

Synthesis and Cure of Liquid Crystalline Diallyl Modifiers for Bismaleimide Resin

Yingfeng Yu, Minghai Wang, Xiaoyun Liu, Lin Zhao, Xiaolin Tang, Shanjun Li

The Key Laboratory of Molecular Engineering of Polymer, Ministry of Education and Department of Macromolecular Science, Fudan University, Shanghai, 200433, China

Received 30 November 2005; accepted 9 February 2006

DOI 10.1002/app.24322

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Three kinds of liquid crystalline aromatic azomethine modifiers were synthesized with high yield, and the modification of bismaleimide resin (BMI) with them was studied by scanning electron microscope, polarizing optical microscope, thermogravimetric analyzer, differential scanning calorimetry, and rheology. Blends cured at the temperature of liquid crystalline phase were found to have oriented liquid crystal-rich phase and improved mechanical

properties. The addition of *o,o'*-diallyl bisphenol A in the blends of BMI decreases thermal properties but shows little effect on phase structures. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 4366–4371, 2006

Key words: liquid crystalline polymers; bismaleimide resin; morphology; mechanical properties; thermal properties

INTRODUCTION

Bismaleimide (BMI) resins are attractive thermosetting polyimides because of their good processability, nonvolatility, high thermal stability, and mechanical properties.^{1–6} However, the main drawbacks of BMIs are their brittleness, poor solubility in organic solvents, narrow processing windows, and high cost. Most of the research efforts on BMIs focused on improving these disadvantages.⁷ For example, toughening agents such as diamines, dithiols, diallyl bisphenols, allylamine, and reactive elastomers were added to improve the toughness of BMI resins.^{8–11}

The toughness of the BMI is increased apparently by blending with reactive liquid rubbers such as carboxyl-terminated butadieneacrylonitrile rubbers¹² or engineering thermoplastics including polysulfone,¹³ poly(ether imide),¹⁴ or poly(ether sulfone).¹⁵ The former modification might reduce either the glass transition temperatures or the modulus and thermal stability of the cured BMI resins. The latter approach, although having the advantage of maintenance of the mechanical and thermal properties for the matrix resins, would certainly increase the viscosity and processing temperatures of the BMI blends. Narrow processing windows of the BMIs were also encountered with these modifications.

Even then, in some two-component BMI systems, such as Matrimid 5292 A and BTM developed by Ciba

Geigy Corp., composed of 4,4'-bismaleimidodiphenyl methane (BDM) and *o,o'*-diallyl bisphenol A (DBA), the mechanical properties and processability are improved at the scarification of thermal properties.¹⁶ Hence, the selection of modifiers is important to improve the toughness of the cured resin in the two-component BMI resin.

Recently, liquid crystalline thermosets (LCTs) have drawn attention as a new type of material, combining the advantages of liquid crystalline polymers and highly crosslinked thermosets.^{17,18} The incorporation of mesogens into thermoset networks as well as the use of new crosslinking reagents results in network passing through a mesophase while curing, and retains a mesophase in the final structure. The retained mesophase structure would increase the fracture toughness of the network, and these materials are expected to have applications as structural and self-reinforced materials.

However, only a few liquid crystals related to BMI are found in literatures.^{19–21} In this paper, three kinds of liquid crystalline modifiers were synthesized and used to modify BDM. Current report examines the influences of mesogenic modifiers concentration on the curing process and physical properties of BMI resin with and without DBA.

EXPERIMENTAL

Materials and samples preparation

BDM was obtained from Fenguang Chemical Co. (China). DBA was supplied by Jianyou Electric Mechanical Material Factory (China). 1,4-Phenylenylene-

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

TABLE I
Mole Ratio of BMI and Modifiers in Samples

Sample	BDM	DBA	Benzally (i)	Totally (iii)
BMI-B	1	–	0.5	–
BMI-BD	1	0.5	0.5	–
BMI-B (1:1)	1	–	1	–
BMI-T	1	–	–	0.5
BMI-BD	1	0.5	0.5	–
BMI-T (1:1)	1	–	–	1
BMI-DBA	1	1	–	–

diamine, 4,4'-biphenyldiamine, 3,3'-dimethyl-4,4'-biphenyldiamine, and 4-hydroxybenzaldehyde etc. were supplied by Sinopharm Chemical Reagent Co. (China) and recrystallized before use.

4-(2-Propenyloxy) benzaldehyde

4-hydroxybenzaldehyde (61.1 g, 0.5 mol), anhydrous K_2CO_3 (82.8 g, 0.6 mol), and DMF (250 mL) were added to a 500-mL three-necked round bottomed flask equipped with a mechanical stirring and a reflux condenser and stirred for 15 min. Allyl bromide (72.6 g, 0.6 mol) in 50 mL of DMF was added slowly over a period of 30 min, and the mixture was refluxed for 24 h under nitrogen. The resulting solution was then poured into water, extracted with ether three times, and dried over anhydrous $MgSO_4$. After evaporating the solvent, slight yellow oil was obtained and further chromatographed over silica gel (benzene).

Yield: 70.5 g (87%). 1H NMR ($CDCl_3$): δ 4.61 (m, 2H, OCH_2), 5.27 (m, 2H, $C=CH_2$), 6.04 (m, 1H, $C=CH$), 6.99, 7.82 (dd, 4H, C_6H_4), 9.92 (s, 1H, $O=CH$).

General procedures for diallyloxy azomethine

A mixture of aromatic diamine and 4-(2-propenyloxy) benzaldehyde in a molar ratio of 1 : 2 was dissolved in DMF with a few drops of acetic acid and heated at 80°C. The reaction was followed by thin-layer chromatography (9 : 1 toluene/acetone) until the initial product disappeared (8 h). After cooling at room temperature, the resulting solution was then poured into water and the solid was filtered off, washed with ethanol, and dried in vacuum.

Diallyloxy azomethines contain different mesogens like benzenoid, biphenyl, and tolyl structures; therefore, compound **i** was abbreviated as **benzally**; **ii** **biphenally**, and **iii** **tolally**.

i (benzally)

Yield: 94%. 1H NMR ($CDCl_3$): δ 4.61 (m, 4H, OCH_2), 5.28 (m, 4H, $C=CH_2$), 6.05 (m, 2H, $C=CH$), 7.02, 7.79 (dd, 8H, C_6H_4), 7.43 (m, 4H, C_6H_4), 8.54 (s, 2H, $N=CH$).

ii (biphenally)

Yield: 89%. 1H NMR ($CDCl_3$): δ 4.61 (m, 4H, OCH_2), 5.28 (m, 4H, $C=CH_2$), 6.05 (m, 2H, $C=CH$), 7.02, 7.79 (dd, 8H, C_6H_4), 7.45, 7.62 (m, 8H, C_6H_4), 8.54 (s, 2H, $N=CH$).

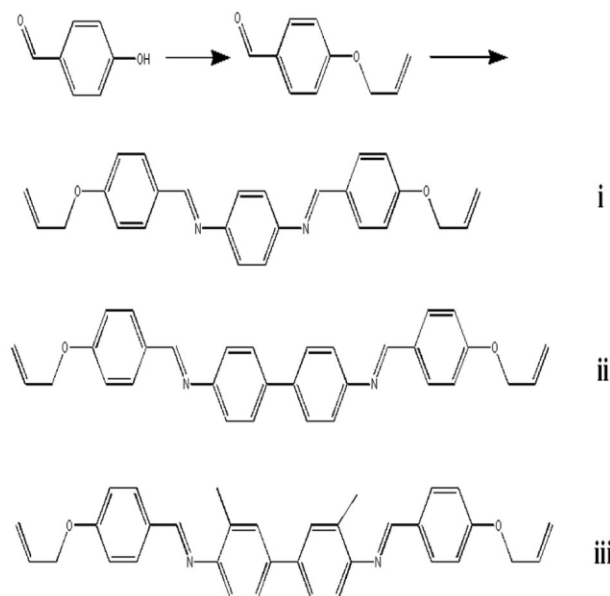
iii (tolally)

Yield: 92%. 1H NMR ($CDCl_3$): δ 2.42 (s, 6H, CH_3), 4.61 (m, 4H, OCH_2), 5.28 (m, 4H, $C=CH_2$), 6.05 (m, 2H, $C=CH$), 7.02, 7.79 (dd, 8H, C_6H_4), 7.38–7.45 (m, 6H, C_6H_3), 8.54 (s, 2H, $N=CH$).

BDM and diallyloxy azomethines (with or without DBA) were blended together at melting state under vigorous stirring until obtaining a transparent solution. The solution was quickly used for various measurements. Four kinds of blends were studied as listed in Table I. The molar ratio between BDM and liquid crystalline diallyloxy azomethine is 1:0.5 and 1:1; DBA was added in 0.5 and 1 mol proportion.

Techniques

Optical microscopy was performed at room temperature and high temperatures using an Olympus polarizing optical microscope equipped with a H-III Polaroid camera (Nikon Co. Ltd). Thermogravimetric analyses were performed between room temperature and 800°C on powdered polymer samples with masses between 8 and 15 mg using a Hi-Res TGA 2950 thermogravimetric analyzer (TA Instruments) at a heating rate of 20°C/min. Dynamic mechanical properties were determined in the dual-cantilever bending



Scheme 1 Synthetic route of diallyloxy azomethine with different structures.

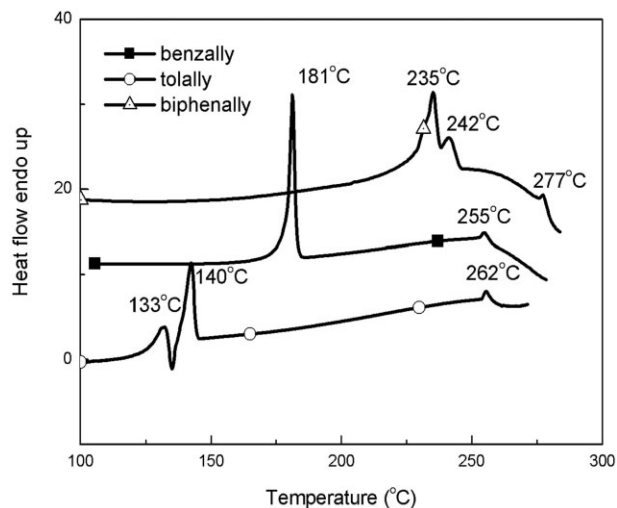


Figure 1 DSC curves of the three diallyoxy azomethines at a heating rate of 10°C/min.

mode between room temperature and 400°C from rectangular polymer samples of approximate dimensions of $1 \times 3 \times 30 \text{ mm}^3$ using a Netzsch DMA 242 apparatus. The measuring frequency was 1 Hz, the sample displacement was 3 mm, and the heating rate was 20°C/min. Rheological measurements were carried out at 170°C on an ARES Rheometer (Rheometrics Scientific, Piscataway, NJ), in steady-shear mode with parallel plate geometry of plate diameter 25 mm and gap 1.0 mm. The mechanical properties of the BMI blends were recorded on an Instron-8500 universal tester according to China State Standard GB 1040-79.

RESULTS AND DISCUSSION

Synthesis and LC behavior of diallyoxy

The synthetic route of the diallyoxy monomers is shown in Scheme 1. 4-(2-Propenyloxy) benzaldehyde

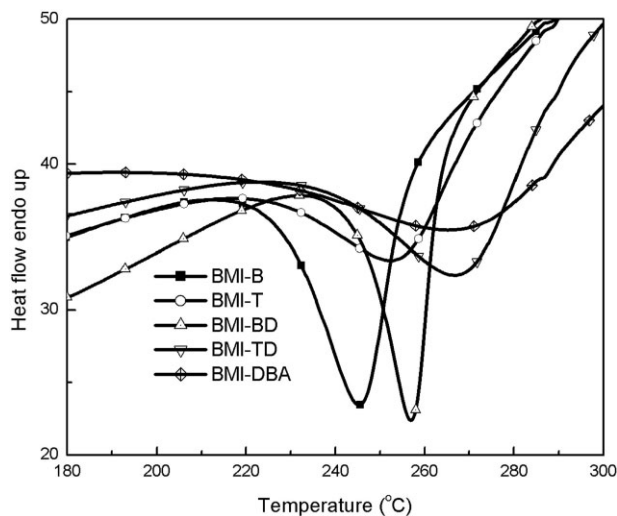


Figure 2 DSC scanning of blends at a heating rate of 20°C/min.

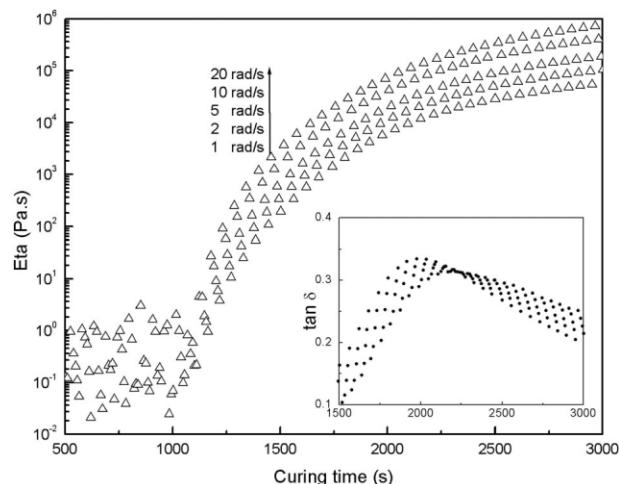


Figure 3 Rheological study of BMI-B blend cured at 170°C.

was synthesized by reaction of 4-hydroxybenzaldehyde with allyl bromide in an alkali solution. The second synthetic step involved the condensation reaction between benzaldehyde and aromatic diamine, obtained by diazocoupling reaction via a reported procedure.²² The condensation, which leads to the formation of azomethine groups, proceeds almost quantitatively in refluxing ethanol or DMF.

The LC behavior of these monomers was examined with differential scanning calorimetry (DSC) and polarized optical microscopy (POM). Figure 1 shows the temperatures of transition evaluated by DSC. Isotropization temperatures were influenced by the homopolymerization or decomposition of allyl, which occurred at high temperatures. Thus, when the same sample was heated twice, the isotropization temperatures were not reproducible. Microscopic examinations after melting show a birefringence characteristic of ordered structures for all modifiers.

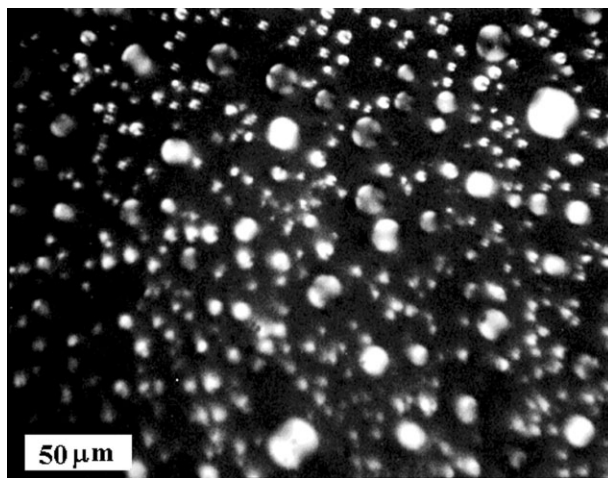


Figure 4 POM of BMI-T (1 : 1) cured at 170°C for 3 h and postcured at 230°C for 5 h.

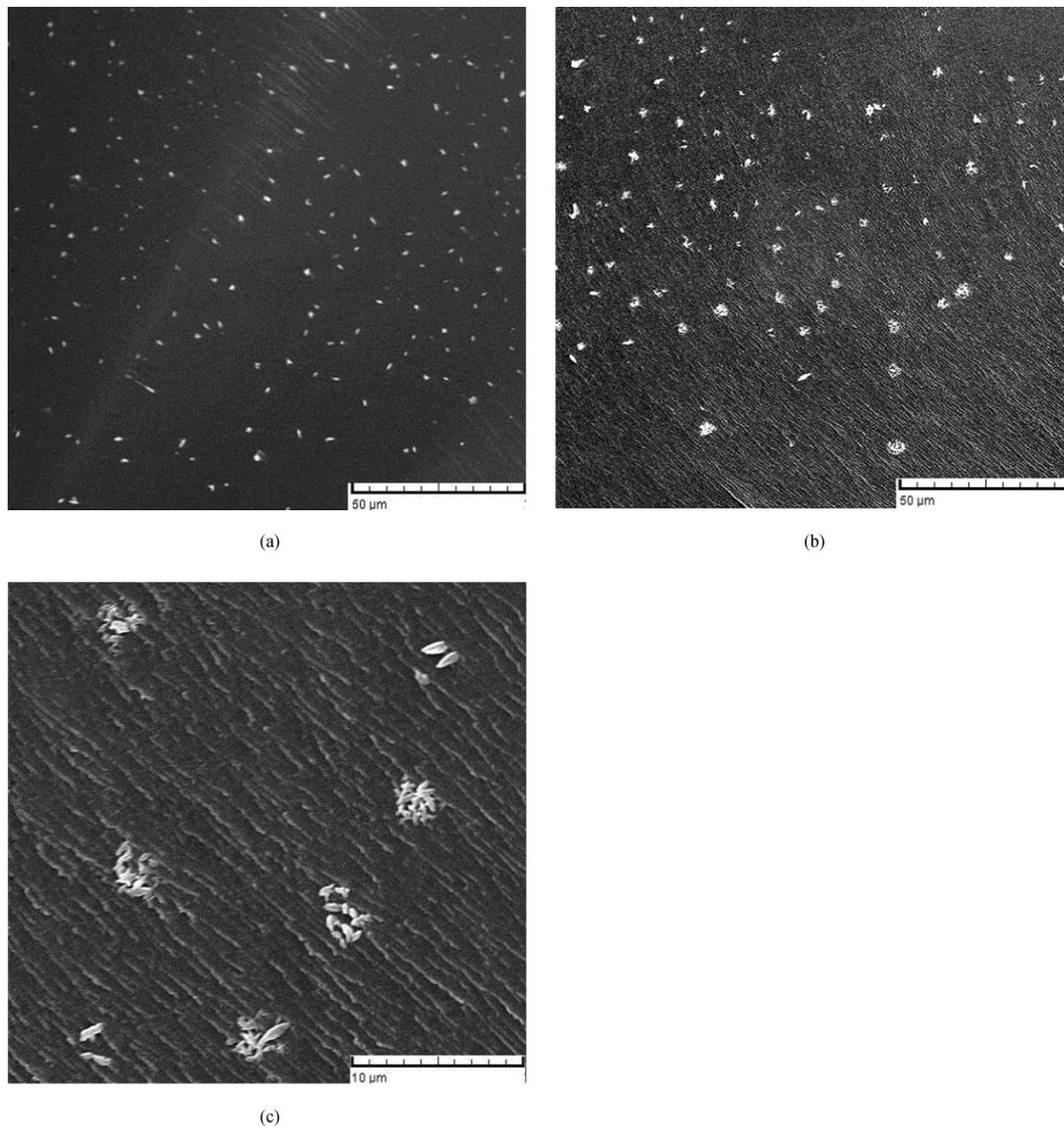


Figure 5 SEM of the samples cured at 170°C for 3 h and postcured at 230°C for 5 h. (a) BMI-T, (b) BMI-TD, and (c) magnification of BMI-TD.

Both benzally and toally show very broad mesogenic range whereas biphenally has a melting point (mp) of 235°C, which is too high to be used as modifiers. It is understandable that the increase of the length of mesogenic unit, as in biphenally, would increase the mp, while incorporation of side groups as methyl group in toally plays an important role in weakening hydrogen bonding and thus significantly depresses the mp. As a result, the toally has a broad mesogenic range from 133 to 262°C, and could be useful in the modification of BMI resin from the view-

point of both processing properties and thermo/mechanical properties.

Curing behavior of blends

DSC curves of BMI blends, BMI-B, BMI-T, BMI-BD, BMI-TD, and BMI-DBA, are shown in Figure 2. Biphenallyl azomethine has a mp of 235°C and cannot be dissolved in BDM at temperature below 210°C; thus, this system was not studied because of its immiscibility. The DSC thermogram of the BMI-B blends exhibits

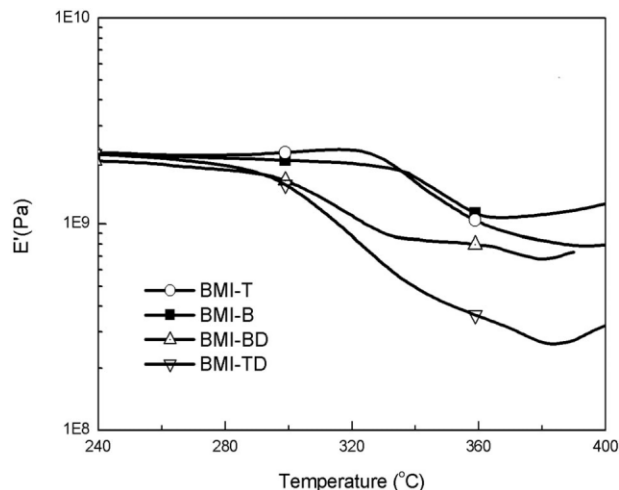


Figure 6 DMA thermograms of full cured blends.

a sharp exothermic peak at 244°C. The exothermic peak of BMI-T appears at higher temperature (253°C at the top), while the DSC thermograms of the samples with DBA are different and exhibit a broad exothermic peak at higher temperature. BMI-DBA shows a weak exothermic peak at high temperatures (272°C). It is well known that allyl groups without electron-withdrawing substitutes as DBA are less reactive than maleimide groups as “ene-ophile” in the ene reaction and “dienophile” in the 4 + 2 cycloaddition. Therefore, higher reaction temperatures were required. However, the addition of liquid crystalline modifiers increases curing rate because of the formation of mesogenic phase at curing temperature.

Rheological behavior is one of the primary aspects to affect BMI processing. As an example, the complex viscosity–time correlation of the BMI-B system is presented in Figure 3. It shows that the viscosity is almost constant for a period of 1000 s and has a value about 0.04 Pa s at a frequency of 1 Hz. The $\tan \delta$ –time curves of the resin system at 170°C are shown in the window of Figure 3. It can be seen that the gel time of the BMI-B system based on the cross-point of $\tan \delta$ at different frequency is 2230 s. Consequently, the times for gelation are 4620 s for BMI-T, 2870 s for BMI-BD, and 5120 s for BMI-TD, which correspond well with the DSC study.

Morphologies of the blends

The evolution of morphologies was followed by POM in the course of polymerization at 170°C in BMI-T (1 : 1) and BMI-B (1 : 1). Before curing reaction, the mesogenic modifiers could be dissolved in BMI completely to form a homogenous solution; thus, POM showed no mesogenic textures. During curing process, the dispersed liquid crystalline particles generated grew with curing time to several decades of

microns and remained stable at full conversion. As an example, Figure 4 shows polarized transmission optical micrographs obtained at 170°C for the fully cured BMI-T (1 : 1).

However, to take full advantage of mechanical properties of the matrix with a liquid crystalline structure, it is necessary to minimize the size of LC phase by decreasing the concentration of LC modifiers. In this respect, some problems could arise by using mesogenic modifiers, because of the low solubility of the liquid crystals in the matrix during curing reaction. For this purpose, the content of mesogenic modifiers was lowered down. As an example, Figure 5 shows the morphology of BMI-T and BMI-TD systems with and without DBA by SEM analysis, where white, liquid crystalline particles are dispersed in the gray BMI-rich matrix. The addition of DBA does not significantly change the morphology of the cured samples with the mesogenic modifiers, and, consequently, allows the preparation of comodifier systems with good processing properties. Microfiber-like LC phase is observed in all the mesogenic hardener cured systems, as shown in Figure 5(c) as an example.

Thermal and mechanical properties

The ability of a polymeric material to withstand loads at elevated temperatures is one of the key aspects of engineering performance to be studied. Thermal and mechanical properties were studied by TGA, DMA, and Instron universal tester.

Dynamic mechanical analysis (DMA) is a method that measures the stiffness and mechanical damping of a cyclically deformed material as a function of temperature. The loss tangent is a sensitive indicator of crosslinking. The representative glass transition temperatures (T_g) of the four samples are shown in Figure 6. The T_g of the mesogenic modifier cured BMI-T and BMI-B blends is shown to be much higher than that of DBA added blends, indicating that the presence of allyloxy in rigid structures may have a positive effect on the glass transition. This could be attributed to the ability of the mesogenic modifiers to form highly crosslinked rigid-rod network both in BMI matrix and liquid crystalline phase. Meanwhile

TABLE II
Thermal Properties of BMI Blends

Sample	T_g (°C)	IDT ^a (°C)	PDT _{max} ^b (°C)	Y_c ^c (%)
BMI-B	324	455	480	59
BMI-BD	294	452	489	59
BMI-T	325	466	511	69
BMI-TD	291	451	489	65

^a Initial decomposition temperature.

^b Maximum decomposition temperature.

^c Char yield at 600°C.

the decrease in the crosslink density in systems with DBA resulted in the decrease of the glass transition, as shown in Table II.

As to the TGA study in nitrogen, the starting temperatures of weight loss are from 452 to 466°C. Figure 7 presents the thermograms obtained for the four systems. It was observed that BMI-B and BMI-TD systems manifest almost identical decomposition pattern, and their curves were nearly superimposable throughout the temperature regime for the benzally systems. While the totally systems have higher IDT (466°C) and char residues at 600°C (69%) (Table II), degradation could be arising from the azomethine moiety in benzally without the protection of methyl groups as in totally systems.

The mechanical properties of all the systems cured at 170°C for 3 h and postcured at 230°C for 5 h are presented in Table III with error about 5%. Compared to the BMI-DBA system, the results revealed the increase of tensile strength, modulus, and strain to break for the cured blends with both liquid crystalline modifiers and DBA, while the blends with only liquid crystalline modifiers revealed slight decrease of tensile strength and strain to break. Thus, it is understandable that the addition of liquid crystalline modifiers increases the toughness of blends in contrast with neat BMI resin, which is too brittle to be tested. Finally, the effect of liquid crystalline modifiers on the toughness of the liquid crystalline blends has not yet been explored. This area is subject to future investigations.

CONCLUSIONS

Three kinds of liquid crystalline aromatic azomethines were synthesized with high yield and broad mesog-

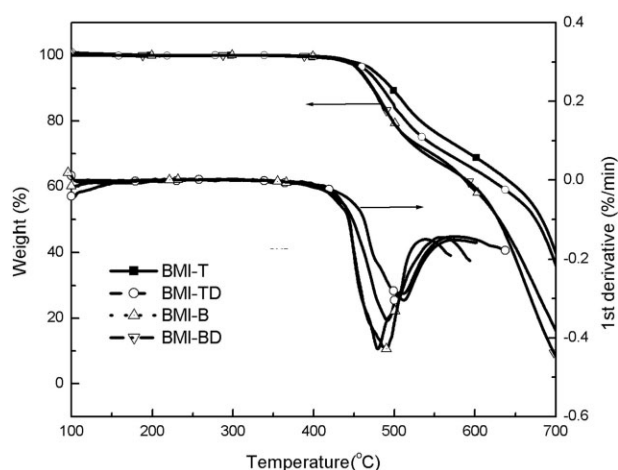


Figure 7 TGA thermograms of full cured blends.

TABLE III
Mechanical Properties of Systems Cured at 170°C for 3 h and 230°C for 5 h

Property	BMI-DBA	BMI-B	BMI-BD	BMI-T	BMI-TD
Tensile strength (MPa)	63.3	61.2	69.6	60.5	73.2
Modulus (GPa)	3.9	4.3	4.1	4.4	4.2
Strain to break (%)	2.6	1.9	2.6	2.1	2.8

inic range. BMI blended with the liquid crystalline modifiers has higher curing rate, and the full cure blend shows high glass transition temperature and heat resistance. Microfiber-like liquid crystal-rich phase was detected in the samples with appropriate content of LC modifiers. Further addition of DBA in the blends show little effect on phase structures of cured blends; however, the mechanical properties increased with a decrease in thermal properties.

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