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Polyimide Derived from the Diels-Alder Polymerization of Difurylmethane with N,N′-bismaleimido-4,4′-diphenylmethane

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Difurylmethane was synthesized and polymerized with N,N′-bismaleimido-4,4′-diphenylmethane *via* the Diels-Alder polycycloaddition reaction to form a polyadduct which was soluble in DMSO, acetone and methylene chloride. FTIR and solution ^{1}H NMR data from the 2 : 1 difurylmethane-N,N′-bismaleimido-4,4′-diphenylmethane model Diels-Alder adduct prepared, facilitated the assignment of spectral features of the polyadduct. Upon treatment of the homogeneous solution of the polyadduct in methylene chloride with borontrifluoride diethyletherate at ambient temperature, aromatization of the bicyclic Diels-Alder adduct moieties in the polyadduct chains occurred resulting in the formation of an insoluble, thermally stable polyimide. Whereas the 2 : 1 difurylmethane-N,N′-bismaleimido-4,4′-diphenylmethane model Diels-Alder adduct and the polyadduct underwent 100% retro-Diels-Alder reaction in the temperature range 115–230°C, the polyimide was stable up to about 420°C in a N_2 atmosphere, forming a high char yield of 40% at 800°C.

Key Words: Diels-Alder polycycloaddition, Bisfurans, Bismaleimides, Polyadduct, Polyimide.

INTRODUCTION

The general properties of aromatic polyimides include tractability, superior thermal properties and good fire resistance, making them suitable for a wide range of technological applications[1–3]. Polyimides prepared from the Diels-Alder (DA) polycycloaddition reaction were first reported by Tesoro *et al.*[4] In their study, difuranic monomers were reacted with bisdienophiles and the resulting linear polyadducts were aromatized to form heat-resistant polyimides which exhibited onset decomposition temperatures ranging from 385–590°C. Diakoumakos *et al.*[5, 6] have applied the Diels-Alder polycycloaddition reaction to a number of bisfuranic monomers and bismaleimides, to prepare polyadducts, which were then aromatized by thermal dehydration to form polyimides with good thermal stabilities. The furan ring being the least aromatic and therefore most pronouncedly dienic of the five-membered heterocycles, its tendency to participate in the Diels-Alder cycloaddition reactions has been studied extensively[7, 8]. Kappe *et al.*[9] in a recent review have provided a comprehensive summary of studies of the synthetic applications of the furan Diels-Alder chemistry. Gandini *et al.*[10, 11] have used bisdienophiles in Diels-Alder reactions to cross-link polymer chains containing furanic moieties and have assessed the relative thermal stabilities of the resulting products. Spectroscopic evidence supported by thermogravimetric measurements indicated the presence of adduct structures which were formed between the bisdienophile and the furanic moieties and which were capable of reverting to their thermoplastic precursors *via* a retro-Diels-Alder reaction. As would be expected on steric grounds, it was also demonstrated that the pendant furanic rings joined to the polymer backbone through the C-2 position were most reactive to cycloaddition. Further, a systematic study of the polycycloaddition reaction that occurs *via* successive Diels-Alder steps has been conducted by the same group[12]. Prior to the polycycloaddition reaction, preparation of model Diels-Alder adducts were examined in terms of reaction conditions, yields and structures. The polymer synthesis consisted of reacting two complementary monomers, one a bisfuranic (A-A) and the other a bismaleimide (B-B). For all the monomer combinations used progressive insolubility of the growing chains was observed and was suggested to account for the low degree of polymerization (DP) obtained. The spectral data for the model adducts facilitated reliable analysis of the structural features of the polyadduct and provided evidence of the polymerization mechanism. Attempts have also been made to prepare a furanic-dienophile monomer and to study its Diels-Alder AB-type polycycloaddition reaction[13]. The FTIR spectra of the insoluble polymer showed the presence of typical characteristic bands of Diels-Alder moieties in the product. Gandini *et al.*[14, 15] in a review of the literature up to 1998, have provided a comprehensive summary of the Diels-Alder polycycloaddition studies of bisfurans with bismaleimide monomers.

In this paper we describe the preparation of a polyadduct by the Diels-Alder polycycloaddition reaction of N,N′-bismaleimido-4,4′-diphenylmethane with difurylmethane. Furanic Diels-Alder adducts have been shown to be readily transformed[9] into aromatic systems at ambient temperatures, by treatment with either boron trifluoride or tetrabutylammonium fluoride reagents. In the present study we report the preparation of a thermally stable polyimide formed by the treatment of a homogeneous solution of the difurylmethane-N,N′-bismaleimido-4,4′-diphenylmethane polyadduct in methylene chloride with boron trifluoride diethyletherate. In order to facilitate the interpretation of the spectroscopic fine structure of the polyadduct and that of the polyimide, a 2 : 1 difurylmethane-N,N′-bismaleimido-4,4′-diphenylmethane Diels-Alder adduct was prepared and characterized. The thermal stability of both the Diels-Alder polyadduct and the polyimide has been investigated by thermal analysis.

EXPERIMENTAL

Analytical grade methylene chloride, acetone and boron trifluoride diethyl etherate (Aldrich Chemicals) were used without further purification. N,N′-bismaleimido-4,4′-diphenylmethane (Aldrich Chemicals) was purified by recrystallization from a 30 vol % CH_3CN in CH_3OH mixture. Difuryl methane was prepared as described elsewhere[16] and its purity confirmed by ^{1}H NMR and elemental analyses.

^{1}H NMR spectra were recorded in DMSO-d_6 on a Bruker AMX-300 MHz spectrometer at room temperature and FTIR (KBr pellets) spectra were recorded on a Perkin-Elmer 2000 FT spectrophotometer. Thermogravimetric analyses were performed on a SDT 2960-DTA-TGA Thermal Analyzer (TA Instruments) using 5–10 mg samples in Pt pans in a N_2 atmosphere at a heating rate of 10°C min^{-1}. Degradation temperatures were determined at the temperature corresponding to a 5% weight loss.

Preparation of the 2 : 1 difurylmethane-N,N′-bismaleimido-4,4′-diphenylmethane Diels-Alder model adduct (3)

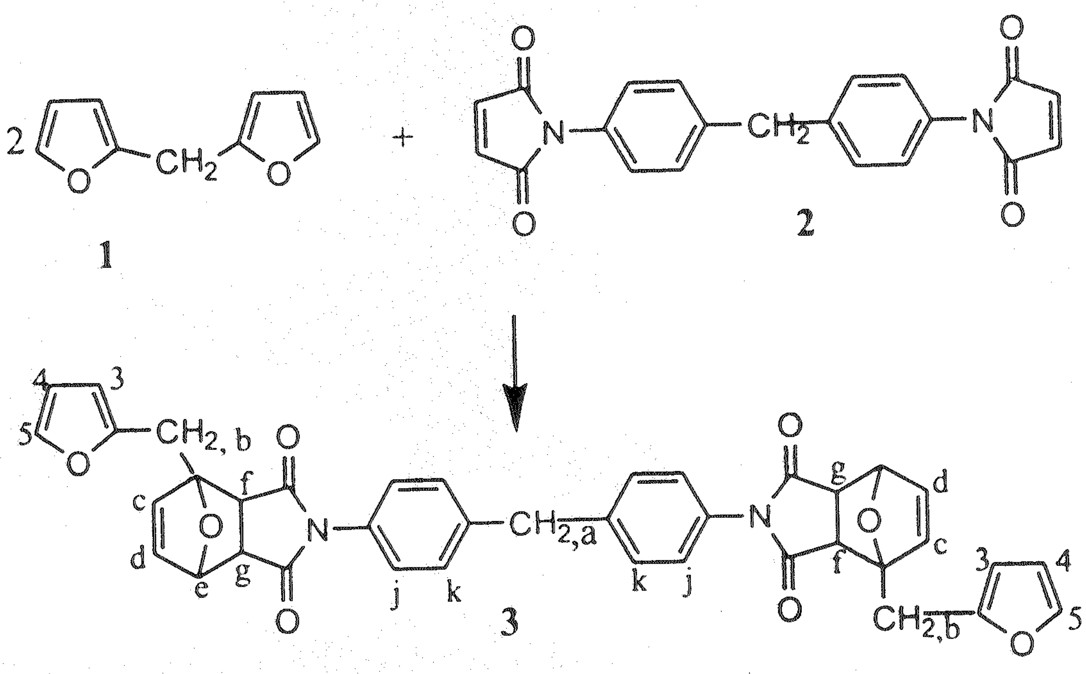
Difurylmethane (**1**) is a dimer that forms in considerable proportions during the preparation of furfuryl alcohol resins[17, 18]. In this study the two co-monomers, with **1** in a thirty-fold molar excess over N,N′-bismaleimido-4,4′-diphenylmethane (**2**) were dissolved in methylene chloride and the solution refluxed for 48 h under an N_2 atmosphere. At the end of this reaction time, the homogeneous solution was poured into an excess of diethyl-ether to precipitate out a white solid of the 2 : 1 Diels-Alder adduct (**3**). This separated **3** from the excess of **1** and trace amounts of the unreacted bismaleimide **2**, both of which are soluble in diethylether. The Diels-Alder adduct **3** was further precipitated twice from the dichloromethane solution into diethyl-ether, filtered and dried to a constant weight under partial vacuum at room temperature, giving a yield of 87%. The structure of the adduct and stereochemistry was confirmed from FTIR and ^{1}H NMR spectroscopy. The adduct was also characterized by thermogravimetric analysis. A mixture of exo and endo-isomers was obtained. The adduct purity was confirmed by elemental analysis. Thus the percentages obtained (compared with those calculated for 100% 2 : 1 difurylmethane-N,N′-bismaleimido-4,4′-diphenylmethane Diels-Alder coupling) were as follows: Found: C, 71.18; H, 4.71; N, 4.35%; C/N, 16.25. Calcd. for $C_{39}H_{30}N_2O_8$: C, 71.59; H, 4.58; N, 4.28%; C/N, 16.72.

Diels-Alder Polymerization

The bisdiene **1** and the bisdienophile **2** were dissolved into CH_2Cl_2 in equimolar quantities (0.5 mol L^{-1}) and the resulting mixture stirred under reflux in a N_2 atmosphere for 48 h. There was no precipitation of products observed throughout the reaction time. The homogeneous reaction mixture was poured in 200 mL of diethyl-ether and the resulting white precipitate of the polyadduct (**4**) filtered, purified by four precipitation procedures from CH_2Cl_2 solution into diethyl-ether and finally dried under partial vacuum at room temperature to a constant weight. The total yield of the dried polymer was 82%. Aromatization of the polyadduct **4** was carried out by dissolving 1 g of **4** into 25 mL of CH_2Cl_2 followed by the addition of 2 mL of boron trifluoride diethyletherate. A light brown precipitate of the polyimide (**5**) formed immediately. The mixture was stirred for 2 h, the precipitate filtered off and washed with several portions of 5% aqueous ammonia to neutralize the Lewis acid. The brown solid was then washed with water followed by methanol and finally soxhlet-extracted with methylene dichloride to remove any traces of the bismaleimide **2**. Elemental analyses percentage values obtained for the polyadduct **4** (compared with those calculated for the repeat unit in a high molecular weight product) were found to be as follows: Found: C, 69.38; H, 4.67; N, 5.13%; C/N, 12.86. Calcd.: C, 71.14; H, 4.38; N, 5.53%; C/N, 13.01; assuming 1 : 1 reaction ratio between monomers **1** and **2** (m.f. $C_{30}H_{22}O_6N_2$).

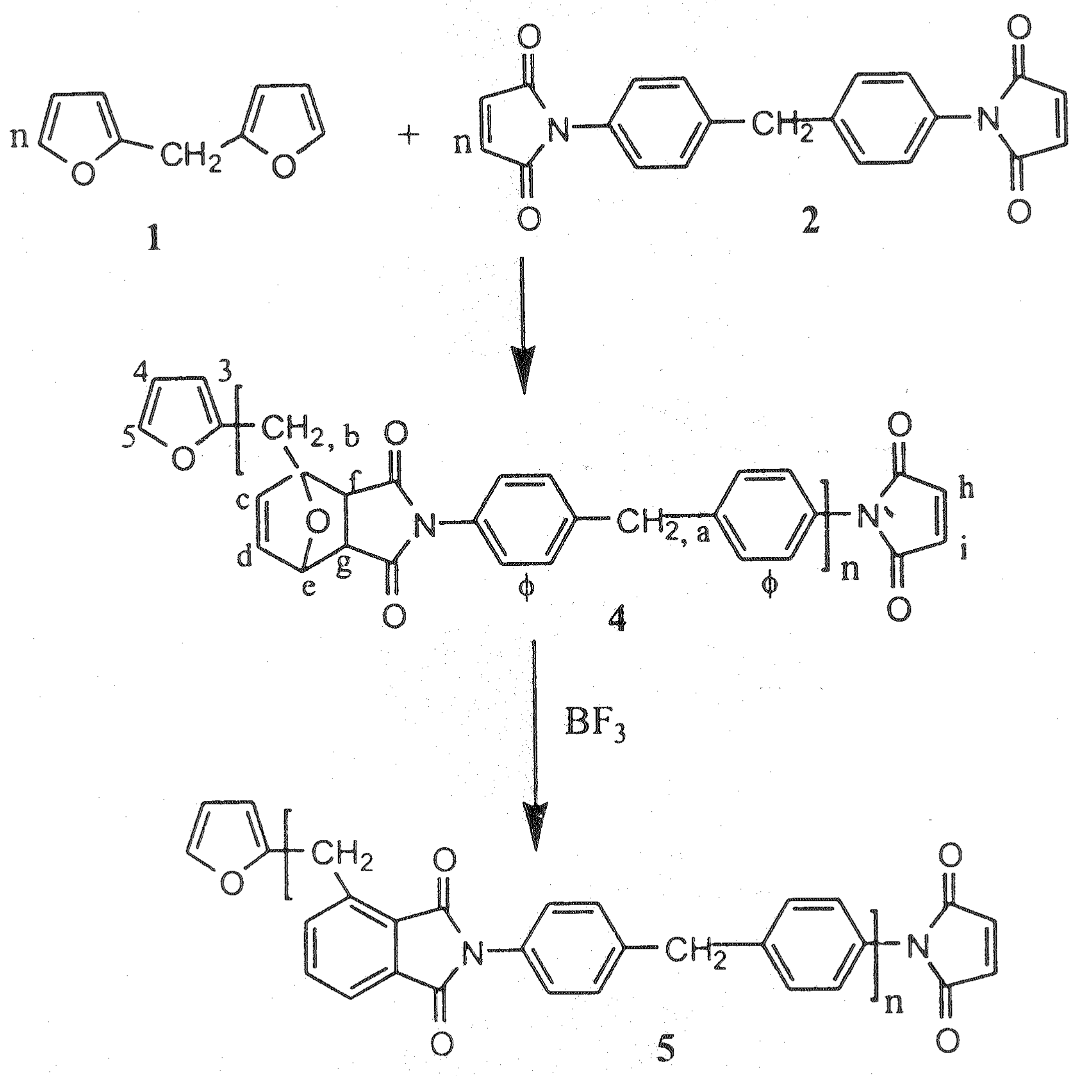
RESULTS AND DISCUSSION

Scheme-1 outlines the synthetic approach applied in this study for the preparation of the 2 : 1 Diels-Alder adduct **3** in which a mixture of a thirty molar excess of **1** over **2** was refluxed for 48 h. Under these conditions, higher molecular weight Diels-Alder adduct oligomers were not formed in any detectable amounts. To the best of our knowledge, the Diels-Alder adduct **3** prepared in these studies has not been reported previously. Its formation was quantitative and the efficiency of the method of its preparation was assessed by elemental analysis which indicated virtually 100% Diels-Alder coupling between **1** and **2**.



Scheme-1. Preparation of the model Diels-Alder adduct 3

The high yields observed for the formation of the model adduct **3** provided good evidence for the feasibility of the Diels-Alder reaction between **1** and **2** and prompted us to apply the same experimental approach to the preparation of the polyadduct **4**. The successive Diels-Alder cycloaddition reactions of monomer **1** with 1 equivalent of **2** (**Scheme-2**) gave a white powder of the polyadduct **4**. We did not observe any progressive insolubility of the growing polymer chains reported elsewhere[12] in similar investigations and the reaction mixtures remained homogeneous throughout the duration of the preparation.



Scheme-2. Synthesis of polyadduct **4** and polyimide **5**

FTIR and ^{1}H NMR Spectroscopy

The FTIR spectrum of the A model adduct **3** (Fig. 1A) and published spectroscopic data on similar Diels-Alder adduct systems[12-14] facilitated the interpretation of the spectral features of polyadduct **4** and the polyimide **5**. In Fig. 1B, we present typical FTIR spectrum (KBr pellets) of the polyadduct **4** for which the following band assignments (cm^{-1}) were made: 3085 ν(=C—H arom. and furan); 3007 ν(=C—H adduct); 2908 ν(CH, =CH_2); 1775, 1711 ν(C=O imide); 1512 ν(C=C arom.); 1384 ν(C—N imide); 1322 and 1281 ν(C—O—C adduct, endo and exo, respectively); 1188 ν(C—O—C adduct + C—N); 1071 ν(C—O—C adduct); 1019 ν(C—H arom. in-plane); 977 ν(=C—H adduct, breathing); 828 ν(C—H arom. out-of-plane); 718, 647 ν(=C—H_α furan, out-of-plane). The high solubility of **4** in DMSO, acetone and methylene chloride, facilitated its transformation into the polyimide **5** when the homogeneous solution of the former was treated with borontrifluoride diethylethyrate **(Scheme-2)**. **5** was insoluble in all solvents tested and was only characterized by FTIR (Fig. 1C) and thermal analysis. Comparison of FTIR spectra for **4** and **5** showed important changes, which clearly confirmed that aromatization of the Diels-Alder, adduct moieties in **4** had occurred.

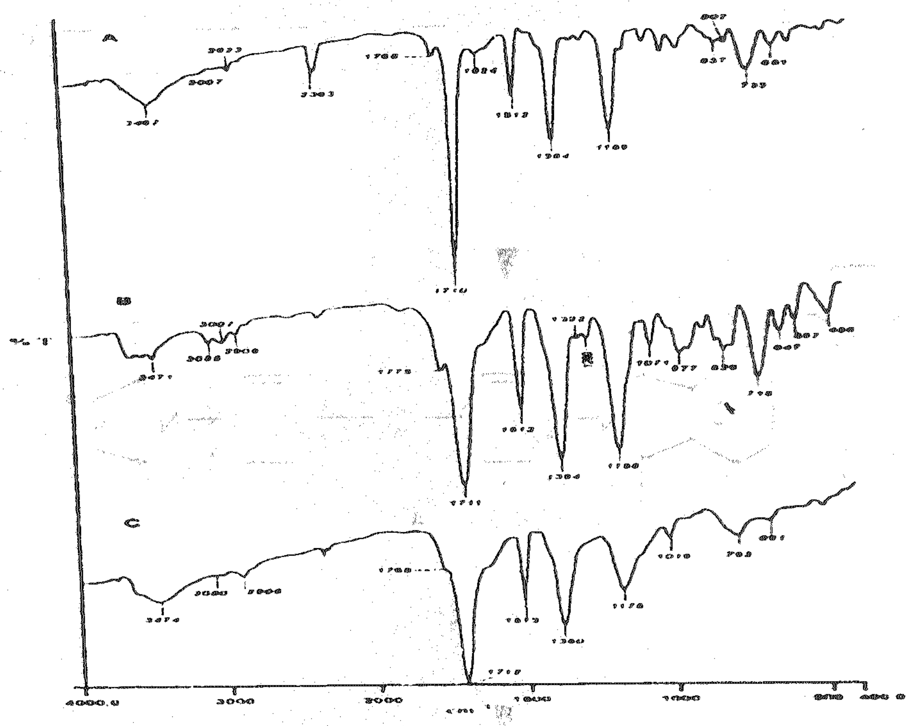


Fig. 1. 1 FTIR spectra (KBr pellets) of Diels-Alder adduct **3** (A), the polyadduct **4** (B) and the polyimide **5** (C)

In particular, the aromatization process caused the intensity of the absorption band around 1775 cm^{-1} attributed to the succinimide rings of the Diels-Alder adduct moieties in **4** to become diminished, while the C—H aryl bands at 1512 and 1019 cm^{-1} increased relative to the band at 1384 cm^{-1} (C—N, imide). The intensity of the small bands at 1322 and 1280 cm^{-1} ν(C—O—C, in the endo and exo bicyclic adduct structures, respectively) disappeared compeletely while that of the band at 1188 cm^{-1} ν(C—O—C, adduct and C—N, imide) significantly diminished leaving a residual broadened band appearing at 1178 cm^{-1} attributed to the C—N stretch alone in the imide structures. Further, the multiple absorption bands centred at 977 cm^{-1} due to the ═C—H breathing modes in the furanic residue of the bicyclic adduct moieties virtually disappeared. There was also a noticeable reduction in the intensity of the band at about 700 cm^{-1} ν(out-of-plane ═C—H_α bending in furan ring) which was attributed to cross-link processes through the α-position of the terminal furanic functions when the boron trifluoride reagent was added. The bands centred around 2908 cm^{-1}, arising from the aliphatic C—H stretch, appear in all the spectra, suggesting that the —CH_2— bridging moieties were not affected by the aromatization process.

In Fig. 2, the ^{1}H NMR spectrum of the Diels-Alder model adduct **3** with peak assignments is shown whereas in Fig. 3 the corresponding spectrum of the polyadduct **4** is presented. The similarity of ^{1}H NMR spectra for **3** and **4** further

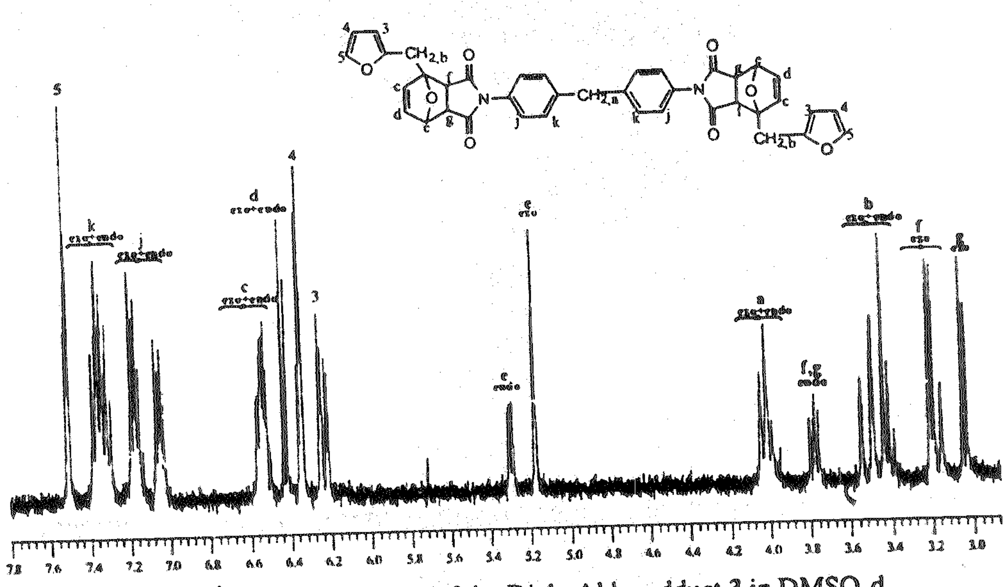


Fig. 2. ^{1}H NMR spectrum of the Diels-Alder adduct **3** in DMSO-d_6

confirms the proposed polyadduct structures and the DA polycycloaddition mechanism presented in **Scheme-2**. By comparison with Fig. 2, the polyadduct proton-peak assignments (Fig. 3) were as follows: ^{1}H NMR (300 MHz, ppm in DMSO-d_6, 298 K) $\delta = 7.48$ (s, H_{-5}, terminal furan function); 7.05–7.38 (m, aryl); 7.04 and 6.77 (d, $H_{h,\ i}$, terminal maleimide function); 6.42, 6.53 (m, $H_{c,\ d}$, endo + exo); 6.34–6.24 (m, $H_{-3,4}$ furan); 5.19 and 5.75 (s, H_e endo and H_e exo, respectively); 4.02–3.94 (s, $CH_{2,\ a}$, exo + endo); 3.95–3.68 (m, $H_{f,\ g}$, endo); 3.52–3.35 (m, $CH_{2,\ b}$); 3.22–3.3.11 (m, H_f, exo); 3.05–2.84 (m, H_g, exo).

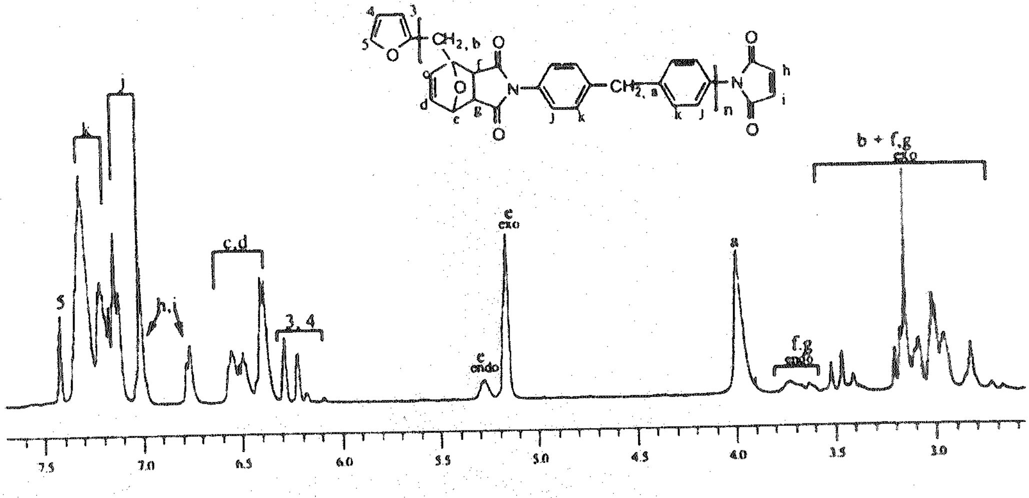


Fig. 3. ^{1}H NMR spectrum of the Diels-Alder polyadduct **4**

As evidenced by the model Diels-Alder adduct **3**, the ^{1}H-NMR spectra of **4** revealed the preponderance of the thermodynamically more stable exo-bicyclic moieties in these short polymer chains and an even distribution of the maleimide and furan end group functions. Thus the DP of the polyadduct **4**, estimated from the ^{1}H NMR was about 9 irrespective of the solvent used in the sythesis. Therefore, the polyadduct showed no distinctive features characteristic of a specific solvent used during preparation. Although the elemental analysis of the

Diels-Alder adduct **3** was in excellent agreement with the calculated percentages, the carbon and oxygen contents of **4** were respectively lower and higher than those expected for the high molecular weight polymer, consistent with the low degree of polymerization observed. However, the measured C/N ratio of 13.01 for **4** closely agreed with the expected value of 12.86 confirming a 1 : 1 combination between monomers **1** and **2**. We were unable to obtain the polyimide **5** in sufficient purity for reliable detailed elemental analysis. We however report the measured C/N ratio of 12.85 for **5** which was comparable to the value observed in the polyadduct **4**.

Thermal stability

The TGA thermograms of the 2 : 1 Diels-Alder adduct **3**, the polyadduct **4** and the polyimide **5** were examined under N_2 atmosphere. Within the temperature range of 115–230°C, the TGA profiles for **3** and **4** were identical and each revealed two well defined decomposition stages (Fig. 4a) corresponding to the retro-Diels-Alder reactions of both the endo and exo adduct structures. The overall volatile mass losses by the Diels-Alder adduct **3** and the polyadduct **4** in this temperature range were 43.2 and 26.3%, respectively. This was in close agreement with the theoretical content (45.3 and 29.2%) of the bisfuran **1** in the Diels-Alder adduct **3** and polyadduct **4**, respectively. The retro-Diels-Alder reaction of **3** and **4** was further investigated in each case, by heating a sample in DMSO-d_6 for 2 h at 160°C and thereafter analysing the mixture with ^{1}H NMR. The spectra confirmed **3** and **4** to have compeletely reverted to **1** and **2** as a result of the retro-Diels-Alder reaction. The low decomposition temperature observed for **4** was in contrast to the good thermal stabilities reported elsewhere[5, 6, 11] for similar Diels-Alder polyadducts derived from bisfurans and bismaleimides. In those cases, no significant retro-Diels-Alder reactions were observed and during heating the thermal dehydration process of endoxide moieties in the Diels-Alder polyadducts was suggested to lead to the formation of polyimide systems with good stabilities up to 350°C. In the present study, the quantitative retro-Diels-Alder decomposition reactions observed for both **3** and **4** at relatively low temperatures precluded the possibility of thermal dehydration as a suitable procedure for the aromatization of the polyadduct. The low thermal stability observed for **4** and the limited degree of polycycloaddition reaction was probably a result of steric crowding along the polyadduct chains. For both **3** and **4** the second major mass loss at 450°C resulted from the thermal decomposition of products formed by the homopolymerization of the bismaleimide **2**[19]. Fig. 4(b) shows **5** to be a remarkably stable thermolysis product that did not exhibit any significant degradation up to a temperature of about 420°C. The small drop in mass (1.5%) observed at around 155°C was confirmed to be associated with the loss of residual BF_3 catalyst (m/e = 68) in the product. When a sample of **5** was heated for 2 h at 160°C in DMSO-d_6 medium and the filtrate analysed by ^{1}H NMR, there was no detectable **1** or **2**. Therefore within the temperature range 115–230°C and beyond, there was no recognizable evidence of a retro-Diels-Alder decomposition reaction exhibited by **5**. Further, the DTG trace revealed no exotherm around 220°C attributable to the exothermic homopolymerization process of the double bond in the bismaleimide **2**[19]. These observations coupled with the FTIR spectroscopic evidence, suggested the bicyclic Diels-Alder adduct moieties in polyadduct **4** to have been completely and irreversibly transformed to thermally stable structures like polyimide by treatment with boron trifluoride diethyletherate since **5** did not suffer any significant degradation below 420°C. Beyond this temperature, the solid decomposed to leave a relatively large proportion of carbonaceous residue at 800°C which resulted from the degradation of graphitized aromatic structures and terminal furanic moieties[20, 21].

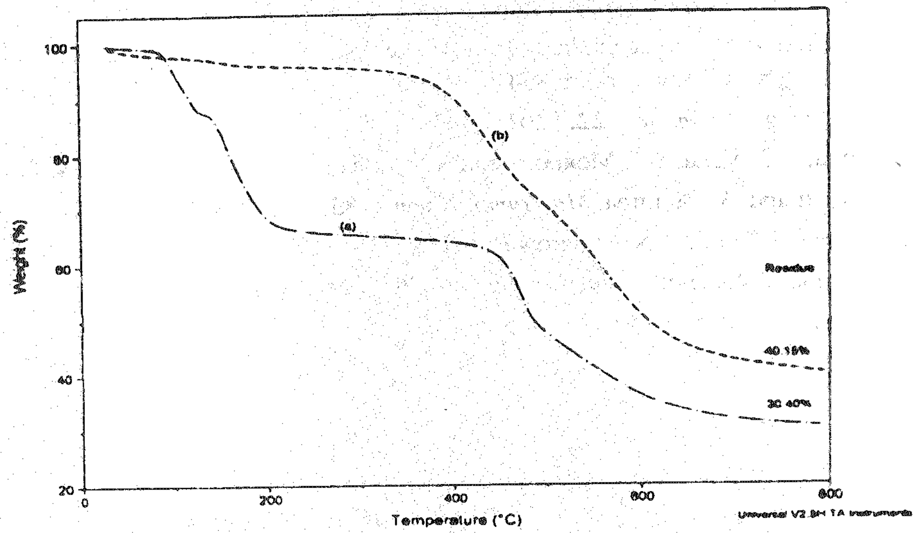


Fig. 4. TGA tracings (10°C min^{-1}, under nitrogen) of the polyadduct 4(a) and the polyimide 5(b).

Conclusion

Our investigations have demonstrated the Diels-Alder polycycloaddition of difurylmethane with bismaleimido-4,4′-diphenylmethane resulting in quantitative yields of a predominantly exo-polyadduct which was completely soluble in DMSO, acetone and methylene chloride. Although there was no observable progressive insolubility of the polyadduct formed, the degrees of polymerization achieved were low possibly due to steric hindrance along the short chains of the polyadduct. Work is in progress to improve on the degrees of polymerization of the polyadduct by use of a more flexible bisfuran co-monomer. The polyadduct was readily transformed into a thermally stable polyimide by treatment of the homogeneous polymer solution in CH_2Cl_2 with boron trifluoride diethylethyrate at room temperature.

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