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Chemical and electrochemical polymerisation of diacetylenes containing thienyl moiety as the side group

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Summary

Two symmetrical diacetylene monomers containing thienyl moiety as the side groups, namely 1,4-bis(2'-thienyl)butadiyne and 1,4-bis(3'-thienyl)butadiyne, are reported which have been successfully polymerised electrochemically. They have also been polymerised chemically in solution using Lewis acid as initiator. The resulting polymers have been characterised by elemental analysis, infrared spectra, absorption spectra and by solid state NMR spectra. The polymers were found to have conjugated π-electron structure and both of them show high environmental stability. The properties of the polymers have been compared with that of poly(3-methylthiophene) which is a conventional and much studied conjugated polymer. The electrical conductivity of the polymers has also been investigated.

Introduction

Research in organic conjugated polymers has been an area of constant attention since quasi-one dimensional conjugation in these polymers offer tremendous potential to moderate optical, non-linear optical, electrical and related properties are concerned(1,2,3). Amongst them, conducting polymers is one of the areas which is being vigorously investigated(4). Recently, development of soluble and melt processible electrically conducting polymers based on 3-alkyl substituted polythiophenes(5) and similar derivatives of polyheterocycles have heralded a new direction in conducting polymer research. Among these, poly(thiophenes) have rapidly become the subject of special interest because of relatively higher environmental stability of the polymer in doped state as well as in undoped state. Moreover, they possess structural versatility required for fine tuning the properties and hence make them viable for specific applications.

A large number of substituted thiophenes and their structural variants eg. thienyl thiophene have been subjected to polymerisation in search for conjugated polymers with suitable properties(6,7,8). Polymerisation of bifunctional α,ω-heterocyclic polyene in search for extended π-conjugated network structures have been investigated. We have been dealing with preparation and polymerisation of diacetylenic monomers containing heteroaryl moieties. In this paper, we report the preparation, electrochemical and chemical polymerisation of 1,4-bis(2'-thienyl)butadiyne, **1** and 1,4-bis(3'-thienyl)butadiyne, **2**. These molecules have potential reactive sites for polymerisation and can form highly conjugated novel structures. Besides, **1** and **2** being conjugated diacetylenes, have also been investigated in our laboratory for the reactivity in solid state topochemical polymerisation to form polydiacetyenes(9, 10). As it turned out, both the diacetylenes **1** and **2** do not undergo polymerisation to form polydiacetylenes, however, **1** and **2** but undergo facile chemical and electrochemical polymerisation in solution. Polymer preparation and characterisation of the polymers are reported in this paper. Also, the electrical conductivity of the polymers is discussed.

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Experimental Part

Synthesis of monomers

Monomer **1** and **2** were synthesised from their precursors, 2-thienylacetylene and 3-thienylacetylene respectively, by oxidative coupling(Glaser's Coupling)(11). Previously, we reported the preparation of 2-thienylacetylene and 3-thienylacetylene(12). The preparation of **1** and **2** from these precursors is detailed below.

Preparation of **1**

To a magnetically stirred suspension of cuprous chloride(190 mg) in dimethoxyethylene (DME) (10 ml), tetramethylenediamine (TMED) (0.5 ml) was added. After 10 minutes at room temperature, 2-thienylacetylene (1g, 0.009 mol) was added while oxygen was bubbled through the solution. The reaction was found to be complete after 2 hours. Extraction from diethyl ether and subsequent column chromatography yielded 40% of **1** as a colourless solid, which upon recrystallisation from methanol at low temperature, yielded colourless needle shaped crystals, m.p. 89°C [lit.(13) m.p. : 88°-90°C]. The product was found to be 99.8% pure (HPLC) after three crystallisation from methanol.

Preparation of **2**

2 was synthesised from 3-thienylacetylene in a similar manner as described for **1**. The product was recrystalled from methanol four times and the purity was found to be 99.5% (HPLC). Yield : 40%, m.p. : 111°C [lit.(14) m.p. : 111.5°-112.5°C].

Electrochemical polymerisation of **1** *and* **2**

Electrochemical polymerisation of **1** and **2** was carried out in a single compartment peer-shaped electrochemical cell by taking a 10^{-2} M solution of the monomers in acetonitrile and using tetraethylammonium perchlorate (TEAPC) (10^{-1} M) in acetonitrile as supporting electrolyte. All reagents were dried using appropriate procedures and the equipments were oven dried for carrying out the polymerisation. The reaction mixture was deaerated by passing nitrogen for 15 minutes prior to the experiment. The polymerisation was done by potentiodynamic method using a PARC 362 Scanning Potentiostat. The potential was cycled between -0.2 V to + 1.2 V vs Ag/Ag^+ at 50 mV/sec. The polymers were obtained as thin films on Pt electrodes or on Indium Tin Oxide (ITO) glass electrodes.

When ITO glass was used as electrode the potential had to be increased upto +1.5 V to initiate the polymerisation reaction due to relatively low conductivity of the substrate as compared to Pt electrode. After the reaction was initiated, however, it was adequate to cycle the potential between -0.2 V to 1.2 V to maintain the propagation of the reaction. For both the monomers **1** and **2**, the potential was cycled for approximately 30 times in order to get a visible thin polymeric film on the electrode.

Polymer films were also grown potentostatically on Pt electrode surfaces by electrochemical polymerisation of **1**, **2** and 3MT below their respective E_{pa} value.

3-Methylthiophene (3MT) was also polymerised in a similar manner for compa5ison. The results for 3MT electrochemical polymerisation are similar to those reported earlier(14).

Chemical polymerisation of **1** *and* **2**

Chemical polymerisation of **1** and **2** was carried out following the method reported in the literature(16). A typical procedure is as follows. Monomer (0.1 mol) was added to a stirred solution of $FeCl_3$ (0.3 mil) in chloroform (1l) purged with nitrogen. The mixture was stirred for two hours. Polymerisation was carried out at two different temperatures (0°C and 25°C). Polymer was precipitated by adding methanol to the reaction mixture. The precipitate obtained was filtered and the residue was extracted in a soxhlet apparatus first with methanol, then with water and finally with acetone. The last step is a slight modification of the reported procedure. Use of acetone made it possible to get the polymers in absolute dry and finely powdered form. The polymers were obtained as amorphous brown solids in all the cases.

Yield for polymer from **1**: 86% (0°C) and 83% (25°C); for polymer from **2**: 81% (0°C) and 82% (25°C).

Polymers were characterised by elemental analysis, FTIR, UV-visible absorption and CP/MAS NMR spectra. Elemental analysis results are tabulated in Table 1.

3MT was also polymerised using the same procedure for a comparative study.

Table 1 : Elemental analysis results for the polymers

Polymer[a]	Elemental Composition (in%)[b] C	H	S	Fe	Cl
{Poly(**1**)$_n$.FeCl$_4$}	56.20 (56.69)	1.62 (1.57)	24.80 (25.19)	2.51 (2.55)	14.05 (13.98)
{Poly(**2**)$_n$.FeCl$_4$}	57.20 (56.69)	1.61 (1.57)	25.05 (25.19)	2.43 (2.55)	14.12 (13.98)
{Poly(3MT)$_n$.FeCl$_4$}	52.50 (51.79)	3.98 (4.32)	24.01 (23.03)	4.24 (4.68)	25.26 (25.54)

[a]number of monomeric units, n = 4
[b]calculated values

Conductivity measurements

Conductivity measurements for the chemically polymerised samples were carried out using 4-probe method using Keithley programmable elecrometer. The neat polymer pellets were used for conductivity measurement. The polymers were doped with iodine and conductivity of the doped polymers were also recorded.

Results and Discussion

Electrochemical polymerisation

1 and **2** could be polymerised to deep golden colour films which are insoluble in common organic solvents. Table 2 summarises the cyclic voltammetric data for the monomers **1**, **2** and 3MT and for their corresponding polymer films. All the monomers show irreversible oxidation peaks indicating that the intermediate radical cation is unstable and quite reactive. The oxidation potentials for **1** and **2** are lower than that of 3MT suggesting that the diacetylene monomers are easier to oxidise. This may be due to greater π-conjugation in their structures.

Table 2 : Cyclic Voltammetric data for **1**, **2** and 3MT measured in 0.1 TEAPC/CH_3CN using Pt. electrode

Compound	E_{pa}(in V) monomer	polymer
1	1.35	0.60
2	1.41	0.62
3MT	1.85	0.75

Figure 1 shows the cyclic voltammogram for poly**1** film on Pt electrode in 0.1 M TEAPC/CH_3CN solution. The film can be cycled repeatedly between conducting(oxidised) and nonconducting(neutral) state with no significant decomposition of the material. Similar results were obtained for **2** also.

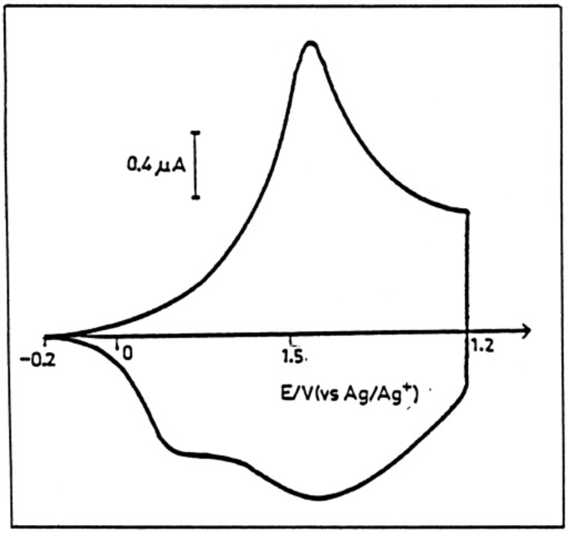


Figure 1 Cyclic voltammogram of poly**1** in 0.1 M TEAPC/CH_3CN solution on Pt; scan rate 50 mVs^{-1}.

Next, ITO glass electrode was used for electropolymerisation of the monomers. As a typical example, the CV for electropolymerisation of **1** on ITO glass elecrode is shown in fig. 2. Although no clear oxidation and reducton peaks could be seen, owing to the less conducting nature of the ITO surface, polymer film grew on the electrode with each cycle. For 3MT also, the oxidation and reduction peaks were less prominent when ITO glass elecrode was used.

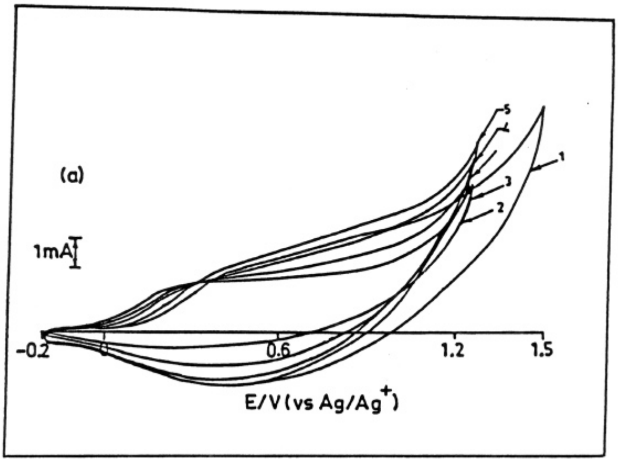


Figure 2 Cyclic voltammogram of electropolymerisation of **1** in 0.1 M TEAPC/CH_3CN solution on ITO glass electrode; scan rate 50 mVs^{-1}.

Absorption spectra of poly**1** and poly**2** on ITO glass showed peaks having λ_{max} at 537 nm and 530 nm respectively. Figure 3 shows the absorption spectra of the polymers alongwith poly[3MT]. The absorption band edge for poly2 extended to significantly longer wavelength(~800 nm) suggesting that the effective conjugation length in the polymer is significantly long. The appearance and absorption spectra of these films remained unaltered on keeping under ambient conditions for several days and on heating at 150°C for several hours.

The polymers on ITO glass were doped with I_2 and the absorption spectra were recorded for varying I_2 intake. It was observed that the λ_{max} shifted by 10 nm to longer wavelength upon I_2 doping indicating increase in conductivity.

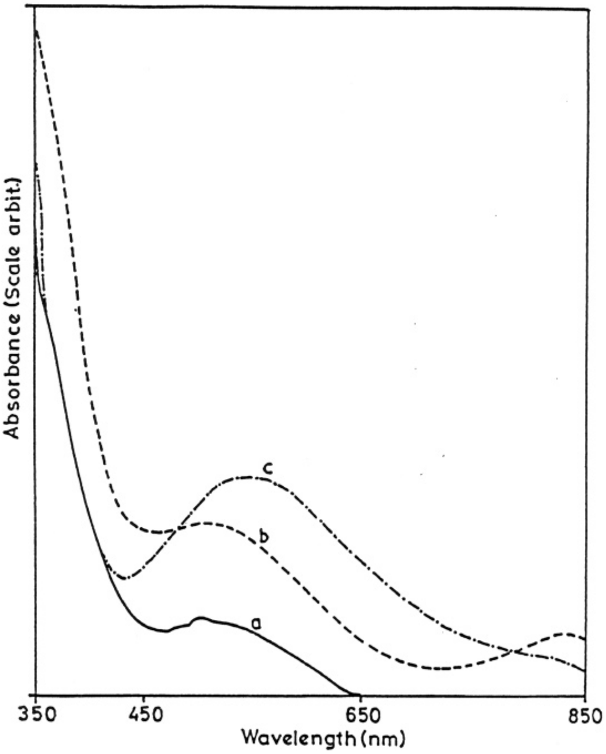


Figure 3 Absorption spectra of (a) poly**1**, (b) poly**2** and (c)poly(3MT) films on ITO glass electrodes.

Chemical polymerisation

Chemical polymerisation of **1** and **2** produced brown powders insoluble in common organic solvents. Elemental analysis for the polymers gave low elemental content even after repeated extractions. However, satisfactory elemental analysis was obtained on inclusion of iron and chlorine contents (table 1). The polymers were kept over concentrated ammonia solution for 24 hours in order to dedope them(17). The undoped samples thus obtained were used for further investigations.

The reflectance spectra of pellets made from poly**1** and poly**2** samples showed broad band absorption stretching over the whole visible region with absorption maximum of approx. 540 nm (band gap energy = 2.29 eV) for both the polymers. The reflectance spetrum of similar pellet of poly[3MT] showed absorption maximum at 480 nm (band gap energy = 2.58 eV) indicating greater effective conjugation length in poly**1** and poly**2** compared to poly[3MT].

The FTIR spectrum of poly**1**, poly**2** and poly[3MT] were recorded to further characterise the polymers. As a typical example, figure 4 shows the FTIR spectra for **1**. The FTIR of polymer is relatively difused than that for the monomer. The FTIR of poly**1** shows a peak, although weak, at 2180 cm^{-1} which indicates the presence of acetylenic bond in the polymer. Also, peaks can be observed in the region 1600-1400 cm^{-1} which correspond to the aromatic ring C=C stretching frequency. Therefore, the acetylenic bonds as well as the aromatic ring seem to be intact after the polymerisation. Peak at 690 cm^{-1} in the monomer is characteristic peak for α C-H bending(18). In the polymer, this peak is absent, indicating that the polymerisation has mainly taken place through the available α carbons of thiophene rings in **1**.

FTIR for sample **2** also provides similar results as for **1**. However, for the monomer **2**, the α C-H bending frequency peak at 690 cm-1 can be seen in the monomer as more intense than the 790 cm^{-1} peak for β C-H bending. In the polymer, the 690 cm^{-1} peak decreases in intensity suggesting that the polymerisation has involved the two free α caron of thiophene.

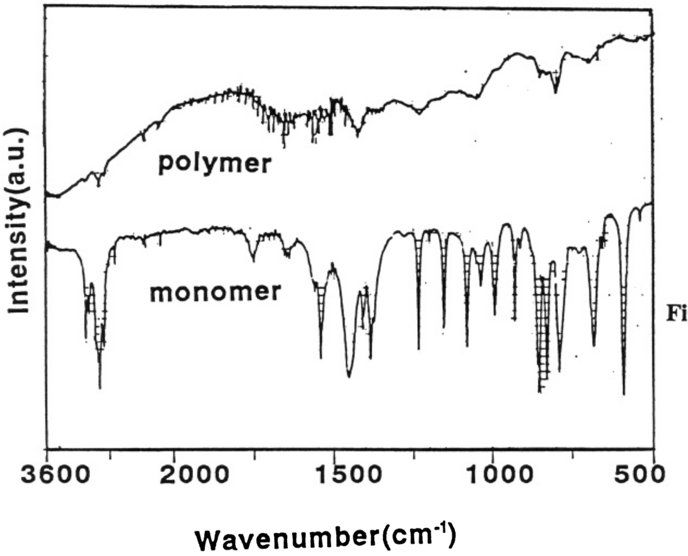


Figure 4 FTIR spectra of **1**

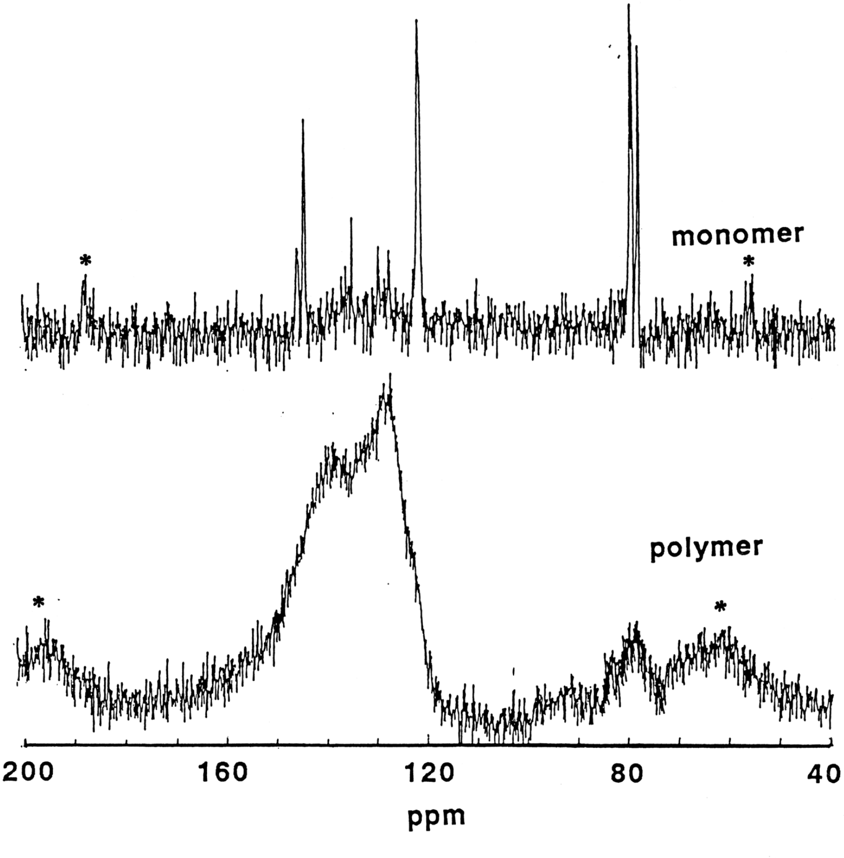
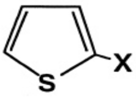


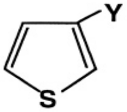
Figure 5 CP/MAS ^{13}C NMR spectra of **1**. The peaks with asterisk mark are for spinning side bands

Further, solid state ^{13}C NMR spectra of the monomers **1** and **2** and their corresponding chemcally polymerised samples were recorded. Figure 5 shows the CP/MAS NMR of monomer **1** and its polymer. Monomer shows peaks at 79 and 82 ppm which can be assigned to the acetylenic carbons. Upon chemical polymerisation, the peaks are still present for the acetylenic carbon atoms. The peaks for thiophene carbons are present in the region 120 to 140 ppm in both the monomer and the polymer. Similar peak patterns are observed for the monomer and polymer of **2** also. Therefore, it follows that the polymerisation has not involved the acetylenic carbon atoms. Consequently, the polymerisation must have taken place at the free α or β carbon of thiophene units.

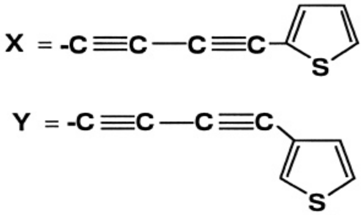
Monomer **1** and **2** can be viewed upon as thiophene units having substitutents X and Y respectively.



1



2



Monomer **2** has a structure similar to 3-alkylthiophene except having a diacetylenic moiety as side group at β-position. Consequently, we expect that **1** should polymerise electrochemically as well as chemically following the mechanism similar to that for the polymerisation of 3-substituted alkyl thiophenes. In fact, it does undergo electrochemical and chemical polymerisation. Moreover, the relatively lower oxidation potential for **2** implies that **2** is easier to polymerise owing to the conjugated structure. However, due to polymerisation at both α carbon position of the thiophene ring, the overall strucutre of the polymer is expected to be a network type.

On the other hand, the structure of **1** is not similar to that of 3MT. But in this case also, the thiophene ring has a free α-carbon atom through which chemical and electrochemical polymerisation could be achieved. In fact, theoretically the conjugation length in poly**1** can extend longer as compared to that in poly**2** by virtue of its structural disposition. However, the nature of the polymer obtained experimentally from **1** is similar to that from **2** as observed from their UV-visible, FTIR and NMR spectra and their electrical conductivity. Consequently, we think that polymerisation has also occured at β carbon position apart from α carbon positions in the thiophene ring of **1** and **2**. Thus the final polymers obtained from **1** and **2** are thought to have a network matrix and similar structure macroscopically.

Electrical Conductivity

The conductivity of chemically polymerised samples of **1**, **2** and 3MT were obtained by measurement using neat sample pellets and are tabulated in Table 3. The conductivities of

Table 3 : Conductivity of chemically polymerised samples

Sample	Conductivity (Scm^{-1}) undoped	doped[a]
poly**1**	5.2×10^{-5}	2.9×10^{-3}
poly**2**	5.9×10^{-5}	2.3×10^{-3}
poly3MT	9.8×10^{-2}	0.8×10^{1}

[a]values are for samples after 12 hours of I_2 doping.

samples from poly**1** and poly**2** were of the order of 10^{-5} Scm^{-1} while for poly[3MT], it was 10^{-2} Scm^{-1}. These pellets were subjected to I_2 doping. The conductivity of the samples were measured after 12 hours of doping. The conductivity increased by almost two order of magnitude for poly**1**, poly**2** and poly[3MT]. Doping above 12 hours could not be continued for poly**1** and poly**2** because the pellet began to crack. This may be because of the sample being fully doped and any more I_2 molecule causes strain to develop in the polymer matrix.

Conclusions

We have reported synthesis of novel conjugated polymers by electrochemical and chemical polymerisation of diacetylene containing thiophenes. The polymers show high environmental stability, long wavelength absorption and moderate electrical conductivities. Further investigations related to the optical and nonlinear optical properties for the polymers are being carried out presently.

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