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Novel heteroarylene polyazomethines: their syntheses and characterizations

S. C. Ng[a,*], H. S. O. Chan[a], P. M. L. Wong[a], K. L. Tan[b] and B. T. G. Tan[b]
[a]*Department of Chemistry, National University of Singapore, Singapore 119260, Singapore*
[b]*Department of Physics, National University of Singapore, Singapore 119260, Singapore*
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Novel thiophene or furan-containing polyazomethines were synthesized by chemical oxidative polymerization with ferric(III) chloride. The structures of the undoped and doped polymers were evaluated by *FT*i.r., elemental analysis, u.v.-vis spectrometry, X-ray photoelectron spectroscopy (XPS) and their thermal stability determined using thermogravimetric analysis (t.g.a.). The conductivities of the undoped polymers were less than 10^{-8} S cm^{-1}, while those of the doped ones were in the range of 10^{-7} to 10^{-6} S cm^{-1}. The low conductivity values were attributed to the low degree of conjugation in the polymers caused by non-planarity of the polymer chains. The thiophene-containing polymers underwent sulfur extrusion during polymerization, resulting in an interruption of conjugation in the polymer backbone with consequent diminished electrical conductivity. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: polyazomethines; thiophene; furan)

INTRODUCTION

Polymers are useful materials on account of their ease of fabrication, flexibility, lightness of weight and chemical inertness. As such, electrically conducting polymers are potential candidates for a wide variety of applications ranging from electrode materials[1,2], microelectronic devices[3,4], catalysts for photoelectrochemical processes[5], organic batteries[6-9] to electrochromic display devices[10,11]. It is not surprising therefore that conducting polymers have been the focus of intense interdisciplinary research over the past 15 years[12-16], where a wide variety of polyenes, polyaromatics, and polyheterocycles were investigated in the search for conducting polymers with improved properties[17-19].

Insertion of azomethine moieties (Shiff's bases) in the backbone of conjugated polymers has been shown to be useful for the preparation of materials with high molecular weights and good physico-mechanical properties[20]. Recently, Destri and co-workers[21,22] reported on the synthesis of a series of polymers, comprising alternating sequences of thienylenic and phenylenic residues linked together by azomethine moieties which have electrical conductivity attaining 10^{-2} S cm^{-1}. With a view to carrying out structure-property correlation studies, we extended this work to a series of polymers (I-IV) incorporating thienylenic or furanylenic and phenylenic residues linked together by azomethine moieties.

EXPERIMENTAL SECTION

Chemicals

Furfuraldehyde (Ajax) was distilled prior to use. Reagent grade thiophene-2-carboxyaldehyde (Fluka), 1,4-phenylene diamine (Fluka) and 4,4'-diaminodiphenyl ether (Fluka) were used as purchased, whilst phenylenediamine hydrogen chloride (Aldrich) was recrystallized from water before use.

Instrumentation

^{1}H and ^{13}C n.m.r. spectra were recorded on a Bruker ACF300 spectrometer using tetramethylsilane as an internal reference. Elemental analyses were performed at the NUS Microanalytical Laboratory on a Perkin-Elmer Model 240 elemental analyser for C, H, N determination. Halogen determination was carried out either by ion chromatography or the oxygen flask method. *FT*i.r. spectra of monomers and polymers dispersed in KBr discs were recorded on a Perkin-Elmer 1725 *FT*i.r. spectrometer. U.v.-vis solution spectra were acquired on a Hewlett Packard 8452A diode array spectrometer with 2-nm resolution, with samples dissolved in methanol. As the polymers were not very soluble in methanol, oligomers were dissolved instead. Mass spectra were obtained using a Micromass 7034E Mass Spectrometer under electron impact. Thermal gravimetric analysis (t.g.a.) of polymer powders (*ca.* 5 mg) were conducted on a Du Pont Thermal Analyst 2100 system with a TGA 2950 thermogravmetric analyser. A heating rate of 10°C min^{-1} with an air flow of 75 ml min^{-1} was used, the runs being conducted from room temperature to 750°C. Conductivity measurements were carried out on a four-point probe connected to a Keithley constant-current source system. X-ray photoelectron spectroscopy (XPS) of the polymer powders was performed by means of a VG ESCA/SIMLAB MKII with Mg Kα radiation. The binding energies were corrected for surface charging by referencing to the designated hydrocarbon C1s binding energy as 284.5 eV. Spectra deconvolutions were carried out using Gaussian component peaks with the same full widths at half-maximum (FWHM) for each component in a particular

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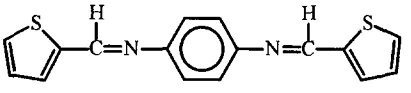
[*] To whom correspondence should be addressed

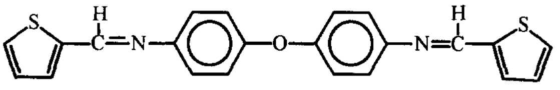
spectrum. Surface elemental stoichiometries were obtained from peak area ratios corrected with the appropriate experimentally determined sensitivity factors.

Monomer synthesis

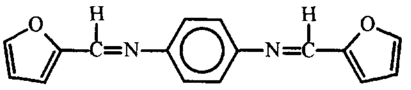
Monomers (I to IV in *Figure 1*) with azomethine linkages have been prepared by condensation of furfuraldehyde or thiophene-2-carboxaldehyde with 1,4-phenylenediamine or 4,4′-diaminodiphenyl ether.



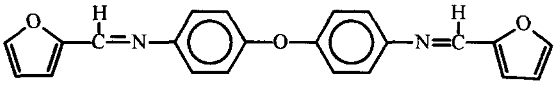
Monomer I



Monomer II



Monomer III



Monomer IV

1,4-Bis(2-thienylmethylideneimino)benzene (I). 2-Thiophenecarboxylaldehyde (21.76 g, 0.19 mol) was added to 1,4-phenylenediamine (10.00 g, 0.09 mol) in isopropanol (100 ml) and the resulting mixture was refluxed over a period of 10 h. Removal of solvent and recrystallization from hexane–chloroform (1:1) afforded the title compound as bright yellow needle-like crystals. Yield 16.2 g (59%). M.p. 169–171°C. *FT*i.r. (KBr): 1613, 1500, 1200, 1050, 975, 856, 813, 738 cm^{-1}. ^{1}H n.m.r.: δ 8.61 (2H, s), 7.54–7.47 (4H, *m*), 7.26 (4H, *s*), 7.13 (2H, *dd*, J = 4.9, 3.91 Hz). *m/z* 296 (M$^+$, 100%). U.v. (methanol) λ_{max} 368 nm (ε 8.1 × 10^4). Anal. calcd for $C_{16}H_{12}N_2S_2$: C, 64.90; H, 4.00; S, 21.60; N, 9.50. Found: C, 65.11; H, 4.19; S, 21.94; N, 9.20.

4,4′-Di(2-thienylmethylideneimino)diphenyl ether (II). 2-Thiophenecarboxaldehyde (17.00 g, 0.15 mol) was added to 4,4′-diaminodiphenyl ether (15.00 g, 0.07 mol) in isopropanol (150 ml) and the resulting mixture was heated under reflux over a period of 10 h. Removal of solvent and recrystallization of the crude product from hexane–chloroform (1:1) afforded the title compound as beige-coloured needle-like crystals. Yield 25.3 g (87%). M.p. 157°C. *FT*i.r. (KBr): 1619, 1500, 1288, 1269, 1200, 856, 706 cm^{-1}. ^{1}H n.m.r.: δ 8.59 (2H, *s*), 7.53–7.46 (4H, *m*), 7.29–6.98 (10H, *m*). *m/z* 388 (M$^+$, 100%). U.v. (methanol) λ_{max} 346 nm (ε 4.5 × 10^4). Anal. calcd for $C_{22}H_{16}N_2S_2O$: C, 68.04; H, 4.12; S, 16.50; N, 7.21. Found: C,68.09; H, 4.44; S, 16.90; N, 7.51.

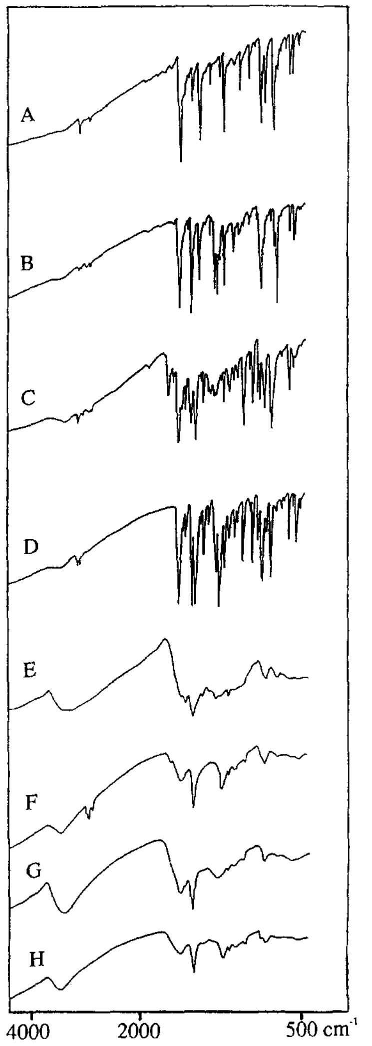


Figure 1 *FT*i.r. spectra of: (A) monomer I; (B) monomer II; (C) monomer III; (D) monomer IV; (E) undoped polymer I; (F) undoped polymer II; (G) undoped polymer III; (H) undoped polymer IV

1,4-Bis(2-furylmethylideneimino)benzene (III). Furfuraldehyde (14.86 g, 0.15 mol) was added to phenylenediamine hydrogen chloride (14.00 g, 0.08 mol) in a solution mixture of methanol (140 ml) and deionized water (140 ml). The resulting mixture was kept under a nitrogen atmosphere and reacted over 3 h. The acid salt of the monomer formed was neutralized with sodium bicarbonate. The monomer was extracted from the mixture with chloroform. Yield 13.4 g (66%). M.p. 132–135°C. *FT*i.r. (KBr): 1732, 1625, 1531, 1475, 1275, 1025, 950, 838, 769 cm^{-1}. ^{1}H n.m.r.: δ 8.39 (2H, *s*), 7.61 (2H, *d*, J = 1.7 Hz), 7.29 (4H, *s*) and 6.96 (2H, *d*, J = 3.4 Hz), 6.59 (2H, *dd*, J = 3.4, 1.7 Hz). *m/z* 264 (M$^+$, 100%). U.v. (methanol) λ_{max} 362 nm (ε 3.1 × 10^4). Anal. calcd for $C_{16}H_{12}N_2O_2$: C, 72.73; H, 4.50; N, 10.60. Found: C, 72.31; H, 4.58; N, 10.82.

4,4″-Di(2-furylmethylideneimino)diphenyl ether (IV). Furfuraldehyde (20.00 g, 0.10 mol) was added to 4,4′-diaminodiphenyl ether (19.22 g, 0.20 mol) in a solution mixture of methanol (200 ml) and deionized water (200 ml). The resulting mixture was kept under a nitrogen atmosphere, and reacted for 3 h. The solid monomer was filtered under suction and recrystallized from chloroform to afford the title compound. Yield 28.6 g (81%). M.p. 115–116°C. *FT*i.r. (KBr): 1625, 1500, 1250, 1025, 931, 837, 750 cm^{-1}. ^{1}H n.m.r.: δ 8.31 (2H, s), 7.62 (2H, *d*, J =

Table 1 Elemental analysis and conductivities of polymer samples

	Bulk elemental ratios[a]	Elemental ratios determined by XPS	Conductivity (doped in iodine for 17 days) (S cm^{-1})
Polymer I	$C_{9.93}O_{2.72}H_{10.15}N_{2.00}S_{0.26}Cl_{0.11}Fe_{0.07}$ $(C_{15.88}O_{0.00}H_{9.91}N_{2.00}S_{0.68}Cl_{0.00}Fe_{0.00})$	$C_{11.16}O_{1.83}N_{2.00}S_{0.21}Cl_{0.09}Fe_{0.01}$	10^{-7}
Polymer II	$C_{18.77}O_{4.07}H_{11.85}N_{2.00}S_{0.59}Cl_{0.19}Fe_{0.26}$ $(C_{21.90}O_{0.00}H_{13.96}N_{2.00}S_{2.00}Cl_{0.00}Fe_{0.00})$	$C_{15.41}O_{2.48}N_{2.00}S_{0.44}Cl_{0.14}Fe_{0.07}$	10^{-6}
Polymer III	$C_{13.76}O_{5.00}H_{12.17}N_{2.00}Cl_{0.24}Fe_{0.06}$ $C_{16.16}O_{2.00}H_{10.08}N_{2.00}Cl_{0.00}Fe_{0.00}$	$C_{13.69}O_{2.39}N_{2.00}Cl_{0.16}Fe_{0.0}$	10^{-7}
Polymer IV	$C_{18.76}O_{4.75}H_{16.25}N_{2.00}Cl_{0.21}Fe_{0.07}$ $C_{22.14}O_{3.04}H_{14.11}N_{2.00}Cl_{0.00}Fe_{0.00}$	$C_{16.64}O_{2.80}N_{2.00}Cl_{0.21}Fe_{0.07}$	10^{-7}
Polymer III (doped in I_2 for 17 days)	$C_{14.66}O_{11.33}N_{2.00}Cl_{1.33}Fe_{0.07}I_{2.29}$	$C_{16.12}O_{2.71}N_{2.00}Cl_{0.00}Fe_{0.03}I_{0.35}$	10^{-7}

[a] Expected values in parentheses.

1.7 Hz), 7.38–6.93 (10H, *m*), 6.56 (2H, *dd*, $J = 3.4$, 1.7 Hz). *m/z* 356 (M^+, %). U.v. (methanol) λ_{max} 340 nm (ε 2.1 × 10^4). Anal. calcd for $C_{22}H_{16}N_2O_3$: C, 67.40; H, 4.50; N, 7.80. Found = C, 67.82; H, 4.44; N, 7.62.

Chemical polymerization

All four monomers were polymerized using modified literature procedures[23]. A 0.2 M solution of the monomer in dried chloroform was added to solid ferric(III) chloride under nitrogen such that the final concentration of the ferric chloride in the reaction flask was *ca.* 0.8 M. The mixture was allowed to react for 48 h at 0–5°C under flowing nitrogen. After the required reaction time, the resulting mixture was added to water to terminate the reaction[24]. The solid polymer that precipitated out was purified by Soxhlet extraction with methanol (18 h) and then acetone (3 h).

Polymer I. Yield 27%; *FT*i.r. (KBr): 1613, 1575, 1513, 838 cm^{-1}; u.v. (methanol) λ_{max} 322 nm. Anal. found: C, 54.83; H, 4.67; S, 3.91; N, 12.91; Fe, 1.89; Cl, 1.72.

Polymer II. Yield 24%; *FT*i.r. (KBr): 1613, 1575, 1513, 838 cm^{-1}; u.v. (methanol) λ_{max} 320 nm. Anal. found: C, 60.81; H, 3.24; S, 5.10; N, 7.60; Fe, 4.12; Cl, 1.69.

Polymer III. Yield 41%; *FT*i.r. (KBr): 1613, 1575, 1513, 825 cm^{-1}; u.v. (methanol) λ_{max} 274 nm. Anal. found: C, 56.18; H, 4.14; N, 9.54; Fe, 0.84; Cl, 2.82.

Polymer IV. Yield 31%; *FT*i.r. (KBr): 1613, 1575, 1500, 838 cm^{-1}; u.v. (methanol) λ_{max} 274 nm. Anal. found: C, 63.10; H, 4.55; N, 7.83; Fe, 1.24; Cl, 2.00.

Doping studies of polymers

Iodine doping was carried out in the vapour phase[25,26]. The polymer powders were compacted into pellets and placed in a desiccator containing iodine crystals. The doping periods ranged from 1 to 17 days.

RESULTS AND DISCUSSION

The *FT*i.r. spectra of all of the monomers show an intense absorption band at 1613–1625 cm^{-1} (see *Figure 1*), which is characteristic for azomethine linkages [–CH=N–]. In monomers I and II, the absorption bands for the C_α–H (706–738 cm^{-1}) and C_β–H (856 cm^{-1}) out-of-plane bend in the thiophene group were clearly evident, whilst the absorption bands for the C_α–H and C_β–H out-of-plane bending in the furan group contained in monomers III and IV can be observed at 750–770 and 838 cm^{-1} respectively. ^1H n.m.r. spectra of the monomers all show signals of –CH=N– protons at *ca.* 8.60–8.30 ppm, while those due to thiophene or furan protons occur around 7.60–6.90 ppm. The u.v.–vis spectra of all the monomers show two absorption peaks, one at around 286–296 nm and the other at around 340–368 nm. The former was assumed to be the π–π^* transition in the benzene component of the structures and the latter is due to the conjugated azomethine linkage. Of the four monomers synthesized, monomers II–IV are novel.

As depicted in *Figure 1*, the *FT*i.r. spectra of the undoped polymers all show that the absorption bands due to the C_α–H out-of-plane bending of the heterocyclic groups have disappeared, while those due to the C_β–H out-of-plane bending have remained. This indicates that the polymerization has occurred through predominant α–α linkages in the heterocyclic moiety[27,28]. The presence of the C=O group in all the polymers is indicated by an absorption band at 1613 cm^{-1}, which suggests aerial oxidation of the polymers. Oxidation during polymerization is unlikely as the reactions were carried out under deaerated conditions. The *FT*i.r. spectra of the doped polymers are very similar to those of the undoped polymers. The u.v.–vis spectra of the undoped polymers show that the bands assigned as the π–π^* transition in the benzene ring have shifted hypsochromically compared to those in the monomers. This is indicative of a low degree of conjugation in the polymer chain, suggesting that the polymer chains may not be planar or that there is a disruption in the conjugation upon polymerization with consequent decrease in conductivity.

The elemental analysis results of polymers *I* and *II* (*Table 1*) show that the sulfur content is lower than expected. This could be ascribable to oxidative ring opening of the thiophene rings in the polymer chains during polymerization with $FeCl_3$. It is known that mineral acids may also attack and open the thiophene ring to form sulfur, H_2S and other products[29]. HCl is formed during polymerization, which goes on to attack the thiophene rings. Oxidizing agents may also cause ring opening. Since the polymerization reaction is essentially one of oxidation, ring opening could have occurred concurrently with sulfur extrusion. The oxygen contents of all of the polymers are much higher than calculated values, which may be attributed to extensive aerial oxidation (supported by *FT*i.r. results).

The XPS analysis indicates that the bulk surface region of the polymer film has a different stoichiometry from that of the bulk. *Table 1* shows the surface and bulk atomic ratios for undoped polymers I–IV and doped polymer III. The surface studies show low sulfur content for polymers I and II and high oxygen content for all polymers, as compared to the calculated results, consistent with the microanalysis results reported above.

The C1s spectra of the doped and undoped polymers all showed asymmetric tailing going from the high to the low binding energy side of the peak. This is a consequence of considerable reorganization of valence electrons in the form of shake-up and/or shake-off phenomena, concomitant with

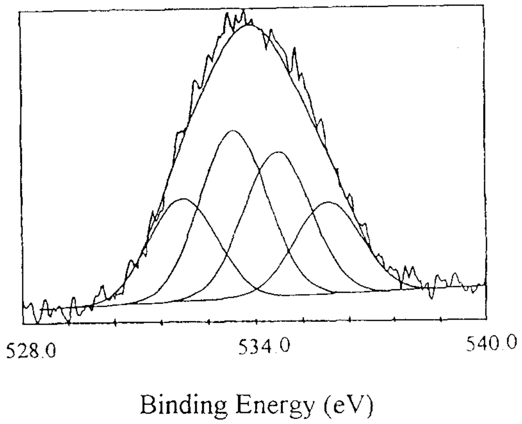


Figure 2 XPS O(1s) spectra of undoped polymer III

the removal of a shielding core electron[30]. It is indicative of long-range disordered conjugation[31,32].

The deconvolution of the C1s envelope for the undoped and doped polymers can be rationalized as follows[33]: 284.8 eV for C atoms of C–C, C–S and C–H linkages. The second environment at 286 eV is due to C–N, C–Cl and C=N. The third environment at 287.1 eV is due to C–N$^+$ and C–N$^+$. The fourth environment is due to C=O at 288.3 eV. A fifth environment at 289.3 eV is observed for some spectra which is assigned to the carboxylate group.

The N1s spectra of the undoped and doped polymers can be deconvoluted into four environments: imine N (398.5 eV), amine N (399.7 eV), protonated imine N$^+$ (401.2 eV) and protonated amine N$^+$ (402.5 eV)[34–36]. Protonated amine and imine peaks were present in the N1s spectra for both the undoped and doped polymers. N$^+$ could have been formed in the undoped polymer due to surface oxidation products[37]. Light doping of the polymers could also have occurred during polymerization with $FeCl_3$.

The S(2p) envelopes for undoped polymers I and II deconvolute into two environments. The first environment is at 164.0 ± 0.1 eV and the second environment is shifted from the first by 1.4 eV to the high binding side, indicating the presence of the S$^+$ species. This species has been reported[38] and could be due to stabilization of the charge on the S atom by polar water molecules. S$^+$ could also be stabilized by the Cl$^-$ counter ion from $FeCl_3$ during the polymerization. The S2p spin orbit doublet has the expected 2:1 intensity ratio[39], and the spin orbit splitting is 1.0 ± 0.1 eV, in accordance with earlier procedures[40].

The O1s envelopes for the undoped and doped polymers are deconvoluted into four environments: C=O (531.0 eV), C–O (532.5 eV), H_2O (533.4 eV) and another environment (533.5–535.0 eV). *Figure 2* shows the deconvoluted XPS O1s core level spectra for undoped polymer III. This figure illustrates the typical O1s spectra obtained from the polymers. In view of its high binding energy, the last environment could be due to an electron-deficient oxygen atom. This oxygen atom could have become coordinated to a chlorine atom during polymerization with $FeCl_3$. Doping does not increase the oxygen content in the last environment in polymer III, suggesting that oxygen does not take part in the conduction mechanism.

The I3d$_{5/2}$ envelope of doped polymer III can be deconvoluted into three components, I_3^- (618.6 eV) and I_5^- (620.0 eV). The small third environment at 621.0 eV could be due to covalent bonding of the iodine to the phenyl group. The absolute binding energies for the various iodine species reported in this work are shifted to the lower binding energies compared to those reported in previous work[26,37], though the chemical shifts are consistent. This discrepancy could be due to the method of normalizing the binding energies to the carbon atom to account for surface charging effects. The assumption that the polymer is uniformly charged throughout may not hold true for the iodine

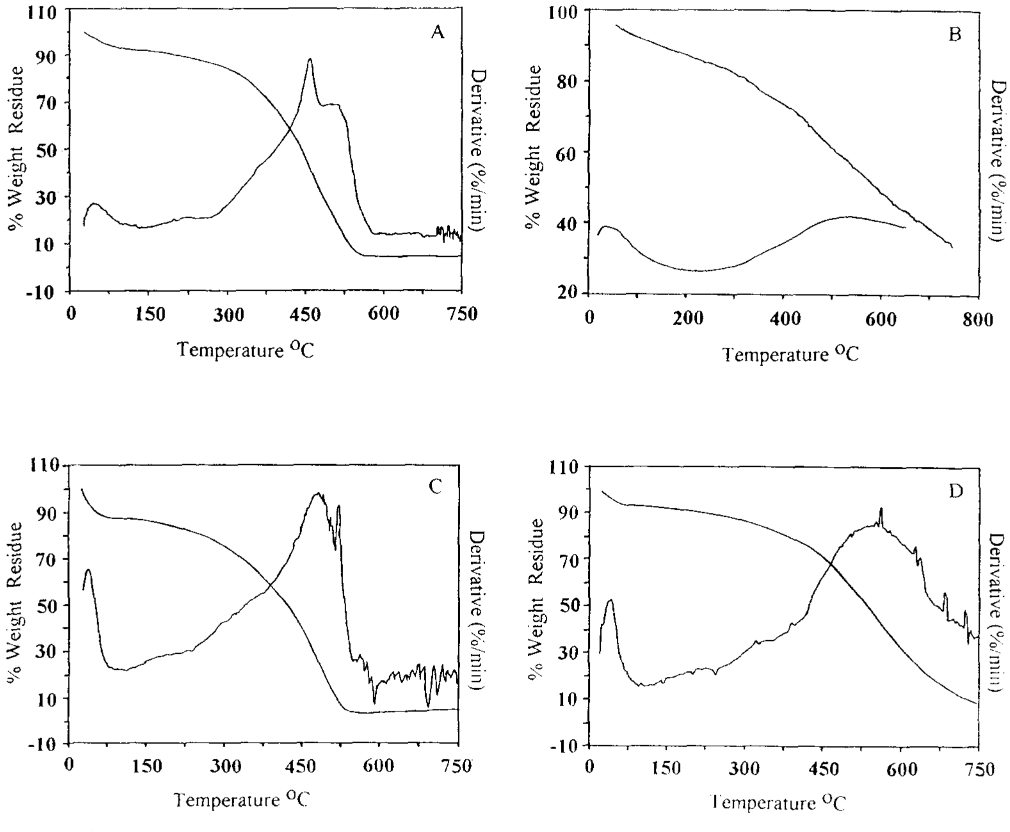


Figure 3 Thermal gravimetric analysis curves of: (A) undoped polymer I; (B) undoped polymer II; (C) undoped polymer III; (D) undoped polymer IV

Table 2 Summary of thermal analysis of undoped and doped polymer samples

	Dopant	Temp. (°C) at 80% weight	Temp. (°C) at 50% weight	Temp. (°C) at 30% weight	Temp. (°C) at greatest rate of weight loss (wt% left)
Polymer I	–	336	450	489	457 (43)
Polymer II	–	334	600	> 750	– (–)
Polymer III	–	264	418	468	482 (24)
Polymer IV	–	389	535	611	557 (42)
Polymer I	Iodine	177	343	450	463 (25)
Polymer II	Iodine	151	269	391	391 (25)
Polymer III	Iodine	167	280	440	512 (15)
Polymer IV	Iodine	162	300	415	400 (33)

spectra. Also, the polymers studied in this report are very different from those of previous studies, thus the absolute binding energies may not be identical. The component at 620.0 eV could also be identified as I_2[26,41]. In this case, since the doped samples were subjected to dynamic vacuum for 48 h prior to the XPS experiment, the amount of I_2 would be expected to be very low.

The thermal stabilities of the undoped polymers are comparable to that of undoped polyaniline[32]. The results are shown in *Figure 3AFigure 3BFigure 3CFigure 3D.* There is an initial weight-loss step of 5–12% weight at 24–140°C, due to volatilization of solvents and moisture. The second weight-loss step is due to the degradation of the polymer backbone, the maximum rate of which is between 450 and 560°C. Polymers II and IV show greater thermal stability than polymers I and III. The greater flexibility of the polymer chain afforded by the inclusion of an oxygen atom between two phenylene rings in the polymer backbone increases the ability of the polymer chain to pack, hence increasing the thermal stability of polymers II and IV due to increased intermolecular interactions. Polymer I is also more thermally stable than polymer III. This could be due to the fact that the sulfur atom in the thiophene ring is less able to donate electrons than oxygen in the furan ring, thus stabilizing free radicals formed during thermal oxidation. A similar trend is seen in polymers II and IV. For iodine-doped polymers, a weight-loss step at 40–200°C is due to the loss of iodine dopant[37]. A summary of the thermal analysis of the undoped and doped samples is shown in *Table 2.*

The undoped polymers show very low conductivities (10^{-8} S cm^{-1} to unconducting). These results are supported by u.v.–vis studies. Iodine doping increases the conductivities of the polymers (see *Table 1*). The conductivities of polymers I and II has increased by one to two orders of magnitude. For polymers III and IV, the conductivities have increased from unconducting to 10^{-7} S cm^{-1}.

The low conductivity observed could be due to the non-planarity of the conjugated polymer backbones of the samples, as shown earlier in u.v.–vis studies. The structure of the polymers containing the thiophene moiety could also have been altered during polymerization, as shown in elemental analysis. Sulfur extrusion had occurred and this could cause interruption of the conjugation in the polymer backbone, thus lowering conductivity. For the polymers containing the furan moiety, loss of the oxygen atom from the furan ring could not be ascertained as elemental analysis could not be used to determine the content of oxygen in the samples. *FT*i.r. studies could not be used to determine the presence of the C–O–C stretch the furan-containing polymers as the spectra were insufficiently resolved.

CONCLUSION

Novel polyazomethines containing thiophene or furan with aniline have been synthesized and polymerized using $FeCl_3$ as the oxidant. The results from *FT*i.r. spectroscopy show that the polymerization occurred through the C_α-position of the heterocyclic group on the monomers, producing regular structures. Aerial oxidation is detected by the appearance of the absorption band due to C=O. This is supported by results from *FT*i.r., elemental analysis and XPS studies. The results from u.v.–vis spectroscopy show that the polymers are less conjugated than the monomers, and that the polymer chains are not planar. Elemental analysis shows that polymers containing thiophene rings underwent oxidative ring-opening during polymerization, leading to sulfur extrusion. XPS studies show that a chemical environment for the oxygen core level at unusually high binding energies is present for doped and undoped polymers. This is attributed to an electron-deficient oxygen species which may have coordinated to the chlorine atom during polymerization with $FeCl_3$. T.g.a. shows that doping has a adverse effect on the thermal stability of some of the polymers.

Conductivity studies show that the undoped polymers are of low conductivities (10^{-12} to 10^{-8} S cm^{-1}) and doping increases the conductivities (10^{-7} to 10^{-6} S cm^{-1}). The low conductivity is attributed to the low extent of conjugation in the polymers because of the non-planarity of the polymer chains as indicated by u.v.–vis studies. Extrusion of the heteroatom in the polymers during polymerization could have altered the structure of the polymers and interrupted the conjugation of the polymer backbones. This could be another cause of the low conductivity observed.

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