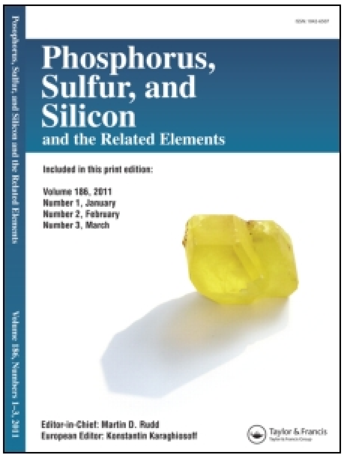

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POLYCHALCONES BASED ON 5,5′-THIO-BIS-2-FURANCARBOXALDEHYDE

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Polychalcones were prepared by aldol condensation of 5,5′-thio-bis-furancarboxaldehyde (TBF) with acetone, methyl ethyl ketone, cyclopentanone, cyclohexanone and cycloheptanone, respectively. All the polychalcones were characterised by elemental analysis, IR spectral data and thermogravimetry. The electrical conductivity of all polychalcones was measured over a wide temperature range.

Key words: Ketone; thiobisfurfural; polychalcones; TGA; electrical conductivity.

INTRODUCTION

There are only few reports about polychalcones found in the literature.[1–4] These polychalcones consist mainly of phenylene moieties. They are found thermally stable, having high chemical resistance and more particularly having good semiconductivity properties. The incorporation of furan rings as well as sulphur atoms in the polychalcone backbone may alter the properties, especially the semi-conductivity of polychalcones to a significant degree. In the present paper the synthesis, characterisation and electrical properties of a number of polychalcones based on 5,5′-thio-bis-2-furan-carboxaldehyde (TBF) are described (Scheme I).

EXPERIMENTAL

Materials: 5,5′-Thio-bis-2-furancarboxaldehyde (TBF) was prepared according to the reported method.[5] The ketones viz. acetone, methyl ethyl ketone, cyclopentanone, cyclohexanone, cycloheptanone and all other chemicals used were of pure grade.

Synthesis of polychalcones: All the polychalcones were prepared by an aldol condensation of TBF with various ketones using the following general procedure.

To a solution of TBF (0.01 mole) and 2.0 g NaOH in methanol (25 ml), a solution of ketone (0.01 mole) (shown in Scheme 1, Table I) in methanol (20 ml) was added dropwise under magnetic stirring at room temperature. The stirring was continued for 24 hrs at room temperature (32 ± 1°C). The precipitated polymeric product was filtered, washed twice with methanol (10 ml) and air dried to yield a yellow powder which did not melt up to 300°C.

The details about all the polychalcones are furnished in Table I.

Measurements: The C, H, and S content in the polychalcone samples was estimated by the C, H, N, O, S Carlo Erba (Italy) analyzer. IR spectra of all the polychalcone samples were obtained using KBr on a Perkin Elmer 983 Spectrophotometer. Thermogravimetric analysis of all the polychalcones was carried out in air at a heating rate of 10°C/min on an Linceise thermobalance.

Prior to the measure the electrical conductivity of polychalcone samples, all the samples were heated twice to 200°C and subsequently cooled to room temperature. This treatment was employed to stabilize the structure of the sample and to remove impurities such as water, organic solvents etc. For the electrical conductivity measurement a pellet (1 cm diameter and 0.45 cm thickness) of the polymer under study was prepared by pressing a finely powdered and dried sample under a hydrostatic pressure at 20,000 p.s.i. per 2 min.

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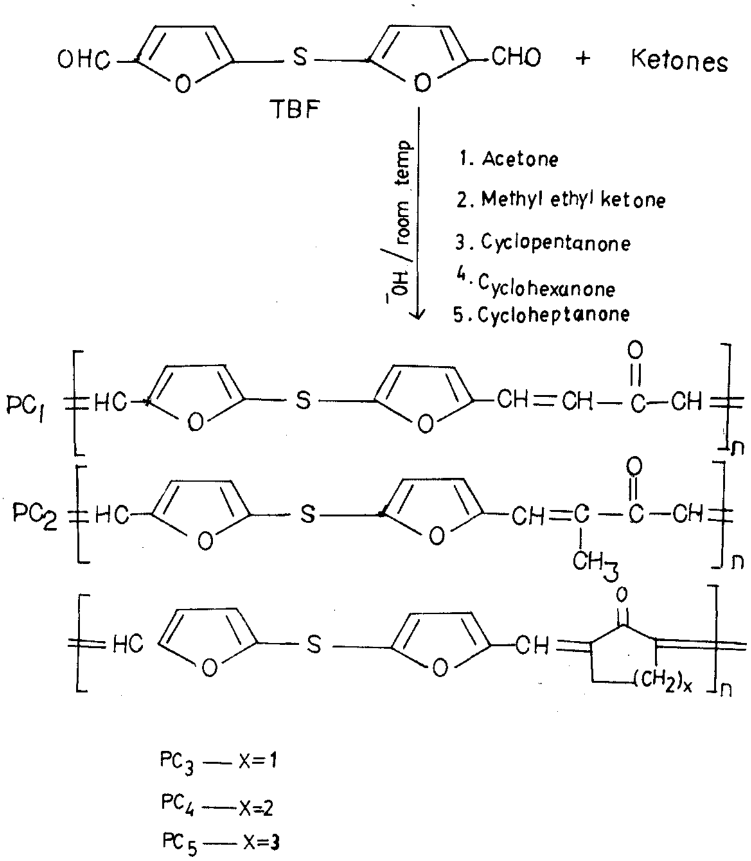


SCHEME I

A uniform thin layer of silver paste was applied on both sides at the pellet providing electrical contacts. The pellet was firmly pressed between two circular metal discs functioning as electrodes. The other ends of the electrodes were pressed through the pellet holder for connections. The entire assembly was placed in a furnace. It was heated at a rate of 1°C min.$^{-1}$ A two probe DC electrical resistivities of the sample was measured by using "Million Megohmeter RM 160 MK 111A BPL India." This instrument is capable of measuring resistivities in the megha ohm range (10^8 to 10^{15}). The specific conductivity (σ) of the sample in pellet was estimated by the usual relation from the knowledge of the resistance of the pellet and its diameter.

The electrical conductivity (σ) of the polymer sample was measured at temperature (T) between 308 to 473°K. The plots of log σ versus $1/T$ were made according to the exponential relation.

$$\sigma = \sigma_0 e^{-ERT} \tag{1}$$

The plots are shown in Figure 1 and values of activation energy E are included in Table II.

RESULTS AND DISCUSSION

As the simple chalcone formation of 2-furaldehyde with aliphatic and aromatic ketones is established as a very facile reaction at room temperature, the synthesis of polychalcones based on thio-bis-furaldehyde and ketones were performed at

TABLE I

Synthesis and characterization of polychalcones

Polychalcone sample	% age yield	Elemental Analysis (%)						(TGA) % age weight loss at °C				
		C		H		S						
		Calcd.	Found	Calcd.	Found	Calcd.	Found	250	300	400	500	600
PC_1	85	63.93	63.85	3.27	3.34	13.11	13.20	2.5	7.5	25	75	92
PC_2	80	65.11	65.21	3.87	3.72	12.40	12.32	3.0	9.0	28	78	94
PC_3	75	66.66	66.54	3.70	3.58	11.85	11.94	4.0	10.0	30	80	96
PC_4	75	67.13	67.08	4.19	4.08	11.18	11.24	5.0	12	32	85	96
PC_5	75	68.45	68.33	4.64	4.72	10.78	10.92	5.0	12	34	85	96

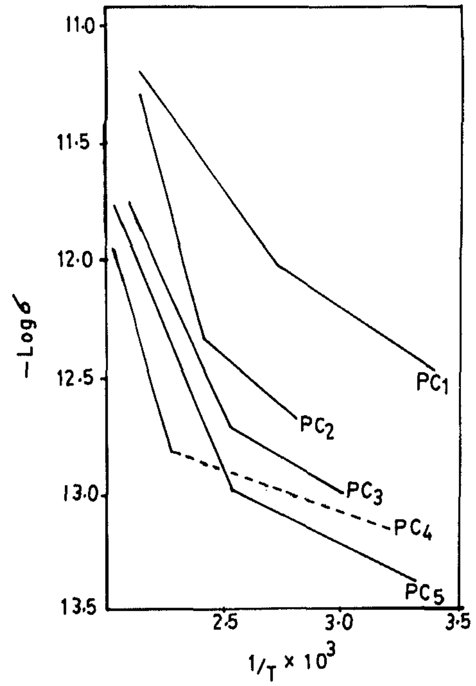


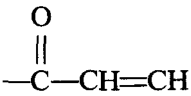
FIGURE 1

TABLE II
Electrical conductivity data of polychalcones

Polymer sample	Electrical conductivity (σ) at 308°K (Ω^{-1}, cm^{-1})	The break temperature range (°K)	Intrinsic electrical conductivity (σ_0) (Ω^{-1}, cm^{-1})	Activation energy for electrical conductivity (ev)
PC_1	3.98×10^{-13}	390–420	3.98×10^{-7}	0.05
PC_2	2.4×10^{-13}	400–430	87×10^{-8}	0.12
PC_3	1.26×10^{-13}	410–430	7.9×10^{-10}	0.95
PC_4	6.3×10^{-14}	410–430	1.9×10^{-10}	1.2
PC_5	2.5×10^{-14}	400–430	1.6×10^{-10}	1.2

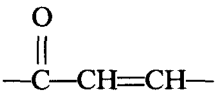
room temperature. All the polychalcone samples were yellow powders. They are insoluble in common organic solvents, but sparingly soluble in conc. H_2SO_4. This agrees with the polychalcones reported earlier.[1–4] Sulphur contents of all polychalcone samples agreed with calculated values of predicted structures of repeat units (Scheme I).

All the polychalcone samples (Table I) showed IR spectra identical in terms of important positions. Each spectrum comprises bands at 3030 and 3070 cm^{-1}. These have been assigned to the aromatic furan ring C—H stretching vibrations. The bands at 2920, 2850 cm^{-1} observed particularly for polychalcones of cyclic ketones are due to νCH_2. In this region the band due to νCH of



$$-\overset{\overset{\displaystyle O}{\|}}{C}-CH{=}CH$$

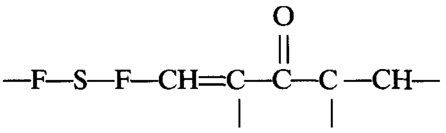
was not observed discernibly. Each spectrum comprises a broad band around 1680 cm^{-1} attributed to $\nu C{=}O$ of the conjugated



$$-\overset{\overset{\displaystyle O}{\|}}{C}-CH{=}CH-$$

system.[7] The band due to conjugated $-C{=}C-$ could not be identified because of series of bands for aromatic ring breathings.

Bromination of the polychalcones yielded the corresponding dibromopolychalcone. It was sparingly soluble in DMF. The bromine content of brominated polychalcones was consistent with the presence of chalcone group in the parent polymer chain. This indicates that all the chalcone groups have participated in the bromination reaction. The IR spectrum of the brominated polychalcones differs slightly from that of parent polychalcone. The band due to $\nu_{C{=}O}$ in the IR spectrum of PC(Br) shifted to somewhat lower region round 1700 cm^{-1} indicating absence of conjugation.[8] All these features suggests that the produced polychalcones comprises



$$-F-S-F-CH{=}\underset{|}{C}-\overset{\overset{\displaystyle O}{\|}}{C}-\underset{|}{C}-CH-$$

repeating units and the polycondensation by aldol reaction occurred in one step by the mechanism shown earlier (Scheme I).

As the produced polychalcones are insoluble in common organic solvents, the estimation of number average molecular weight ($\bar{M_n}$) of polychalcones and solution viscometric study of polychalcones were not attempted.

The results of the TG analysis of all polychalcones are listed in Table I. Examination of thermograms of polychalcones reveals that the polychalcones start to decompose at a perceptible rate at temperatures around 250°C. Above this temperature, the polymers degrade very rapidly and lose their weights completely (i.e. disappear) at around 700°C depending upon the nature of the polymer. The thermal behaviour of the produced polychalcones appeared to be similar to that reported behaviour of the polychalcones obtained from aryl derivatives.[1-4]

Examination of Figure 1 (plots of 10 g σ vs $1/T$) for the electrical conductivity reveals that the conductivity increases with temperature, slowly initially, and then very rapidly after some point between 130°C and 200°C depending on the nature of polymer. This indicates that in the low temperature region the polymer samples present extrinsic conduction. In the high temperature region, where a linear dependence of log σ versus $1/T$ was observed, the polymer samples possess intrinsic conductance. The shape of the plots below the break temperature in which the conductivity increases slowly may be depends on the nature and type of the sample, or on the partical size of the sample.[9] Hence the portion below the break temperature is of secondary interest. In the intrinsic conductance domain, the temperature dependence of the electrical conductivity obeys the well known equation (1). Hence the linear portion of the plots of log σ versus $1/T$ in the higher temperature range beyond the break temperature is used for estimate the activation energy E and intrinsic conductivity.

Examination of the results presented in Table II reveals that the polychalcone samples have an electrical conductivity in the range from 2.5×10^{-14} to $3.98 \times 10^{-13}\ \Omega^{-1}$, cm^{-1} at room temperature depending upon the nature of the polymer. The linear nature of the plots above the break temperature indicates that polychalcone samples can be ranked as a semiconductor materials at high temperature.

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