This is an interesting and important parameter for the applications. Tan δ is often assimilated to the temperature of glass transition[37,55]. The BMIs were crosslinked according to the specific conditions of each product (see experimental part). These conditions make it possible to obtain conversion degrees similar crosslinkages. They are near the unit. The conversion degrees were specified by DSC. The results are provided in TABLE 1.

As a whole, Tan δ are relatively high for molecules presenting long flexible groups. Apart from BMI series II n=8 and III (EO), Tan δ of BMI serie I are the highest ones. These higher values could be due to their stronger rigidity relativy to the presence of ether junctions. BMI series II n=8 and III(EO) reveal the highest Tan δ(280°C and 264⁰C). Within the framework of this work these results could not be explained precisely. But these high Tan δ could be due to the higher order that was obtained during crosslinking with these BMIs. This higher order was characterized, but no quantified within the frame work of this work, by the intensity of the reflection of polarized light observed by PLM. With these BMIs, the decrease of the thermomechanical properties takes place under very high temperatures. As suggested by other authors, this improvement of thermomechanial properties might be related to the attaining of very high conversion degrees due to the proximity of the active centers which is involved by the smectic ordered structure of the material[37].

Moreover, BMI serie III(EO) presents a mesogenic group of the aramide type which promotes high Tan δ in presence of hydrogen bonds. These hydrogen bonds limit the motions of the chain segments. Works carried out on diepoxydes show that the presence of a liquid crystalline state makes it possible to improve their Tan δ.

CONCLUSION

This work made it possible to show that bismaleimides with mesogenic groups and flexible

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groups, could present, a true liquid crystalline behaviour according to temperatures and undergo many thermal cycles without crosslinking. The relatively low melting point of these of thermotropic BMIs enable crosslinking in good conditions, that gives of crosslinked material with a smectic C mesophase. Tan δ of these liquid crysta lline BMIs are high. The size of the order could strongly increase Tan δ. The bismaleimide "arylate" with ester junction and flexible group with eight carbons keeps good thermomechanical properties up to 280°C after crosslinking in the smectic C state.

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