

New aromatic diamines containing a multiring flexible skeleton for the synthesis of thermally stable polyimides

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Abstract

Multi-ring aromatic diamines bearing a long alkyl chain (C_6 , C_8 or C_{16}) were obtained from the corresponding dinitro compounds synthesized by a Friedel–Crafts alkylation of substituted mesitylenes by paranitrobenzyl chloride. The bismaleimide synthesized from the diamine bearing a C_{16} chain formed a thermostable polyimide. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

While crosslinked polyimides continue to be studied for electronic and electro-optic devices [1,2], attention is now being focused on the synthesis of flexible and thermostable polyimides, which can be processed in the melt or in solution in organic solvents. Many of these polyimides are synthesized by condensation between aromatic dianhydrides and flexible aromatic diamines. The latter have the structure $H_2N-Ar-X-Ar-NH_2$ where X represents the flexible link between the two aromatic rings bearing the amine function. In order to enhance the thermal stability of these diamines, an ether, sulfonyl or carbonyl function is used to join the aromatic rings [3–8]. For a better processability, alkyl groups can be incorporated in *ortho*-position to the flexible linkages. In addition, such substituents also prevent coplanarity of the aromatic rings and therefore minimize strong intra- and intermolecular interactions [9]. In previous papers [10,11] the authors described highly soluble new polybenzyl materials synthesized by Friedel–Crafts polycondensation of mesitylenes bearing a long pendant alkyl chain with α,α' -dichloroparaxylene. The presence of an aromatic ring substituted by methyl groups and a long alkyl chain in modified linear or crosslinked polyimides appeared to enhance both the flexibility and the solubility of these polymeric materials without important loss of thermal stability.

This paper reports the synthesis of aromatic multi-ring diamine precursors of these materials. In order to confirm its thermal stability in a polymeric network, the diamine with a C_{16} chain was condensed with maleic anhydride and the thermal behavior of the crosslinked bismaleimide thus obtained studied.

2. Experimental

2.1. Instrumentation

Elemental analyses were performed with a Fison EA 1108 CHONS apparatus. IR spectra were recorded on a BRUKER IF66V spectrometer in KBr. NMR spectra were run on a AC 200 BRUKER spectrometer in $CDCl_3$, at 297 K. Chemical shifts are given from tetramethylsilane as the external reference. Differential scanning calorimetry (DSC) was carried out on a TA Instruments MDSC 2920 apparatus at a $10^\circ C\ min^{-1}$ heating rate. Thermogravimetry was performed using a TA Instruments High Resolution TGA 2950 or a SDT 2960 TGA-DTA at a $10^\circ C\ min^{-1}$ heating rate under air and nitrogen atmospheres.

Commercial, analytical grade solvents and reagents were used throughout.

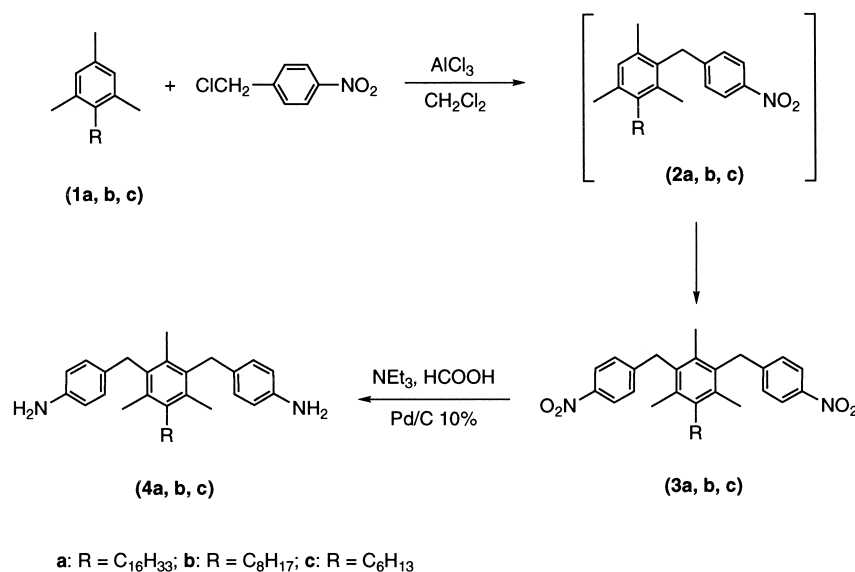
2.2. Syntheses

2.2.1. Dinitro compound 3a

p-nitrobenzyl chloride (20 g, 0.116 mol) and aluminum trichloride (13.5 g, 0.102 mol) were stirred under reflux in

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Scheme 1.

100 ml of anhydrous dichloromethane until they completely dissolved. **1a** (20 g, 0.058 mol) dissolved in 50 ml of dichloromethane, was then added and the mixture was heated under reflux in a nitrogen atmosphere for 4 days. The resulting deep green solution was cooled to 0°C and 50 ml of water was added dropwise. After decantation, the organic layer was washed with water until neutral and dried over magnesium sulphate. The solution was evaporated to dryness and the resulting creamy powder was recrystallized in acetone to give 21 g of **3a**. Yield 60%, m.p. 55°C.

¹H NMR: 8.12–8.08 (d, 4H), 7.18–7.14 (d, 4H), 4.20 (s, 4H), 2.19 (s, 6H), 2.01 (s, 3H), 1.55–1.20 (m, 30H), 0.90–0.80 (t, 3H). I.R.: 2920, 2850, 1600, 1510, 1355, 729 cm⁻¹. Analysis calculated for C₃₉H₅₄N₂O₄: C, 76.18; H, 8.85; N, 4.56. Found: C, 77.07; H, 9.16; N, 4.35.

Compounds **3b** and **3c** were synthesized using the same procedure in 50–60% yield. **3b**: m.p. 60°C. Analysis calculated for C₃₁H₃₈N₂O₄: C, 74.08; H, 7.62; N, 5.57. Found: C, 74.24; H, 7.97; N, 5.39. **3c**: m.p. 62°C. Analysis calculated for C₂₉H₃₄N₂O₄: C, 73.39; H, 7.22; N, 5.90. Found: C, 73.22; H, 7.40; N, 5.72. IR and NMR spectra are very similar for compounds **3a**, **3b** and **3c**.

2.2.2. Diamino compound **4a**

Dinitro compound **3a** (20 g, 0.033 mol) and palladium 10 wt% on activated carbon (1.3 g) were stirred under reflux in triethylamine (41 ml, 0.293 mol) until complete dissolution of **3a** under nitrogen. 97% formic acid (10.5 ml, 0.280 mol) was slowly added and a highly exothermic and effervescent reaction took place. The mixture was heated for 1 h under reflux before cooling and diluted with 50 ml of dichloromethane and filtered. The organic layer was washed with water until neutral. After removal of the solvent, the product was recrystallized in ethanol to give 16 g of **4a**. Yield 90%, m.p. 65°C.

¹H NMR: 6.82–6.78 (d, 4H), 6.59–6.55 (d, 4H), 3.98 (s, 4H), 3.61 (s, 4H), 2.20 (s, 6H), 2.08 (s, 3H), 1.40–1.20 (m, 30H), 0.90–0.80 (t, 3H). IR: 3410, 3360, 3323, 2950, 2850, 1622, 1271, 821 cm⁻¹. Analysis calculated for C₃₉H₅₈N₂: C, 84.42; H, 10.53; N, 5.05. Found: C, 84.01; H, 10.62; N, 4.65.

Compounds **4b** and **4c** were obtained in high yield using the same procedure. **4b**: m.p. 70°C. Analysis calculated for C₃₁H₄₂N₂: C, 84.10; H, 9.56; N, 6.34. Found: C, 83.88; 9.45; N, 5.99. **4c**: m.p. 73°C. Analysis calculated for C₂₉H₃₈N₂: C, 84.00; H, 9.24; N, 6.76. Found: C, 83.80; 9.50; N, 6.40. NMR and IR spectra of compounds **4a**, **b**, **c** are very similar.

2.2.3. Bismaleimido compound **6a**

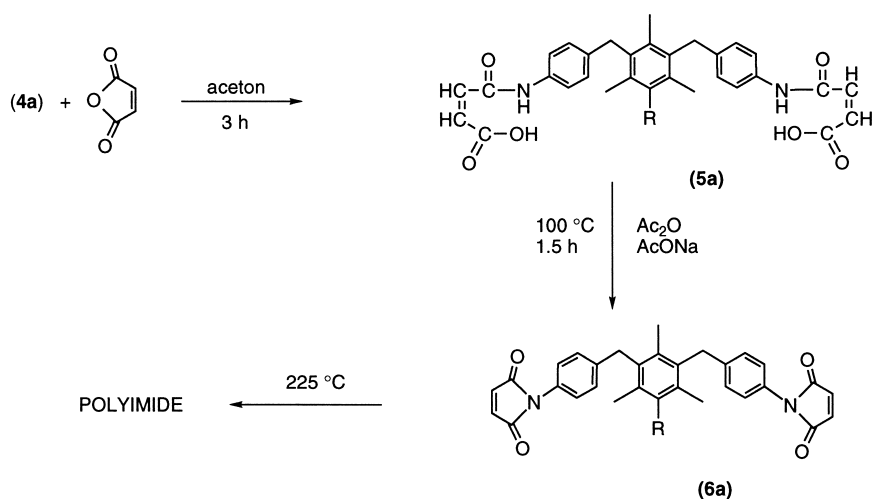
Diamino compound **4a** (2 g, 0.0036 mol) and maleic anhydride (0.7 g, 0.0072 mol) were stirred under reflux in 15 ml of acetone for 3 h. Removal of acetone gave a pale brown powder identified by IR as **5a**. IR: 3283, 3201, 2950, 2850, 1700, 1631 cm⁻¹.

Crude **5a** was dissolved in 10 ml of acetic anhydride. Sodium acetate (0.2 g, 0.0024 mol) was added and the mixture was stirred under reflux for 3 h. The bismaleimido compound was precipitated in water, isolated by filtration and washed with water until neutral. The crude product was dried under vacuum for 24 h and recrystallized in methanol to give 2 g of **6a**. Yield 80%, m.p. 45°C.

¹H NMR: 7.21–7.17 (d, 4H), 7.12–7.18 (d, 4H), 6.82 (s, 4H), 4.12 (s, 4H), 2.20 (s, 6H), 2.09 (s, 3H), 1.60–1.20 (m, 30H), 0.90–0.80 (t, 3H). IR: 3100, 2950, 2850, 1720, 1149, 830 cm⁻¹. Analysis calculated for C₄₇H₅₈N₂O₄: C, 78.95; H, 8.17; N, 3.92. Found: C, 78.60; H, 8.39; N, 3.81.

2.2.4. Polymerization of **6a**

One gram of **6a** in an aluminum pan was heated for 1 h at 200°C and 1 h at 250°C under air. 0.97 g of a deep brown solid was obtained.



Scheme 2.

3. Results and discussion

The synthesis of the diamines **4** requires two steps (Scheme 1). The first step is a Friedel–Crafts alkylation of substituted mesitylenes (**1a–c**) by *p*-nitrobenzyl chloride to give the dinitro compounds (**3a–c**). The reaction is performed in dichloromethane, under reflux from **1a**, at room temperature from **1b** and **1c**, to avoid polysubstitution, which occurs at higher temperature. The reaction, which requires 4–5 days to be complete, is monitored by ¹H NMR until the complete disappearance of the characteristic singlet of the aromatic protons of the starting material at 6.80 ppm and of the singlet of the monosubstituted product **2** at 6.90 ppm. The amount of AlCl₃ must not be higher than 1.75 mol for 2 mol of the chloro compounds to avoid undesirable substitutions.

After hydrolysis and washing of the organic layer with water until neutral to remove HCl, the dinitro compound **3a** is recrystallized in acetone to give a brown microcrystalline powder in 60% yield. Both **3b** and **3c** are purified on a silica–gel column (eluents petroleum ether/dichloromethane (7/3) and petroleum ether/diethyl ether (8/2), respectively). After removal of the solvents, these compounds are recrystallized in ethanol to give yellow powders in ca. 50% yield.

The reduction of the dinitro derivatives **3** takes place in the triethylammonium formate complex in the presence of Pd/C as catalyst [12]. Compounds **3** are dissolved in boiling triethylamine, then formic acid is added slowly (Scheme 2).

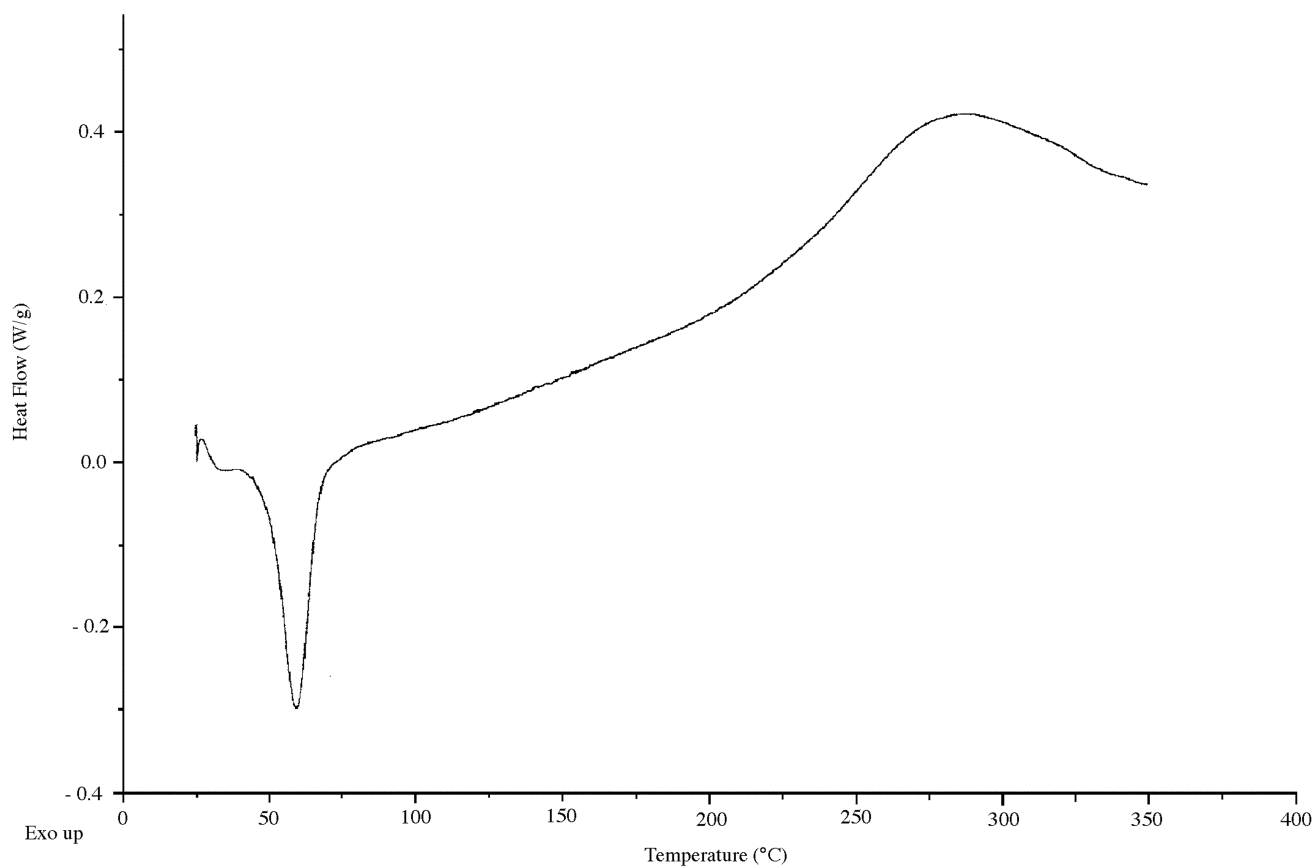
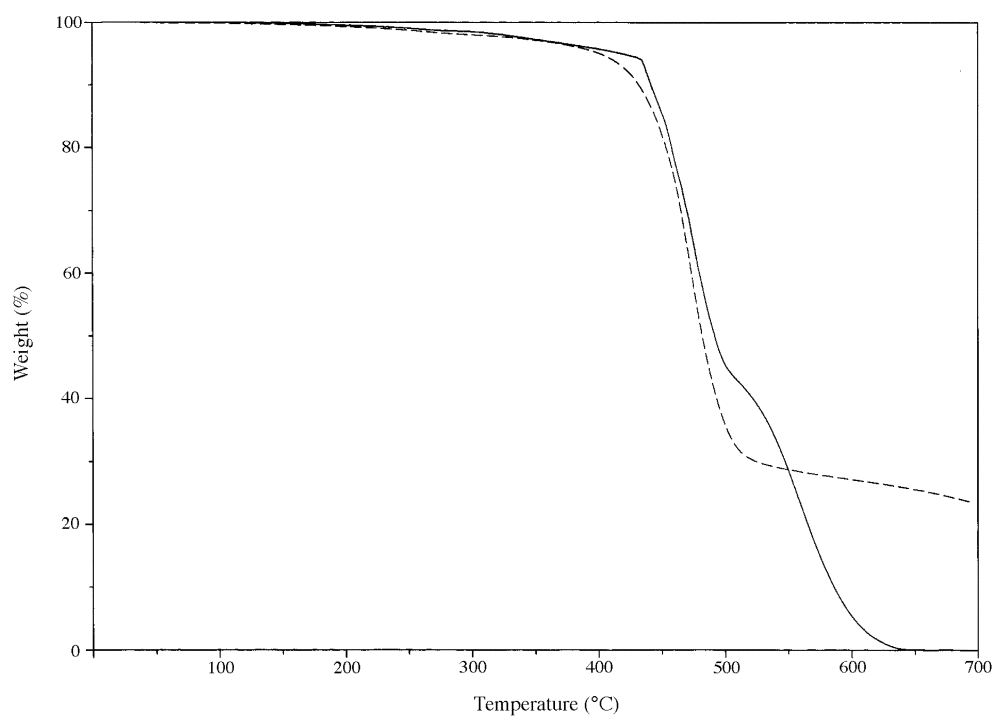
The reduction is exothermic and evolves CO₂. After addition of dichloromethane, filtration to remove the catalyst, washing with water and removal of the solvents, the diamines **4** are recrystallized in ethanol to give pale brown microcrystals in ca. 90% yield. All the dinitro (**3**) and diamino (**4**) compounds were characterized by ¹H and ¹³C NMR, IR spectrometry and elemental analysis. The

diamines show a good thermal stability, degradation occurs at 450 °C (10% weight loss, heating rate 20 °C min⁻¹) under nitrogen.

To check the thermal stability of polymeric chains obtained from these diamines, the synthesis of the bismaleimide **6a** was performed from diamine **4a**, bearing the longest alkyl chain. A solution of maleic anhydride in acetone is added to a solution of **4a** in acetone. After 3 h heating under reflux, the solvent is removed and the amidoacid **5a** is obtained as a brown solid. This compound, clearly identified by IR spectroscopy (N–H bands at 3283 and 3201 cm⁻¹), is used without further purification. Crude **5a** is dissolved in acetic anhydride and sodium acetate is added, the reaction mixture is then heated to 100 °C for 3 h. The bismaleimide **6a** is precipitated after pouring the mixture in water. The crude product is washed with NaHCO₃ and with water until neutral pH, then recrystallized from ethanol.

DSC shows that **6a** melts under nitrogen at 45 °C and polymerizes between 225–350 °C (Fig. 1). From thermogravimetry, information on the stability of the polymeric material is easily obtained. The weight loss curves of bismaleimide **6a** in air and nitrogen are shown in Fig. 2. In nitrogen, the degradation appears to begin at ca. 400 °C and stops at ca. 550 °C with a maximum rate at 480 °C. The thermal stability is a little better in air than in nitrogen, the degradation commencing at 410 °C. This degradation proceeds in two steps, the first one being very close to that observed in nitrogen. A second stage appears between 520 and 650 °C and affords a very small residue (less of 2% at 650 °C). This second reaction, which is not observed in nitrogen, corresponds to complete oxidation of the polymer. It is noteworthy that these curves are very close to those obtained for unsubstituted bismaleimidodiphenylmethane [13].

Polymerization of **6a** has been performed under air by heating for 1 h at 200 °C and an additional 1 h at 250 °C. Crosslinking was complete as shown by the disappearance

Fig. 1. DSC of bismaleimide compound **6a** under nitrogen.Fig. 2. Thermogravimetry of bismaleimide compound **6a** under air (—) and under nitrogen (---).

of the IR band of the maleimido group at 3100 cm^{-1} . The black polybenzylimide material is insoluble in common organic solvents.

4. Conclusions

This paper describes the synthesis of a series of new multiring aromatic diamines bearing long alkyl pendant groups. These flexible chains confer very good solubility in organic solvents to the diamines, which remain also thermally stable up to 450°C .

Reaction with maleic anhydride leads to a bismaleimide, which can be thermally polymerized. The properties of the cross-linked polybenzylimide so obtained is not strongly modified by the presence of the alkyl chain and therefore allows the use of such modified diamines for the synthesis of linear thermoplastic polyimides with good thermal stability.

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