New semi-interpenetrating polymeric networks from linear polyimides and thermosetting bismaleimides. 1: Synthesis and characterization of starting components

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Starting from two aromatic diamines carrying meta phenoxy linkages, 3,3′-[2,6-pyridinediylbis(oxy)]bisbenzeneamine (BAPPY) and 3,3′-[1,3-phenylenebis(oxy)]bisbenzeneamine (BAPB) we have synthesized two thermoplastic linear polyimides by polycondensation with 3,3′;4,4′ benzophenone dianhydride (BTDA) and two thermosetting bismaleimides by condensation with maleic anhydride. The characterization of these different compounds was achieved by d.s.c., t.m.a., t.g.a. and d.m.a. Each linear polyimide was then mixed with the corresponding bismaleimide, or with another bismaleimide having a different chemical structure, 1,1′-(methylenedi-1,4-phenylene)bis(1H-pyrrole-2,5-dione). The mixtures blended in *N*-methylpyrrolidone solution were cast onto glass plate and were thermally dried following a cure cycle of 1 h at 100°C, 1 h at 150°C and 1 h at 200°C. This did not allow the polymerization of maleimide groups. The thermomechanical analysis of the resulting films showed a reduction of the glass transition temperature of polyimides in agreement with a plasticizing by bismaleimides.

(Keywords: 3,3′-[2,6-pyridinediylbis(oxy)]bisbenzeneamine; 3,3′-[1,3-phenylene bis(oxy)]bisbenzeneamine; polyimide; bismaleimide; blends of polyimide and bismaleimide; thermomechanical analysis)

INTRODUCTION

The concept of the semi-interpenetrating polymeric networks (semi-IPN) has been developed to obtain macromolecular systems which combine the processability of thermoplastic polymers and the high temperature properties of thermosetting polymers.

Semi-IPNs are composed of two chemically different polymers. One is crosslinked and the other is linear. If the crosslinked material is polymerized into the linear matrix, the resulting system is called semi-2-IPN.

A blend of polymers is often thermodynamically unstable, and during the chain extension a phase separation occurs[1–6]. From the point of view of the morphology, a semi-2-IPN can be described as a two-phase system with microphases dispersed in a homogeneous medium[7,8]

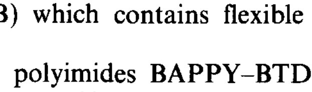
Recently the semi-2-IPN concept was used to prepare heat resistant plastics with potential applications as composite matrix resins. Two novel semi-2-IPNs based on acetylene-terminated imide oligomers and thermoplastic polyimides, such as LARC-TPI, have been synthesized at NASA Langley[9,10]. Semi-2-IPNs coming from bismaleimide compounds and thermostable polymers have been investigated, for instance, with starting blends composed of PI 2080 and 1,1′-(methylenedi-1,4-phenylene) bis(1H-pyrrole-2,5-dione)[7] or with a new bismaleimide resin called HG 9107[11].

Polysulphone mixed with acetylene end-capped phenylsulphone monomers was also characterized by dynamic mechanical analysis showing a microphase separation structure[12].

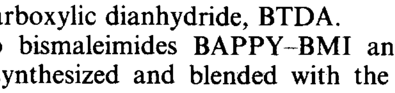
To improve the miscibility of the blend components, we studied thermoplastic and thermosetting resins prepared from the same type of starting compounds, the aromatic diamines, 3,3′-[2,6-pyridinediylbis(oxy)]bisbenzeneamine (BAPPY) and 3,3′-[1,3-phenylene bis(oxy)]bisbenzeneamine (BAPB) which contains flexible meta phenoxy linkages.

Two linear polyimides BAPPY–BTDA and BAPB–BTDA were prepared by polycondensation between these two aromatic diamines and the 3,3′;4,4′-benzophenone tetracarboxylic dianhydride, BTDA.

Two bismaleimides BAPPY–BMI and BAPB–BMI were synthesized and blended with the corresponding polyimides in *N*-methylpyrrolidone solution. The thermomechanical properties of resulting films were studied after a drying cycle which prevented the bismaleimide polymerization. In addition, the blend coming from linear BAPPY–BTDA and 1,1′-(methylene-1,4-phenylene) bis(1H-pyrrole-2,5-dione), MDA–BMI, was investigated in order to evaluate the influence of chemical structure of the bismaleimide component on the final properties.



BAPPY : X = N
BAPB : X = CH



BAPPY - BTDA : X = N
BAPB - BTDA : X = CH

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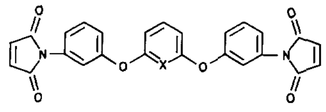
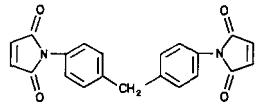


BAPPY - BMI : X = N

BAPB - BMI : X = CH



MDA - BMI

EXPERIMENTAL

Instrumentation

Elemental analyses were performed by the Service Central d'Analyses du CNRS (Vernaison). I.r. spectra were recorded with a Perkin-Elmer 377 spectrophotometer. *FT*i.r. spectra were recorded with a Nicolet 20 SX FT-IR spectrophotometer. ^{1}H n.m.r. spectra were obtained at 393 K with a Bruker WP 80 CW spectrometer using an Me_4Si reference. Inherent viscosities were obtained from 1 g dl^{-1} polyimide solution in *N*-methylpyrrolidone at 30°C using a Ubbelohde capillary viscometer.

Melting points were determined in an electrothermal melting point apparatus. All melting points are uncorrected. D.s.c. data were obtained from 10 mg samples in a nitrogen atmosphere at a 2°C min^{-1} heating rate using a Mettler TA 3000 thermal analyser. T.g.a. data were obtained from 100 mg samples in a nitrogen or air atmosphere at a 5°C min^{-1} heating rate using a Setaram TG85 thermogravimetric analyser. T.m.a. spectra were recorded at a 5°C min^{-1} heating rate with a 0.3 N penetrating strength using a Mettler TMA 40 thermomechanical analyser. Dynamic mechanical tests were performed by a Du Pont 981 mechanical analyser at a 5°C min^{-1} heating rate. The polyimide specimens used for the dynamic mechanical tests were obtained from moulded samples prepared as described below.

Preparation of films

An *N*-methylpyrrolidone solution with 30 wt% of linear polyimide ($\eta_{inh} \simeq 0.5$ dl g^{-1}) was cast on a glass plate using a 0.2 mm thickness doctor blade. The solvent was evaporated in a convection oven at 100°C for 1 h and at 150°C for 1 h. Final drying was performed at 300°C for 1 h. The film was removed from the glass plate by soaking it in cold water. The final film thickness was about 0.05 mm.

An identical workup procedure was used to obtain cured films coming from bismaleimides or dried films coming from polyimide/bismaleimide blends except for the concentration of the starting solution which was 45 wt%. In addition, the final cure temperature was 200°C in place of 300°C for the blends.

Preparation of moulded samples

A 60 mm diameter cylindrical mould filled with about 5 g of linear polyimide was preheated at 120°C for 5 h in a primary vacuum.After vacuum removal, the mould was placed in a press at 120°C and heated at 5°C min^{-1} up to 370°C. The mould was then pressed at 10 bars for 30 min. The pressure was then maintained at 10 bars during the natural cooling of the mould. The specimen was a disc with a thickness of about 1 mm.

Synthesis

All solvents and common reagents were commercial and of analytical grade.

Reagent synthesis: 3,3'-[2,6-pyridinediylbis(oxy)]bisbenzeneamine (BAPPY) **1**. In a 500 ml three-neck flask fitted with a magnetic stirring bar, thermometer and nitrogen inlet tube 200 ml of dimethylsulphoxide and 40 ml of toluene were added and azeotropically distilled for 2 h. After cooling, 62.1 g (0.45 mol) of potassium carbonate was added and dried by azeotropic distillation.

After the addition of 45.83 g (0.42 mol) of 3-aminophenol and 29.6 g (0.2 mol) of 2,6-dichloropyridine, the solution was heated to 140°C in nitrogen and maintained at this temperature for 20 h. The reaction mixture was slowly poured into 2000 ml of 0.1 M sodium hydroxide solution. The white precipitate was filtered, washed with 1500 ml of water, collected and twice crystallized in methanol to yield 53 g (92%) of **1**. The characteristics are listed below.

m.p. 123°C;
^{1}H n.m.r. (DMSO): 7.5–7.9 (*t*, 1H), 6.9–7.2 (*t*, 2H), 6.2–6.7 (*m*, 8H), 4.7 (*s*, 4H);
I.r. (KBr): 3445. 3320, 1630, 1595, 1565, 1425, 1220, 1140, 735;
Analysis calculated for $C_{17}H_{15}N_3O_2$: C, 69.63; H, 5.12; N, 14.33; O, 10.92;
Found: C, 69.67; H, 5.09; N, 14.50; O, 10.90.

3,3'-[1,3-phenylenebis(oxy)]bisnitrobenzene **2'**. In a 1000 ml three-neck flask fitted with a magnetic stirring bar, thermometer and nitrogen inlet tube, 500 ml of dry freshly distilled pyridine and 27.5 g (0.25 mol) of resorcinol were added. The solution was kept for 30 min under nitrogen circulation and 19.6 g (0.49 mol) of 60% sodium hydride dispersion in paraffin oil was progressively added. The reaction was terminated after 1 h at 20°C. 202 g (1 mol) of 3-bromonitrobenzene and 7.5 g of cuprous chloride were introduced. After stirring in nitrogen at 110°C for 24 h, the reaction mixture was poured into 2500 ml of water and neutralized by dropwise addition of concentrated hydrochloric acid. The product was extracted with 400 ml of toluene after work up. The viscous crude product was dissolved in 200 ml of ethanol and precipitated by cooling to 0°C. A crystallization with ethanol yields 31.6 g (36.6%) of **2'**. The characteristics are listed below.

m.p. 104°C;
^{1}H n.m.r. ($CDCl_3$): 7.1–8.2 (m, 12H);
I.r. (KBr): 3090, 1585, 1520, 1470, 1350, 1280, 1215, 875, 735 cm^{-1}
Analysis calculated for $C_{18}H_{12}N_2O_6$: C, 61.36; H, 3.41; N, 7.95; O, 27.28;
Found: C, 61.20; H, 3.18, N, 7.98; O, 27.32.

3,3'-[1,3-phenylenebis(oxy)]bisbenzeneamine (BAPB) **2**. In a one litre metal hydrogenation reactor, 122.7 g (0.349 mol) of nitro compound **2'**, 5 g of palladium charcoal 5% and 300 ml of tetrahydrofuran were introduced blanketed with nitrogen. Then hydrogen was introduced under 20 bars during 3 h at 40°C. After cooling and filtration, the solvent was removed in a vacuum. The viscous product dissolved in 200 ml of ethanol was poured in 1 litre of ice water. The white precipitate was collected, dissolved in 500 ml of ethanol, heated with charcoal, filtered and poured into 500 ml of water to yield 100.2 g (98.4%) of **2**. The characteristics are listed below.

m.p. 109°C;
^{1}H n.m.r. (Me_2SO–d_6): 6.2–7.4 (m, 12H), 3.6 (s, 4H);
I.r. (KBr): 3460, 3360, 1620, 1600, 1575, 1475, 1180, 1150, 765 cm^{-1};
Analysis calculated for $C_{18}H_{16}N_2O_2$: C, 73.97; H, 5.48; N, 9.59; O, 10.96;
Found: C, 74.19; H, 5.55; N, 9.47; O, 11.05.

3,3′-[2,6-pyridinediylbis(3,1-oxyphenylene)] bis(1H-pyrrole-2,5-dione) (BAPPY–BMI) **4**: *bisamic-acid* **4′**. In a 500 ml three-neck flask fitted with a magnetic stirring bar, thermometer and nitrogen inlet tube, 43.95 g (0.15 mol) of BAPPY **1** and 200 ml of acetone were added. After cooling to 0°C, 31.96 g (0.32 mol) of maleic anhydride in 100 ml of acetone was added dropwise with stirring. The temperature was maintained at 0°C during the addition and was raised to 20°C for 3 h. The reaction mixture was filtered, washed with icy acetone and dried to yield 72.25 g (98.5%) of **4′**.

Bismaleimide **4**. Using the preceding flask, 68.46 g (0.14 mol) of **4′** and 191.7 g (1.88 mol) of acetic anhydride were added, followed by 20 ml of toluene and 17.36 g (0.207 mol) of sodium acetate. The reaction mixture was stirred in nitrogen at 90°C for 3 h.

After toluene removal in a vacuum, the reaction mixture was slowly poured into aqueous sodium carbonate (320 g in 2000 ml). The yellow product was filtered and washed with vigorous stirring in 2000 ml of water for 5 h. After work up, the product was crystallized from a 1:2 chloroform/ethylacetate mixture to yield 38.7 g (61%) of **4**. The characteristics are listed below.

m.p. 137°C;
^{1}H n.m.r. (Me_2SO–d_6): 7.8–8.1 (t, 1H), 6.9–7.6 (m, 12H), 6.6–6.9 (d, 2H);
I.r. (KBr): 3090, 1760, 1710, 1590, 1425, 1370, 1295, 1220, 1140, 695;
Analysis calculated for $C_{25}H_{15}N_3O_6$: C, 66.23; H, 3.31; N, 9.27; O, 21.19;
Found: C, 66.07; H, 3.50; N, 9.59; O, 21.07.

1,1′-[1,3-phenylenebis(3,1-oxyphenylene)] bis(1H-pyrrole-2,5 dione) (BAPB–BMI) **5**: *bisamic-acid* **5′**. By a work up procedure identical to that of the preceding synthesis, 43.8 g (0.15 mol) of **2** was reacted with 31.96 g (0.35 mol) of maleic anhydride in an acetone solution to yield 71.7 g (98%) of **5′**.

Bismaleimide **5**. In a 500 ml three-neck flask fitted with a magnetic stirring bar, thermometer and nitrogen inlet tube, 69 g (0.141 mol) of **5′** and 200 ml of tetrahydrofuran were added, followed by 36 g (0.61 mol) of triethylamine and 120 g (1.176 mol) of acetic anhydride. The reaction mixture was stirred in nitrogen at 50°C for 5 h. After cooling, the reaction mixture was poured into aqueous sodium carbonate (198 g in 2000 ml). The yellow product was collected and washed with vigorous stirring in 2000 ml of water for 5 h. A crystallization from a 1:2 H_2O/acetone mixture yields 50.0 g (78.1%) of **5**. The characteristics are listed below.

m.p. 116°C;
^{1}H n.m.r. (Me_2SO–d_6): 6.6–7.7 (m, 16H);
I.r. (KBr): 3100, 1770, 1710, 1590, 1480, 1380, 1245, 1145, 830, 700;
Analysis calculated for $C_{26}H_{16}N_2O_6$: C, 69.03; H, 3.54; N, 6.19; O, 21.24;
Found: C, 68.95; H, 3.51; N, 6.14; O, 21.36.

1,1′-(methylenedi-1,4-phenylene)bis(1H-pyrrole-2,5-dione) (MDA–BMI) **6**. Using the preceding procedure, 29.7 g (0.15 mol) of diamino-4,4′-diphenylmethane was reacted with 31.96 g (0.35 mol) of maleic anhydride with further imidization in an acetic anhydride–sodium acetate–toluene mixture. After removal of toluene under reduced pressure, the reaction mixture was filtered and washed with 300 ml of methanol and 300 ml of icy acetone to yield 33.58 g (67%) of **6**. The characteristics are listed below.

m.p. 159°C;
^{1}H n.m.r. (Me_2SO–d_6): 6.7–7.5 (m, 12H), 4.0 (s, 2H);
I.r. (KBr): 3100, 1760, 1700, 1510, 1390, 1375, 1150, 840, 690;
Analysis calculated for $C_{21}H_{14}N_2O_4$: C, 70.39; H, 3.91; N, 7.82; O, 17.88;
Found: C, 70.12; H, 3.70; N, 7.49; O, 19.02.

Polymer synthesis

Polyimide BAPPY–BTDA, I, or BAPB–BTDA, II. In a 250 ml three-neck flask fitted with a mechanical stirrer, thermometer and nitrogen inlet tube, 20 g or 19.932 g (0.0682 mol), respectively of **1** or **2** and 60.26 g of *N*-methylpyrrolidone were added, followed by 22.630 g (0.0703 mol) of 3,3′;4,4′-benzophenone tetra carboxylic dianhydride **7**. The reaction mixture was stirred in nitrogen at room temperature for 1 h. The temperature was then progressively raised to 80°C for 2 h, 120°C for 1 h and finally 200°C for 2 h.

The solution contained 40 wt% of dry polymer. By pouring in a cold 1:2 methanol/water mixture, the polymer was obtained in a powder form. The polymers exhibited an inherent viscosity in the range of 0.5 dl g^{-1} in *N*-methylpyrrolidinone solution with a concentration of 1 g dl^{-1}.

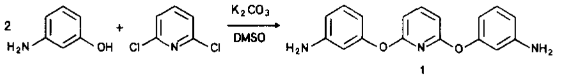
RESULTS AND DISCUSSION

Synthesis of bismaleimides and polyimides

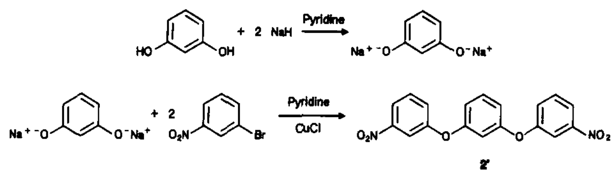
Synthesis of starting aromatic diamines BAPPY and BAPB. The synthesis of 3,3′-[2,6-pyridinediylbis(oxy)] bisbenzeneamine, BAPPY, **1** was achieved by condensation of the 2,6-dichloropyridine with 3-aminophenol in the presence of potassium carbonate in a polar aprotic solvent (*Scheme 1*).

The preparation of the 3,3′-[1,3-phenylene*bis*(oxy)] bisbenzeneamine, BAPB, **2** required the preliminary synthesis of the corresponding dinitro compound **2′** by condensation of disodium salt of resorcinol with 3-bromonitrobenzene[13] (*Scheme 2*). This reaction was achieved in Ullman's conditions by using a cuprous chloride/pyridine system as a catalyst[14].

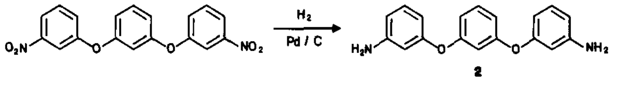
The diamine was then obtained by hydrogenation of



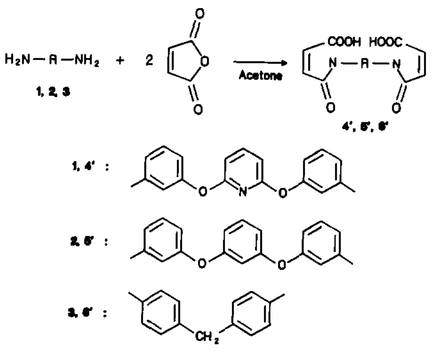
Scheme 1



Scheme 2



Scheme 3



Scheme 4

the dinitro compound **2′** with a palladium charcoal catalyst in a tetrahydrofuran solution (*Scheme 3*).

Synthesis of bismaleimides BAPPY-BMI, BAPB-BMI and MDA-BMI. The bismaleimides BAPPY-BMI **4**, BAPB-BMI, **5** and MDA-BMI, **6**, were prepared in a two-step synthesis. The synthesis involved first the preparation of the bisamic acid precursors **4′**, **5′** or **6′** by reacting the maleic anhydride with the corresponding diamine in acetone solution (*Scheme 4*). Cyclization of the bisamic acid precursor was then achieved by a conventional treatment[15] with acetic anhydride and sodium acetate to give the bismaleimide compound **4** or **6** (*Scheme 5*).

For the bisamic acid **5′** obtained from BAPB **2**, the imidation reaction was performed in the presence of triethylamine, acetic anhydride and tetrahydrofuran as cosolvent. This synthetic method produced BAPB-BMI, **5**, with a higher yield than the usual procedure described above.

Synthesis of polyimides BAPPY-BTDA and BAPB-BTDA. The polyimides BAPPY-BTDA, I, and BAPB-BTDA, II, were synthesized by condensation of the aromatic diamines BAPPY, **1**, and BAPB, **2**, respectively, with BTDA, **7**, in *N*-methylpyrrolidone solution at room temperature (*Scheme 6*). The final imidation of the first polyamic acid formed was performed by heating at 200°C for 2 h in solution.

A 1.03 molar excess of BTDA yielded polyimides I and II with respectively inherent viscosities of 0.53 dl g^{-1} and 0.48 dl g^{-1} at 30°C in an *N*-methylpyrrolidone solution. The excess of BTDA was used to prevent amino end groups which might be able to react with the maleimide double bond according to a Michael addition[16] during the formation of semi-IPNs.

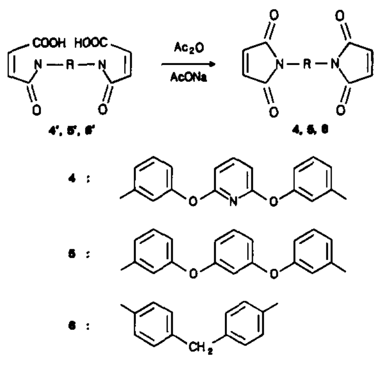
Characterization of bismaleimides and polyimides

Bismaleimides. The d.s.c. traces of BAPPY-BMI, BAPB-BMI and MDA-BMI showed an endothermic transition due to melting followed by a broad exotherm corresponding to maleimide polymerization. Analytical data from the d.s.c. study are summarized in *Table 1*.

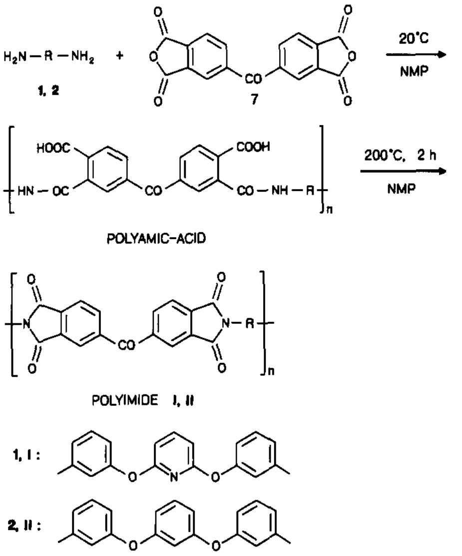
BAPPY-BMI and BAPB-BMI required higher curing temperatures to become polymerized compared to MDA-BMI. It seems that the exotherm was shifted to a higher temperature as the length of the bridge between the two maleimide groups was increased[17]. The polymerization enthalpy of BAPPY-BMI was far higher than those of BAPB-BMI and MDA-BMI.

The radical polymerization of maleimide double bonds might be modified by the presence of the pyridinic ring which is able to react by nucleophylic attack with maleic anhydride to give cyclic intermediate compounds[18].

The three bismaleimides were cured according to the following programme: 1 h at 100°C, 1 h at 150°C and 1 h



Scheme 5



Scheme 6

Table 1 Calorimetric characteristics of bismaleimide compounds

Bismaleimide	Melting point (°C)	ΔH melting (kJ/mole)	Maximum exotherm (°C)	ΔH exotherm (kJ/mole)
BAPPY-BMI	137	65.72	258	186.2
BAPB-BMI	116	51.9	277	77.1
MDA-BMI	159	61.86	206	62.5

Table 2 Thermomechanical and thermogravimetric characteristics of polymerized bismaleimide compounds

Bismaleimide	T_s[1] TMA[2] (°C)	ε[3] 20–350°C (%)	T_d[4] ATG[5] (°C)	ΔP 500°C (%)	ΔP 550°C (%)
BAPPY–BMI	386	3.2	400	32.5	37
BAPB–BMI	372	4.4	386	30.2	38.4
MDA–BMI	390	0.6	410	27.9	43.3

[1] Softening point of the network determined with the intersection of the base line tangent and the inflection point tangent on the TMA curve
[2] TMA on films with about 0.05 mm in thickness with a 5°C/min heating rate
[3] Relative penetration of TMA probe measured between room temperature and 350°C
[4] Onset of degradation temperature corresponding to the first base line deviation
[5] Dynamic TGA from grinding samples with a 5°C/min heating rate

Table 3 Glass transition temperatures of polyimides

Polyimide	T_g by t.m.a.[1] (°C)	T_g by d.s.c.[2] (°C)
BAPPY–BTDA	198	185
BAPB–BTDA	191	181

[1] T_g determined by t.m.a. on polymer films as explained for the softening point in the *Table 2*
[2] T_g determined by d.s.c. on precipitate polymer powders

at 300°C. The thermogravimetric determination during the cure cycle confirmed that the thermal crosslinking of the bismaleimides was achieved without volatile evolution. The thermomechanical and thermogravimetric characteristics of the corresponding networks are summarized in *Table 2*.

From the mechanical point of view, the three networks exhibited a rather low relative deformation at 350°C (less than 5%). The most rigid network was obtained from the MDA–BMI compound in that it had a higher softening point and lower relative deformation. Concerning thermal stability, we compared the onset of decomposition and the loss of weight at 500°C and 550°C in a nitrogen atmosphere. It could be observed that the polymerized MDA–BMI seemed a little bit more thermostable than polymerized BAPPY–BMI and BAPB–BMI. The more rigid structure and better stability of the network coming from MDA–BMI was probably due to its higher crosslinking density.

Polyimides. The glass transition temperatures of the polyimides BAPPY–BTDA and BAPB–BTDA given in *Table 3* were below 200°C, which was consistent with the presence of flexible meta phenoxy linkages in the polyimides backbone. The polyimide BAPPY–BTDA has a higher glass transition temperature than the polyimide BAPB–BTDA. This is probably caused by the polar character of the pyridinic ring which brings higher cohesion to the macromolecular system. The thermogravimetric analysis results of both polymers in air and nitrogen atmosphere are given in *Table 4*. The polymer BAPPY–BTDA carrying a pyridinic ring showed lower degradative stability than the polymer with only an aromatic ring.

The dynamic mechanical analysis achieved with moulded samples using a Du Pont 981 apparatus gave the evolution of the oscillating frequency and relative damping *versus* temperature for each polymer. The d.m.a. spectra reported in *Figure 1* showed a rapid decrease of the frequency and a maximum of the damping profile when the glass transition temperature was reached. The corresponding temperatures and the elastic moduli E' at 20°C and 160°C are given in *Table 5*. The elastic modulus of the polyimide BAPPY–BTDA was higher than the one of the polyimide BAPB–BTDA in relation to the intramolecular association properties attributed to the pyridinic heterocycle.

Thermomechanical study of blends

N-methylpyrrolidone solutions of both components were cast and the resulting films were cured for 1 h at 100°C, 1 h at 150°C and 1 h at 200°C. The following polyimide/bismaleimide blends with different proportions of each components were studied:

Blend PPY/PPY: polyimide BAPPY–BTDA and bismaleimide BAPPY–BMI.

Table 4 Thermogravimetric characteristics of polyimides[1]

	Powder			Film		
Polyimide	T_d[2] (°C)	ΔP 500°C (%)	ΔP 550°C (%)	T_d[2] (°C)	ΔP 500°C (°C)	ΔP 550°C (°C)
			Nitrogen			
BAPPY – BTDA	377	6.3	14	380	8.2	15.5
BAPB–BTDA	385	3.1	14.2	378	6.5	15.5
			Air			
BAPPY–BTDA	343	12.8	26.4	352	13.2	28.8
BAPB–BTDA	356	4.2	14.2	371	5.4	16.8

[1] Dynamic TGA with a 5°C/min heating rate
[2] Onset of degradation temperature

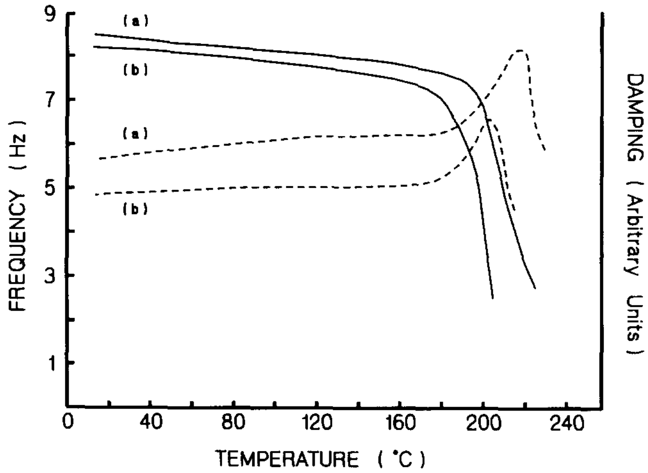


Figure 1 DMA diagrams of polyimide moulded sampled, (a) BAPPY–BTDA, (b) BAPB–BTDA.——, Oscillating frequency; – – –, relative damping

Table 5 Dynamic mechanical characteristics of polyimides[1]

Polyimide[2]	T maximum damping (°C)	E' 25°C (dynes/cm^2)	E' 160°C (dynes/cm^2)
BAPPY–BTDA	216	3.4×10^{10}	3.11×10^{10}
BAPB–BTDA	201	3.17×10^{10}	2.85×10^{10}

[1] DMA with a 5°C/min heating rate
[2] Samples moulded at 370°C under 10 bars

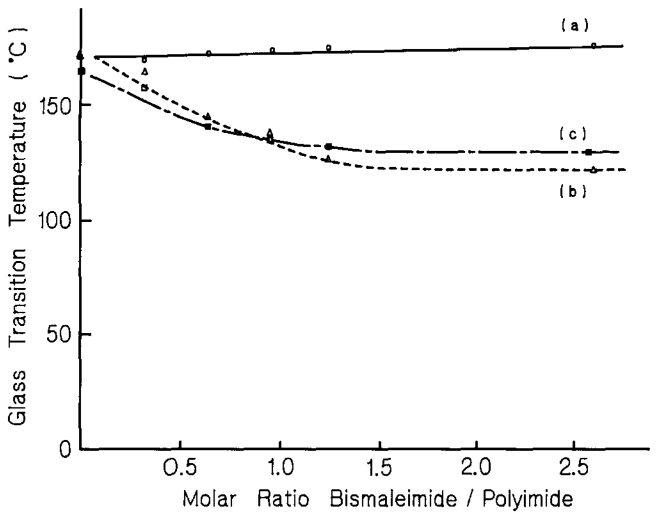


Figure 2 Evolution of the T_g of the linear polyimide *versus* the bismaleimide concentration in the blend: (a) blend PPY/PPY; (b) blend PPY/MDA; (c) blend PB/PB

Blend PPY/MDA: polyimide BAPPY–BTDA and bismaleimide MDA–BMI.
Blend PB/PB: polyimide BAPB–BTDA and bismaleimide BAPB–BMI.

The thermomechanical analysis of the films showed only one mechanical transition corresponding to the T_g of the linear polyimide except in the case of the films coming from blend PPY–MDA, which displayed a second transition at about 330°C.

Figure 2 shows the evolution of the T_g *versus* the concentration of bismaleimide for the three types of blend. As shown in *Table 3*, the T_g of the free linear polyimides were 198°C for BAPPY–BTDA and 191°C for BAPB–BTDA after a cure cycle of 1 h at 100°C, 1 h at 150°C and 1 h at 300°C. As shown in *Table 6*, which summarizes the analytical data from the t.m.a. of the blends, these two temperatures were 172°C and 165°C, respectively, with a final cure temperature at 200°C. This behaviour could be explained by the presence of residual *N*-methylpyrrolidone in the films. A final cure temperature higher than 200°C was not used because it could promote the polymerization of bismaleimides in the three blends studied.

Thus, the constant T_g observed in the case of the blend PPY/MDA was explained by a full polymerization of the MDA–BMI which showed a crosslinking temperature of nearly 200°C. Therefore, the second mechanical transition at 330°C could be attributed to the softening point of the crosslinked bismaleimide structure.

For the two other blends, PPY/PPY and PB/PB, a decrease of the T_g was observed as the concentration of the unreacted bismaleimide increased. Although residual *N*-methylpyrrolidone remains in the films, this decrease of T_g as a function of the bismaleimide concentration is in agreement with a plasticizing of the linear polyimide by the bismaleimide due to miscibility between the blend components.

Table 6 Evolution of the T_g of the linear polyimide *versus* the concentration of bismaleimide

Ponderal ratio bismaleimide/polyimide	Molar ratio[1] bismaleimide/polyimide	T_g[2] (°C)
Semi-IPN PPY/PPY		
0	0	172
0.256	0.327	165
0.509	0.650	145
0.750	0.959	137
0.996	1.273	127
2.030	2.595	124
Semi-IPN PPY/MDA		
0	0	172
0.201	0.325	170
0.395	0.639	172
0.593	0.959	175
0.791	1.279	176
1.569	2.537	176
Semi-IPN PB/PB		
0	0	165
0.258	0.330	158
0.512	0.655	142
0.746	0.954	136
0.986	1.261	133
2.017	2.579	131

[1] Molar ratio: mole of bismaleimide/mole of repeating unit of polyimide
[2] T_g determined by t.m.a. on films of about 0.05 mm thickness

CONCLUSION

Starting from 3,3′-[2,6-pyridinediylbis(oxy)]bisbenzeneamine (BAPPY) and 3,3′-[1,3-phenylenebis(oxy)]bisbenzeneamine (BAPB) both linear polyimides with 3,3′;4,4′, benzophenone tetracarboxylic dianhydride (BTDA), and two bismaleimides were prepared and characterized.

The incorporation of a pyridinic ring instead of a benzenic ring induced a higher T_g for the linear polymer and a higher melting point for the bismaleimide. Moreover the polymerization mechanisms of pyridinic bismaleimide and benzenic bismaleimide could be different.

The thermomechanical study of the polyimide/bismaleimide blends showed a plasticizing of the linear thermoplastic polymer by the thermosetting compound. The formation of semi-2-IPNs with high mechanical and thermal properties could be expected starting from mixtures of these both miscible components.

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