Synthesis and characterization of elastomer-modified addition polyimides

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Elastomer-modified polyimides, based on *N*,*N*′-bismaleimido-4,4′-diphenylmethane and 1,4-piperazine, have been prepared by chemically incorporating 0–50 wt% of a butadiene–acrylonitrile oligomer into the polyimide chain by a two-step procedure. Thermal, dynamic mechanical and thermogravimetric analyses were carried out on the copolymers prepared. Thermograms of all the samples investigated show an exotherm in the temperature range 230–280°C due to a curing process probably involving chain-end reactions. The dynamic mechanical characterization indicates microphase separation for all the copolymers prepared. Different high-temperature mechanical behaviours were observed depending on the elastomer content. Thermogravimetric analysis indicates that modification of the polyimide occurs at a modest sacrifice of thermal stability if the elastomer content does not exceed 30 wt%.

(Keywords: polyimide; block copolymer; elastomer modification; butadiene–acrylonitrile; *N*,*N*′-bismaleimido-4,4′-diphenylmethane)

INTRODUCTION

Aromatic polyimides are suitable polymeric materials when high performance or use in extreme environmental conditions are required. Their use and applications, however, are limited mainly because of problems related to the high processing temperature and poor solubility. The introduction of flexible rubbery segments along the rigid polyimide chains has been used to improve some specific properties such as tear resistance, impact strength and processability[1–3]. Toughening is especially required in the case of addition polyimides, as the crosslinks formed during the curing process lead to brittle materials.

In the present paper we report some preliminary results on the synthesis of a series of addition polyimides, based on 1,4-piperazine and *N*,*N*′-bismaleimido-4,4′-diphenylmethane, containing different amounts of a chemically bound elastomeric component, and on the effect of rubber incorporation on the thermal and mechanical properties.

EXPERIMENTAL

Materials

N,*N*′-Bismaleimido-4,4′-diphenylmethane (Aldrich reagent, purity 95%) was recrystallized from chloroform/methanol. 1,4-Piperazine (Aldrich) was distilled under reduced pressure in the presence of NaOH and of A-4 molecular sieves.

The amine-terminated butadiene–acrylonitrile elastomer (ATBN) (kindly supplied by Goodrich Chemical Italia) had an acrylonitrile content of 16 wt%, a molecular weight of 3500 and a functionality close to 2. It was purified from free *N*-aminoethylpiperazine according to the following procedure: a sample was dissolved in methylene chloride, the resulting solution filtered and the solvent removed under vacuum. The recovered product was kept at 10^{-2} mmHg and 80°C for 14 h. *N*-Methylpyrrolidone (NMP) was used as received. *m*-Cresol was distilled at reduced pressure before use.

Typical preparation of a polyimide–elastomer copolymer

NMP solution (35 ml) containing 3.10 g (0.88 mmol) of ATBN was added dropwise under nitrogen to 35 ml of *m*-cresol solution containing 5.96 g (16.62 mmol) of *N*,*N*′-bismaleimido-4,4′-diphenylmethane at 105°C with vigorous stirring. The resulting solution was reacted at 105°C for 2 h and thereafter 1.36 g (15.74 mmol) of 1,4-piperazine, dissolved in 35 ml of *m*-cresol, was also added. After 3 h the very viscous solution was poured in 1 litre of methanol and the precipitated polymer was repeatedly washed with methanol and finally dried at 60°C in a vacuum oven: 9.65 g of a white powder were obtained (yield 93%). The polymer had 32 wt% of ATBN as found by C and N elemental analyses.

Polymer characterization

The dynamic mechanical analyses were carried out in the temperature range −50 to 300°C using a DMTA Analyser (Polymer Laboratories) equipped with a Hewlett–Packard series 2000 Computerized System on films obtained by slow evaporation of NMP/acetic acid mixtures (film thickness > 150 μm). A 10 Hz excitation frequency and a heating rate of 4°C min^{-1} were used.

The infrared spectra were performed on films obtained as before or on nujol mulls using a Perkin–Elmer 457 Spectrophotometer.

The thermal analyses were carried out by means of a Mettler TA 3000 differential scanning calorimeter on 4 mg samples at a scanning rate of 10°C min^{-1}.

The thermogravimetric analyses were performed by using an STA 409 Netzsch Geratebau Thermobalance under a nitrogen flow at a 10°C min^{-1} heating rate.

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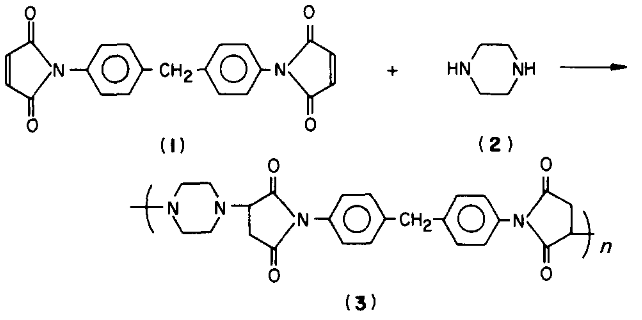
RESULTS AND DISCUSSION

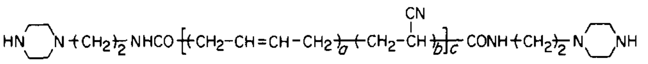
Synthesis

The nucleophilic addition of diamines to aromatic bismaleimides, Michael-type polyaddition, is a well known route to high-molecular-weight linear polyaspartimides[4]. The polymerization is performed in protic solvents, generally *m*-cresol, to avoid the formation of crosslinked, insoluble products[5].

In the present work, *N*,*N*′-bismaleimido-4,4′-diphenylmethane (**1**) and 1,4-piperazine (**2**) were chosen as low-molecular-weight reagents as they yield a rigid polyimide (**3**):

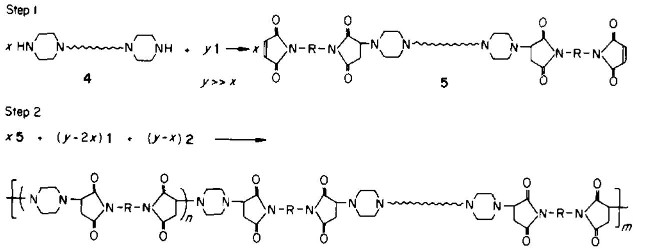


A telechelic amino-terminated butadiene–acrylonitrile elastomer (ATBN, **4**) was used as rubber component to modify **3**:



ATBN (**4**) $a=5$, $b=1$, $c=10$

The synthesis was accomplished by a two-step procedure as shown in *Scheme 1*. First, the telechelic rubber **4** was reacted with a large excess of **1** (step 1): the addition of the secondary amino end-groups of ATBN to the maleimide double bonds yields a maleimide-terminated rubber (**5**). In the second step the macromer (**5**) and the unreacted (**1**) are chain-extended with piperazine (**2**), thus forming random multiblock copolymers characterized by the alternation of rigid polyimide sequences and flexible ATBN blocks.



Scheme 1

The experimental conditions of the synthesis strongly affect the molecular characteristics of the copolymers. We have confirmed that the use of polar aprotic solvents, such as NMP or *N*,*N*′-dimethylacetamide (DMA), leads to gel formation due to extensive crosslinking[5]. In *m*-cresol a high-molecular-weight sample of **3** was obtained, but copolymers of low inherent viscosities were formed when the rubber was introduced. Better results were obtained using mixtures of protic and polar aprotic solvents. A 2/1 v/v mixture of NMP and *m*-cresol was employed throughout this work.

Step 1 was carried out at 105°C for 2 h by slowly adding a solution of the telechelic rubber to a solution of **1** in order to avoid an undesired chain extension of ATBN. The increase of molecular weight in step 2 is strongly dependent on the reaction temperature and time. A temperature of 105°C and a reaction time of 3 h enable one to obtain copolymer samples with reasonable values of inherent viscosity without gel formation. The results of the polymerization runs performed according to the above experimental conditions are reported in *Table 1*.

The amount of ATBN was varied in the range 0–50 wt% by a proper choice of the x/y stoichiometric ratio (see *Scheme 1*), and it is indicated in the polymer code. Assuming a random multiblock architecture for the copolymers, the increase in the weight fraction of ATBN should lead to a rapid fall in the *MW* of the polyimide blocks.

The rubber incorporation was checked by benzene extraction of the crude polymerization products, which gave a low amount of soluble fraction (see *Table 1*), and was confirmed by i.r. analysis of the extracted copolymers. Absorption bands, characteristic of ATBN (2235 cm^{-1}, –C≡N; 965 and 910 cm^{-1}, 1,4-*trans*- and 1,2-diene units, respectively) were found together with imide bands centred at 1775 and 1720 cm^{-1} (=C=O) and 1380 cm^{-1} (C–N–C).

The elemental analyses, performed on the purified polymers, yielded actual values of rubbery content very close to those expected on the basis of the reactant ratios.

The parent polyimide and the copolymers are soluble in *m*-cresol and sparingly soluble in strong polar solvents such as NMP, DMA and dimethylsulphoxide. Their solubilities increase with increasing content of ATBN. Concentrated solutions suitable for film casting could be obtained in NMP/acetic acid mixtures.

Physical properties

The prepared polymers are amorphous, as generally found for addition polyimides obtained by the Michael reaction. Wide-angle X-ray diffraction patterns of the PI–O homopolymer and of the copolymers show, in fact, only a broad amorphous halo with a flat maximum at $2\theta \sim 17°$.

The thermal behaviour was investigated by d.s.c. and the thermograms of PI-0 and PI-30 are reported in *Figure 1* as an example. Both thermograms are characterized by a broad endotherm having a maximum at 80–100°C and by an exotherm occurring in the 230–280°C temperature range. Moreover, the PI-30 sample also shows a sharp second-order transition at −50°C. Since similar low-temperature transitions were observed in the case of PI-15 and PI-50, they are attributed to the ATBN

Table 1 Polyimides prepared from *N*,*N*′-bismaleimido-4,4′-diphenylmethane, 1,4-piperazine and ATBN

Polymer code	ATBN (wt%) Calc.	ATBN (wt%) Found[a]	Yield (%)	Benzene-soluble fraction (wt%)	η_{inh}[b] (dl g^{-1})
PI-0	0	–	90	–	0.94
PI-15	15	15	92	3.6	0.50
PI-30	30	32	93	1.1	0.90
PI-50	50	47	88	5.5	0.71

[a] By elemental analysis

[b] Inherent viscosity in NMP at 25°C; $C=0.50\,\mathrm{g\,dl^{-1}}$

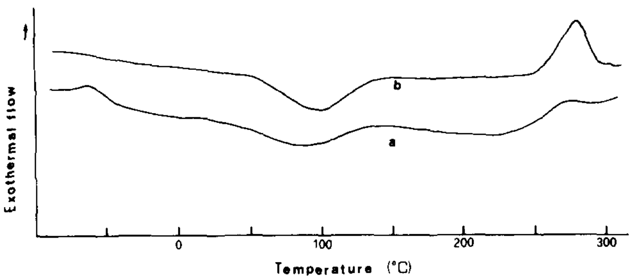


Figure 1 D.s.c. thermograms of (a) PI-30 and (b) PI-0 in the −100 to 300°C range

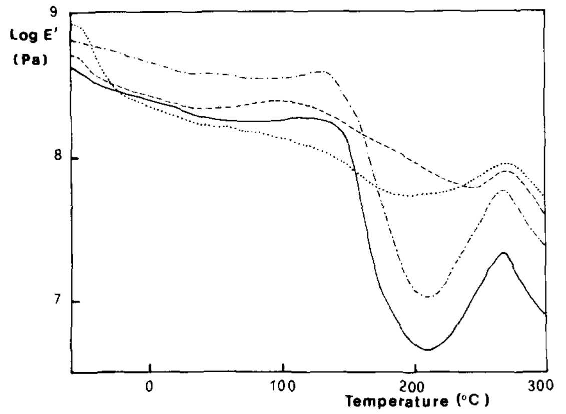


Figure 2 Temperature dependence of the storage modulus E' for the polyimides investigated: (—·—·—) PI-0; (——) PI-15; (– – –) PI-30; (······) PI-50

rubbery component. Clear evidence of a high-temperature glass transition was not found in any case. The exotherms were not reproduced in second runs and can reasonably be ascribed to irreversible chemical reactions.

As far as the endotherm is concerned, it was found that the absorbed heat decreases with increasing ATBN weight fraction. Owing to the absence of a crystalline component, as shown by X-ray diffraction profiles, the absorbed heat can hardly be related to a melting process. The possibility that it is due to the evolution of solvent (or other low-molecular-weight components) tightly bound to the polyimide chains appears unlikely. The endotherm, in fact, is still present in the d.s.c. thermograms of polymer samples kept under vacuum at 120°C for 3 days. Moreover in the t.g.a. thermograms (see below) no evidence of a weight loss was observed below 200°C. The nature of this endotherm is still under investigation.

The dynamic mechanical spectra are reported in *Figures 2* and *3* as the logarithm of the elastic modulus, log E', and the loss term, tan δ, plotted against the temperature. The PI-0 presents a large tan δ band with a maximum at 170°C and a shoulder at 210°C; in the same temperature range the elastic modulus shows a drastic drop of about two decades. This behaviour is ascribed to the glass transition of the polymer. Immediately above T_g, the modulus increases with increasing temperature, reaching a maximum at 280°C. This stiffening can be related to the exothermic peak observed in the d.s.c. thermogram and may be explained by the occurrence of a curing process starting at temperatures higher than 220°C. It is conceivable that most of the curing process consists of reactions between two chain ends, particularly maleimido terminal groups, leading to both *MW* increase and crosslink formation. The latter point is consistent with the fact that the bismaleimide (**1**) undergoes double-bond polymerization at $T > 200$°C, yielding highly crosslinked systems, as reported by other authors[6,7]. The drop in modulus observed for temperatures higher than 280°C is due to the onset of thermal degradation as shown by thermogravimetric analysis (see below). The dynamic mechanical behaviour of PI-15 closely resembles that of the unmodified polyimide. The T_g, 165°C, is practically unchanged and the elastic modulus is only slightly lowered by the introduction of 15% of elastomeric component. A weak low-temperature band, however, is observed in the tan δ plot of the PI-15 copolymer; its intensity increases with increasing elastomer weight fraction in the PI-30 and PI-50 (see *Figure 3*). A corresponding drop in the modulus is associated with this loss band (see *Figure 2*). The transition temperature (−45°C), which is independent of the composition, compares well with that of the second-order transition observed in the d.s.c. thermograms and is only slightly higher than that of pure ATBN (−55°C)[8]; this transition is therefore identified as the glass transition of the elastomeric component. Thus, on the basis of the above findings, a two-phase model with a sharp microphase separation is suggested for the elastomer-modified polyimides.

It is to be noted that the temperature of the initial modulus drop of PI-30 and PI-50 (~100°C) is about 50°C lower than that of PI-0 and PI-15, in agreement with the increased overall chain flexibility expected for the ATBN-rich polyimides. On the other hand, the drop in the elastic modulus is less pronounced and the loss peak is weaker and shifted to higher temperatures compared with those of PI-0 and PI-15. It is therefore rather difficult to identify unambiguously the T_g of the hard segments in the polyimides having high ATBN contents.

The high-temperature behaviour shown by PI-30 and PI-50 may be explained by assuming that chain-end reactions are favoured in these copolymers by the higher chain flexibility and, consequently, curing starts at lower temperatures. Therefore, the drop in the elastic modulus related to the glass transition is partially masked because of a stiffening of the system due to the onset of the curing process.

As polyimides are particularly attractive for high-temperature uses, it was interesting to test their thermal stability after ATBN incorporation. T.g.a. profiles of the

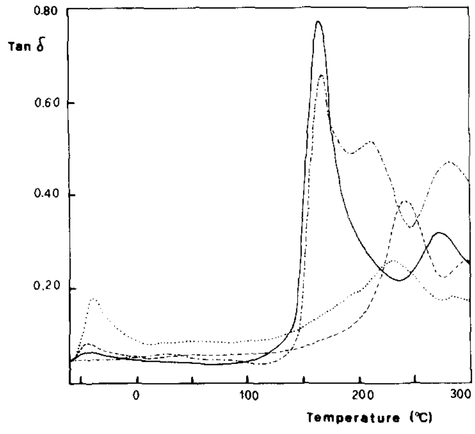


Figure 3 Temperature dependence of the loss factor tan δ for the polyimides investigated: (—·—·—) PI-0; (——) PI-15; (– – –) PI-30; (······) PI-50

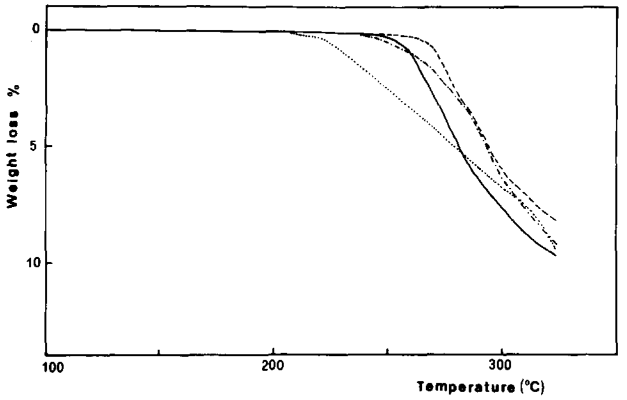


Figure 4 Thermogravimetric analysis under nitrogen of the polyimides investigated: (—·—·—) PI-0; (——) PI-15; (- - -) PI-30; (······) PI-50

investigated polymers in the range 100–300°C are shown in *Figure 4*. At 270°C the weight loss is close to 5% for all the samples. The thermal stability of the polyimides appears to be scarcely affected by the presence of ATBN up to 30 wt%. In the case of PI-50, the onset of thermal degradation is shifted to a lower temperature (~200°C) with respect to the other copolymers. These results are in agreement with those obtained by other groups on different polyimide systems, showing that reasonable thermal stability is retained after ATBN incorporation[1–3], at least for low elastomer contents.

CONCLUSIONS

We have shown the possibility of incorporating a telechelic rubber (ATBN) in addition-type polyimides obtained via Michael addition. The results obtained by d.s.c. and dynamic mechanical analysis point to a complete microphase separation of ATBN and polyimide chains. High elastomer contents markedly influence the thermal and mechanical behaviours and also affect the temperature of the curing process. In the copolymers with low ATBN contents, curing occurs above T_g in a narrow temperature range, while at high ATBN contents T_g falls in the temperature range of the curing process, which is broadened towards low temperatures because of the increased chain flexibility. Preliminary t.g.a. results indicate that the thermal stability is scarcely affected by the presence of the elastomer up to 30% content.

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