



*Dedicated to Professor Ionel Haiduc
on the occasion of his 80th anniversary*

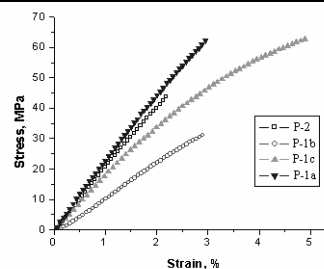
THERMAL AND MECHANICAL PROPERTIES OF SOME BISMALIMIDE POLYMERS CONTAINING AZOBENZENE SIDE GROUPS

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Two series of polymers with azobenzene units were synthesized by the reaction of bismaleimide monomers with aromatic diamines (Michael addition). Azobismaleimides containing azobenzene groups were obtained by the condensation of aromatic diamines with maleic anhydride followed by cyclodehydration with triethylamine and acetic anhydride. Thermal and mechanical properties of the polymers with various chromophore-loading levels were studied.



INTRODUCTION

Bismaleimide (BMI)-based resins have been attracted a great attention because of their excellent heat resistance, mechanical and electrical properties, radiation resistance, good flame resistance and good retention of thermo-mechanical properties, even after long aging times at 250°C.¹⁻⁷ In addition, these resins are of great interest because of their easy processability by resin transfer molding, without formation of volatile by-products.

The reactivity of bismaleimide monomers is determined by the ability of their double bonds to add monomers bearing an active hydrogen atom acting as a dienophile in Diels-Alder reaction and to enter into reactions of radical and anionic homopolymerization, and copolymerization with other monomers containing unsaturated bonds or with cyclic compounds (cyclobutane derivatives or heterocy-

cles). All these properties make polyaspartimides attractive for various applications such as advanced composite components for aerospace, electronic and nuclear industries, high-performance composite matrices for multilayer printed circuit boards, for large-scale computers, and structural adhesives.⁸⁻¹³

At the same time, the second-order nonlinear optical (NLO) polymers have been extensively investigated due to their potential application in integrated opto-electronics.^{14,15} The chromophore is attached to the polymer network by one end functional group.

Unfortunately, these resins evidence some drawbacks, such as brittleness (due to their high crosslinking density), poor solubility in ordinary solvents, and high melting and curing temperature, which considerably restrict their applications.¹⁶⁻¹⁸

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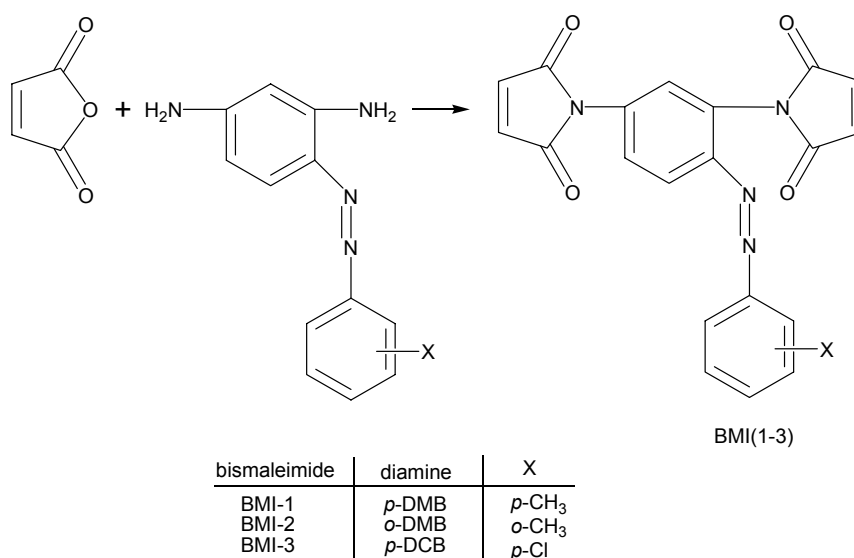
A series of properties can be adjusted by varying the nature of aromatic ring systems and the number of flexible linkages within the polymer chain. Much effort has been dedicated to improve the processability of polyaspartimides, *e.g.* to find new solution systems and to modify their structures by introduction of bulky substituents and flexible linkages into backbone, or by polymerization.

The present communication reports on the synthesis of two series of resins with azobenzene side groups starting from various bismaleimides bearing azobenzene in their structures and aromatic diamines or from bismaleimide and aromatic diamines containing side azobenzene groups, and their characterization.

RESULTS AND DISCUSSION

Bismaleimide monomers containing azobenzene groups BMI(1-3) were obtained by the condensation reaction of various azoaromatic diamines with maleic anhydride followed by cyclodehydration with triethylamine and acetic anhydride (Scheme 1).¹⁹ Bismaleimide BMI-4 was synthesized following the procedure described in literature.²⁰

The FTIR spectra of monomers BMI(1-3) showed characteristic carbonyl bands in the 1777-1771 and 1720-1713 cm^{-1} range. Monomer BMI-3 exhibited an absorption band at 1087 cm^{-1} attributed to the Cl atom. Figure 1 presents the FTIR spectrum of monomer BMI-1.



Scheme 1 – The structure of bismaleimide monomers BMI(1-3).

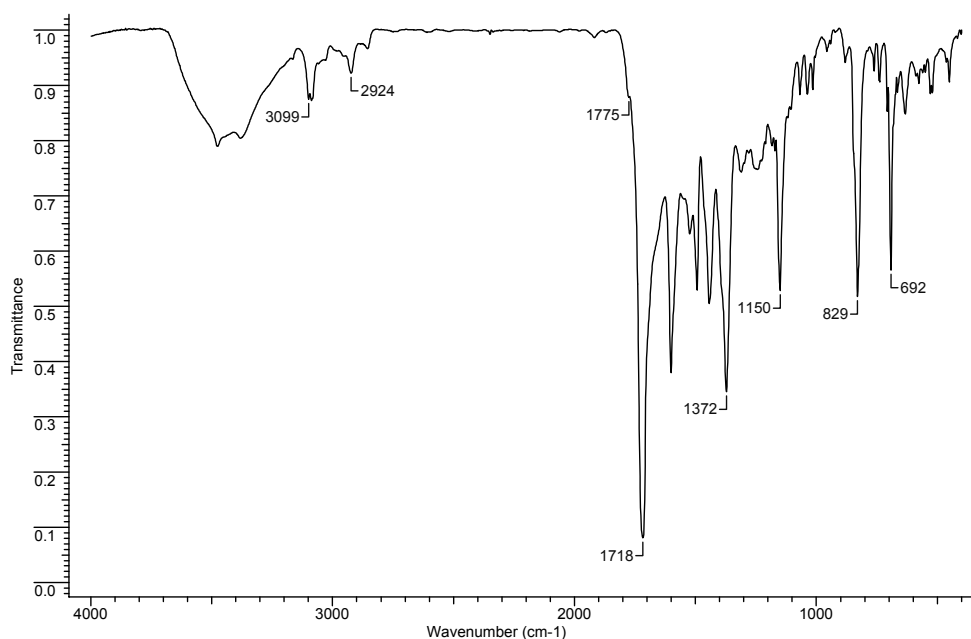
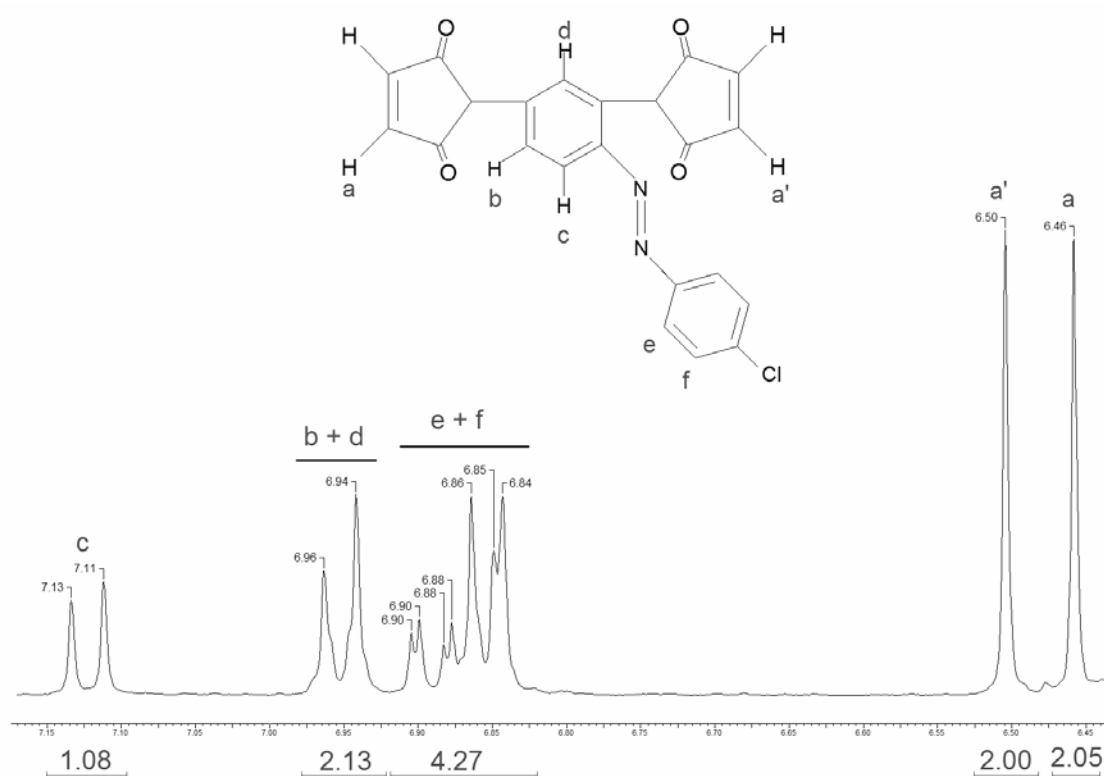
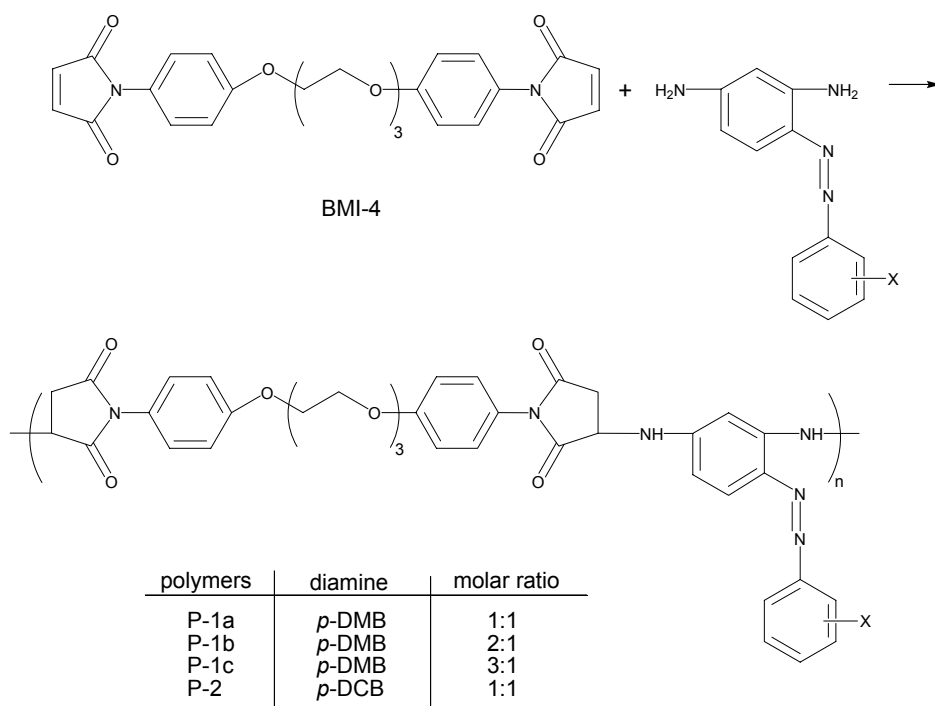


Fig. 1 – FTIR spectrum of bismaleimide BMI-1.

Fig. 2 – ^1H -NMR spectrum of monomer BMI-3.

Also, all monomers BMI(1-3) were characterized by ^1H -NMR spectra which confirmed their chemical structure. Figure 2 shows the ^1H -NMR spectrum of compound BMI-3 and the corresponding ascribing of protons.

The polymers with various structures containing azobenzene units were synthesized by the Michael addition of aromatic diamines to various bismaleimides²¹ and the results are summarized in Table 1.



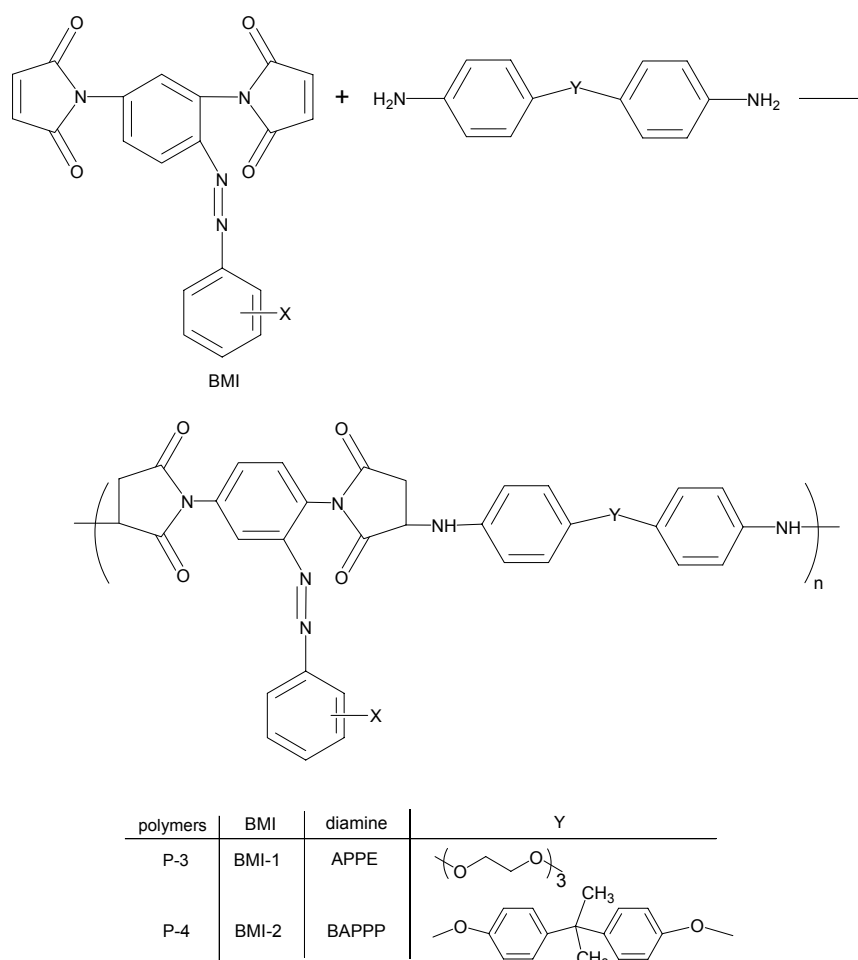
Scheme 2 – Structure of polymers P-1(a-c) and P-2.

The first series of polymers was prepared by the reaction of BMI-4 and *p*-DMB 2,4-diamino-4'-methylazobenzene using molar ratios of 1:1, 2:1, and 3:1, and BMI-4 with 2,4-diamino-4'-chloroazobenzene (*p*-DCB) (Scheme 2). The second series of polymers was prepared by reaction of bismaleimides BMI-1 and BMI-2, and aromatic diamines APEE and BAPPP (Scheme 3).

The structure of the polymers was confirmed by means of FTIR spectroscopy. Figure 3 presents the spectrum of polymer P-1b. Two characteristic carbonyl bands around 1776 and 1714 cm^{-1} are due to asymmetric and symmetric stretching vibration.

Other bands were observed in the range 2962-2874 cm^{-1} and ascribed to aliphatic groups (CH_2). At the same time, the band at 1150 cm^{-1} , due to maleimide ring, disappeared and a band at 1170 cm^{-1} , due to succinic ring, appeared, which indicated that maleimide C=C bond reacted.

The thermal properties of polymers were evaluated by TGA and DTG. The representative curves of these polymers obtained in nitrogen atmosphere are shown in Figures 4 and 5. The thermal behavior data of these compounds are summarized in Table 2.



Scheme 3 – Structure of polymers P-3 and P-4.

Table 1

Reaction between bismaleimides and diamines

Polymer	BMI	Diamine	Molar ratio	Reaction temp ($^{\circ}\text{C}$)	Reaction time (h)	Film
P-1a	BMI-4	<i>p</i> -DMB	1:1	95	35	Flexible
P-1b	BMI-4	<i>p</i> -DMB	2:1	95	55	Flexible
P-1c	BMI-4	<i>p</i> -DMB	3:1	90	40	Flexible
P-2	BMI-4	<i>p</i> -DCIB	1:1	95	30	Brittle
P-3	BMI-1	APEE	1:1	90	40	Flexible
P-4	BMI-2	BAPPP	1:1	90	60	Brittle

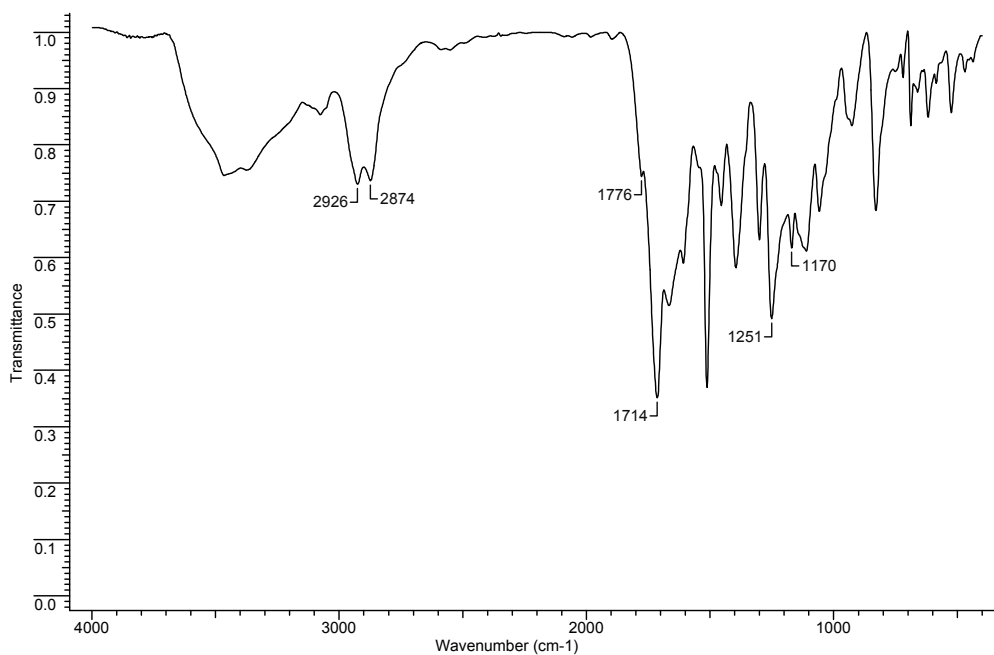


Fig. 3 – FTIR spectrum of polymer P-1b.

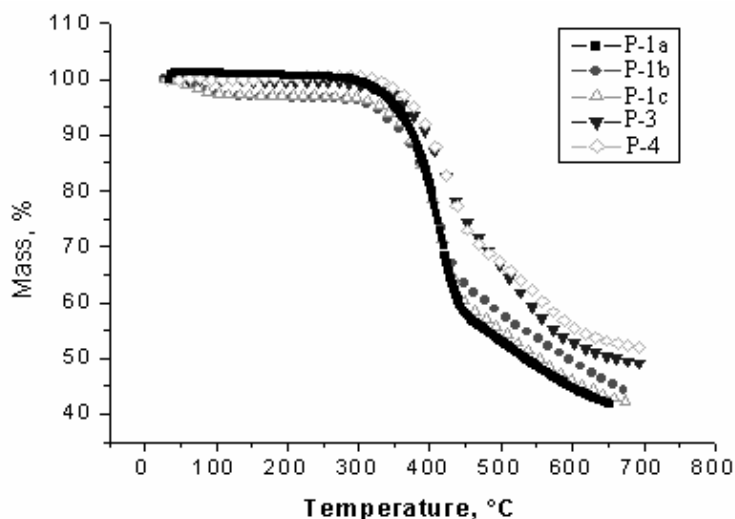


Fig. 4 – TG curves of polymers P-1(a-c), P-3 and P-4.

The polymers P-1b, P-1c and P-3 exhibited their initial decomposition temperatures (IDT) between 356 and 373°C while polymer P-4 was stable up to 298°C in N₂ atmosphere and the weight loss (1-2%) observed in this interval is associated with the evaporation of humidity and solvent traces. A rapid weight loss occurred between 335 and 503°C in the region of maximum decomposition temperature (PDT_{max}). In the interval 357-473°C were located the temperatures at which a 25% weight loss (T₂₅) was recorded. The polymers P-1b, P-1c and P-3 afforded a char yield (Y_c) of 42-56% at 675°C. Thermal stability of polymer P-1a and P-2 was carried out in air atmosphere. Polymers P-3 and P-4 showed two

maxima of decomposition. The multistage decomposition observed for these polymers is due to the combination of chemical different segments in the polymer chain. The first PDT_{max} is due to the thermal destruction of the groups more sensitive to degradation. The second PDT_{max} is ascribed to the degradation of the polymer chain itself.

Some polymers possess film forming ability. Their solutions in NMP having a concentration of 10% were cast onto glass substrates and dried to yield thin reddish-brown films. The quality of such films was studied by AFM. A typical AFM image is shown in Figure 6. This film is smooth and relative homogeneous and it does not show any pinholes or cracks.

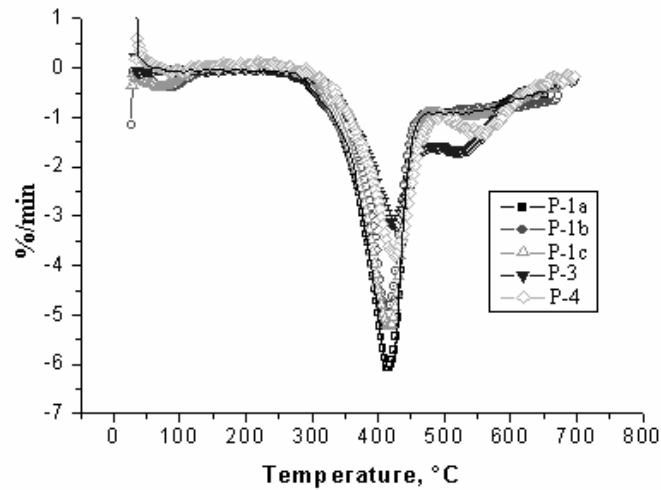


Fig. 5 – DTG curves of polymers P-1(a-c), P-3 and P-4.

Table 2

Thermal properties of polymers P-1(a-c) and P(2-4)

Polymer	IDT (°C)	PDT _{max} (°C)	T ₂₅ (°C)	Y _c (%)
P-1a	363	415	408	42 ^a
P-1b	373	406	414	44
P-1c	367	417	411	42
P-2	298	335	357	38 ^a
P-3	356	410, 525	412	53
P-4	289	503, 560	473	56

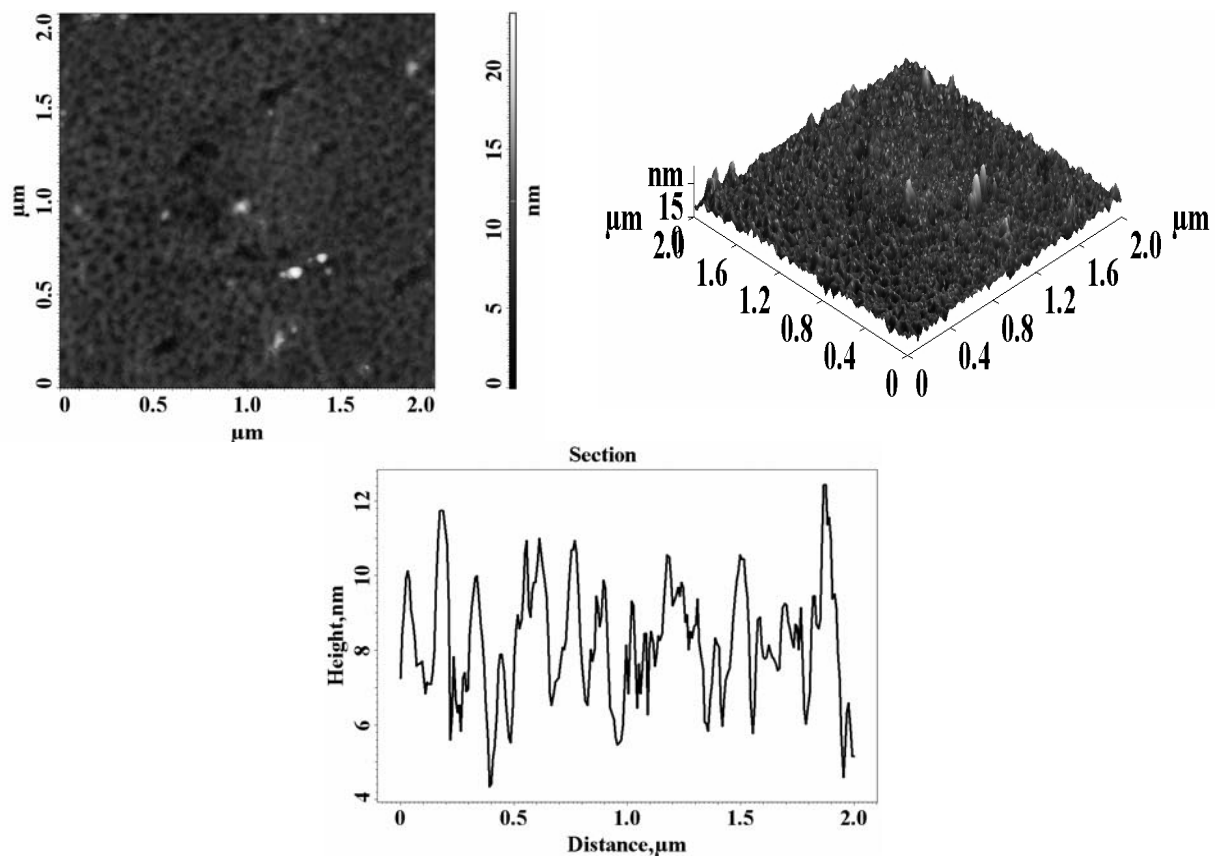
^a Thermogravimetric measurements were carried out in air

Fig. 6 – AFM picture of the film made from polymer P-1a.

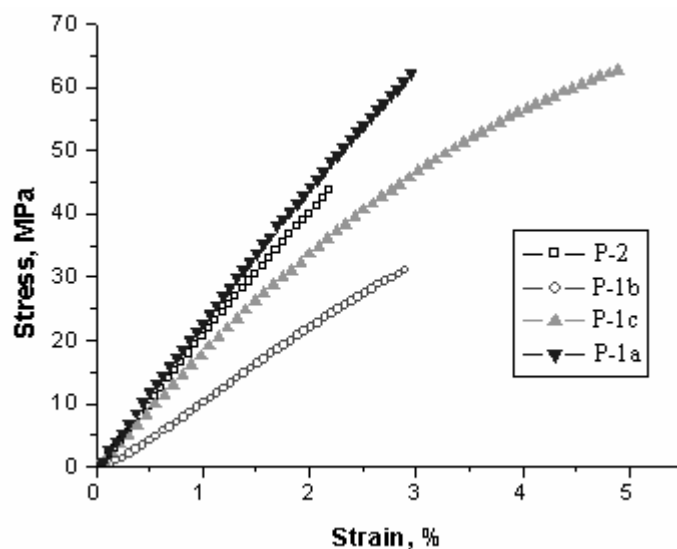


Fig. 7 – Stress-strain curves of polymers P-1(a-c) and P-2.

Table 3

Mechanical properties of the polymer films

Polymer	Tensile strength at break (MPa)	Tensile modulus (GPa)	Elongation at break (%)
P-1a	63.0	2.20	3.06
P-1b	31.0	1.17	2.04
P-1c	63.0	1.72	4.89
P-2	44.0	2.12	2.23

The stress-strain curves are shown in Figure 7. The polymer composition and reaction parameters influence the tensile strength values, which are between 31–63 MPa (Table 3). The elongation at break values are between 2.23–4.89 % and the maximum value was 4.89 % for sample P-1c. The polymer films had tensile modulus varying between 1.17 and 2.20 GPa. The high level of rigidity of these polymers is reflected by their modulus values. The polymers P-1a and P-2 have higher rigidity values. The modulus values are mainly due to the high crystallinity of polymers. It is possible that the molecular orientation to contribute to the observed effect.

EXPERIMENTAL

Materials. 2,4-Diamino-4'-methylazobenzene (*p*-DMB), 2,4-diamino-2'-methylazobenzene (*o*-DMB) and 2,4-diamino-4'-chloroazobenzene (*p*-DCB) were prepared according to literature.²² 1,2-Bis[2-(4-aminophenoxy)ethoxy]ethane (APEE) and 2,2-bis[4-(4-aminophenoxy)phenyl]propane (BAPPP) were prepared according to the method reported by Feld.²³ Maleic anhydride (Fluka, Buchs, Germany), acetic anhydride (Merck, Darmstadt, Germany), triethyl amine and magnesium acetate (Fluka, Buchs, Germany) are commercially available products and were used as received. Commercial solvents as acetone and *N*-methyl-2-pyrrolidone (NMP) (Fluka, Germany) were dried and purified by standard methods.

Synthesis of bismaleimide monomers. Monomers BMI(1-3) and BMI-4 were synthesized following the literature, *via* the reaction of maleic anhydride with various diamines according to Scheme 1. Diamine (0.02 mol) dissolved/suspended in 50 mL acetone was reacted with maleic anhydride (0.04 mol)

in 40 mL acetone to give the corresponding bismaleamic acid. The mixture was stirred for 30 min at 20–25 °C, and then the temperature was raised to 40°C. Over a period of 10 min, triethylamine (TEA) (0.02 mol), acetic anhydride (0.15 mol) and magnesium acetate (0.04 g) were added. The mixture was refluxed for 1.0 h under nitrogen atmosphere. The hot solution was filtered, cooled and poured into cold water. The product was washed with a solution of sodium carbonate (10%) until free from acetic acid. Finally, it was washed with water and dried in vacuum.

Synthesis of polymers. Into a 50-mL three-necked flask fitted with a mechanical stirrer, a thermometer, and a nitrogen inlet, bismaleimide (0.02 mol), diamine (0.02 mol) in *N*-methyl-2-pyrrolidone (NMP) or *m*-cresol as solvent (up to 10–15% of monomer concentration) and a small amount of acetic acid were charged. The reaction mixture was kept in a water bath at 90–95°C, for different time intervals. The polymer was isolated by pouring the reaction mixture into a large amount of methanol. All polymers were redissolved in fresh solvent, precipitated in a nonsolvent medium, and dried for 20 h in a vacuum oven at 90°C.

Measurements. The FTIR spectra were recorded on a Bruker Vertex 70 spectrophotometer and the ¹H-NMR spectra were recorded on a Bruker NMR Spectrometer Avance DRX 400 MHz, using DMSO-*d*₆ as solvent and tetramethylsilane as an internal standard. Differential scanning calorimetry (DSC) measurements were done with a DuPont of 10°C/min in air. Melting points were determined with a Gallenkamp hot-block melting point apparatus. Thermogravimetric analysis (TGA) was carried out using a Mettler Toledo TGA/SDTA 851e-thermogravimetric analyzer, under nitrogen flow (20 mL/min) at a heating rate of 10°C/min from room temperature to

700°C, and 3-5 mg of sample mass. AFM images were collected in semicontact mode with a solver PRO-M, NT-MDT, atomic force microscope (Russia).

CONCLUSIONS

Several bismaleimide monomers bearing azobenzene moieties were synthesized. BMI-based polymers have been prepared by a Michael addition reaction of aromatic diamines to bismaleimides. The polymers were stable up to 289-373 °C and these thermal properties were influenced by the rigidity, symmetry and conditions of reaction. Degradation process for polymers P-1(a-c) in the first series occurred between 363-373 °C while for polymer P-2 the initial degradation temperature was 298 °C because this polymer contained chlorine atoms in its structure and the thermal degradation was performed in air. Concerning the second series of polymers that contained azo group in aromatic diamine structure, the two polymers had different values of initial degradation temperature. The thermal behaviour of the polymers reported was due to the combination of different chemical segments in the polymer chains and different positions of substituents in their structures.

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