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POLYSCHIFF BASES—I

SYNTHESES AND PROPERTIES OF POLYSCHIFF BASES FROM 5,5'-THIOBISFURFURAL

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Abstract—PolySchiff bases have been synthesized from 5,5'-thiobisfurfural and various diamines such as *o*-, *m*- and *p*-phenylenediamines, benzidine, 3,3'-dimethoxybenzidine, 3,3'-dimethylbenzidine, 4,4'-diaminodiphenylmethane, 4,4'-diaminodiphenylsulphone and aliphatic diamines such as ethylenediamine and hexamethylenediamine under various experimental conditions. The polymers have been characterized by i.r. spectral and thermal studies and by measurement of electrical conductivity at various temperatures.

INTRODUCTION

PolySchiff bases are known for their high stability but more particularly for their semiconducting properties [1-3]. The polySchiff bases containing S-bridges are reported to have been prepared from diamines such as 4,4'-diaminodiphenylsulphone [4-7] but there are no reports about such polySchiff bases having been prepared from a dicarbonyl compound with such a bridge. It has been reported that the polySchiff bases with a sulphur bridge in the polymer chains have thermal properties comparable with those of all aromatic polySchiff bases [2]. Such polymers based on the condensation of 5,5'-thiobisfurfural (TBF) and various aromatic and aliphatic diamines listed in Table 1 are reported in the present communication. These polySchiff bases are characterized by i.r. spectral and thermal studies and by measurement of electrical conductivities at various temperatures.

EXPERIMENTAL

Furfural (SDS grade) was purified by distillation (b.p. 162°C) adding 0.05% of hydroquinone. The *o*-, *m*- and *p*-phenylenediamines, benzidine, 3,3'-dimethylbenzidine, 3,3'-dimethoxybenzidine, 4,4'-diaminodiphenylmethane, 4,4'-diaminodiphenylsulphone, ethylenediamine and 1,6-hexamethylenediamine were laboratory grade reagents and were purified by the usual methods. The solvents, dioxane and DMF, were purified by double distillation.

Monomer synthesis

5-Bromofurfural (m.p. 82°C) was prepared by bromination of furfural by a published method [8].

5,5'-Thiobisfurfural (*TBF*). To a refluxing mixture of 5-bromofurfural (70 g, 0.4 mol) and water (800 ml), a solution of sodium sulphide (24 g, 0.3 mol) in a mixture of water (800 mol) and alcohol (100 ml) was added. The reaction mixture was refluxed for 15 to 20 min after addition of sodium sulphide was completed. The reaction mixture was cooled. The product separated as brown leaflets and was collected and then washed with water. It was crystallized from 60% ethanol–water mixture in golden coloured leaflets (m.p. 132°C) [9]. PolySchiff bases were prepared from TBF and the required diamines under different experimental conditions. The polymer samples are so designated as to indicate the monomers from which the polymer was prepared.

Polycondensation of TBF with p-*phenylenediamine*. TBF (1.11 g, 0.005 mol) was dissolved in DMF (20 ml) at 150°C. To this solution *p*-phenylenediamine (*p*-Ph) (0.54 g, 0.005 mol) was added at 150°C. The reaction mixture was heated for 30 min at 150–155°C. The brown coloured powder was filtered. The solid mass was powdered and washed twice with boiling ethanol. It was refluxed in benzene (50 ml) and filtered. The yield of polymer was 98%. It did not melt up to 360°C and was insoluble in all organic solvents except formic acid. The sample is designated as TBF–*p*-Ph-1. When this polycondensation was carried out over a period of 1 hr, the resulting polySchiff base TBF–*p*-Ph-2, was insoluble even in formic acid.

The polycondensation of TBF with *p*-phenylenediamine was effected in other solvents at reflux temperature over a period of 6 hr. It was observed that, when benzene, ethyl acetate and chloroform were used as solvents, the resulting polySchiff bases were insoluble in all solvents except formic acid.

Polycondensations of TBF with *m*-phenylenediamine (*m*-Ph), benzidine (Bz), tolidine (Tol), dianisidine (Dian) and 4,4'-diaminodiphenylmethane (DDM) were carried out similarly in DMF solution affording the corresponding polySchiff bases, TBF–*m*-Ph, TBF–Bz, TBF–Tol, TBF–Dian and TBF–DDM respectively in 95 to 98% yield. Under similar conditions *o*-phenylenediamine failed to react with TBF and diaminodiphenyl sulphone afforded the corresponding polySchiff base TBF–DDS in about 50% yield.

The polycondensations of TBF with ethylenediamine and 1,6-hexamethylenediamine in DMF at reflux temperature afforded TBF–Et and TBF–HMD as yellow powders in nearly quantitative yield even when the reaction time was only 2 hr.

For melt polycondensation of TBF with *p*-phenylenediamine, the monomers TBF (1.11 g, 0.005 mol) and *p*-phenylenediamine (0.54 g, 0.005 mol) were mixed and heated at 160–170°C for 4 hr. The mixture was scraped at intervals with a glass rod. The dark solid was washed with boiling ethanol (50 ml) and was then refluxed in benzene (50 ml) for 1 hr and filtered. It was treated again at 60°C in the same manner and dried at 60°C. The yield was 1.45 g. This sample is designated as TBF–*p*-Ph(melt).

In another such synthesis, the reaction mixture after in-

Table 1. Properties of formic acid-soluble polySchiff bases prepared from TBF

Diamine used	DMF-solution time (hr)	Polymerization temp. (°C)	Analysis						(TGA) % wt loss at 500°C
			Calculated %			Found %			
			C	H	S	C	H	S	
p-Ph	1/2	150	65.3	3.4	10.9	62.9	3.6	10.5	70
m-Ph	1/4	150	65.3	3.4	10.9	63.3	3.7	10.4	72
Bz	1/2	150	71.3	3.8	8.6	69.0	3.9	8.3	78
Tol	1/2	150	72.4	4.5	8.1	71.3	5.0	7.7	85
Dian	1/4	150	66.4	4.2	7.4	64.8	4.6	7.0	95
DDM	1/4	150	71.8	4.2	8.3	69.0	4.9	8.0	95
DDS	2	150	60.8	3.2	14.7	58.9	3.6	13.9	85
E	1/4	100	58.5	4.1	13.0	58.0	4.7	12.4	75
HMD	1/4	80	63.6	5.9	10.6	62.7	6.2	9.9	99

itial heating for 4 hr, was heated in vacuum for 2 hr at 160–170°C. The nature of the polymeric product, designated TBF–*p*-Ph(melt), was apparently the same as the polymer sample, TBF–*p*-Ph(melt).

The other polymer samples *viz.* TBF–*o*-Ph(melt), TBF–*m*-Ph(melt), TBF–Bz(melt), TBF–Tol(melt), TBF–Dian(melt), TBF–DDM(melt) and TBF–DDS(melt) were prepared in the same manner. The use of N_2 atmosphere in the reaction made no apparent change in the colour of the product. All the polymer samples prepared in absence of solvent were insoluble in all solvents including formic acid.

In order to prepare some polymer samples fairly soluble in formic acid, the polycondensations were carried out under milder conditions.

Measurements

i.r. Spectra of these polySchiff bases were scanned in KBr on Carl-Zeiss Jena UR-10 spectrophotometer.

The TG analysis of some of the polymer samples was carried out on "Linseis thermogravimetric analyser" in air at a heating rate of 10°C min^{-1}. The thermal characteristics of these polymer samples are presented in Table 2.

For the electrical conductivity measurements, a pellet of the polymer under study was prepared by pressing a finely powdered and dried sample under a hydrostatic pressure of 20,000 lb/in^2 for 2 min. Polymer samples obtained by the melt technique are very hard and it is difficult to convert them to fine powders. For this reason, the formation of good compact pellets from such polymer samples was not possible except for TBF–*o*-Ph(melt) and TBF–Bz(melt).

A uniform thin layer of silver paste was applied on both the sides of the pellet providing electrical contacts. Average diameter and thickness of each pellet were measured. The pellet was firmly pressed between two circular metal discs functioning as electrodes. The other ends of the electrodes were passed 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}. The resistance of the pellet was measured by an "Electrometer Amplifier EA 814". The specific conductivity (σ) of the sample in the pellet was estimated by the usual relations from knowledge of the resistance of the pellet and its dimensions.

The electrical conductivity (σ) of the polymer sample was measured at temperatures between 308 to 443°K. The plots of logσ vs $1/T$ were made to examine whether variation of σ with temperature follows the exponential relation $\sigma = \sigma_0 e^{E/RT}$ or not. Selected plots are shown in Fig. 1.

RESULTS AND DISCUSSION

The polySchiff bases described here are yellow to dark-brown solids, insoluble in common organic solvents except that some of the polymer samples are

Table 2. Data from TG thermograms of polymer samples showing weight loss (±2in %) at various temperatures in air and application of $\log \sigma = \log \sigma_0 + -E/2.303\,kT$

Polymer	TG data weight loss in % at given temperature (°C)				Electrical conductivity (σ) at 308°K (ohm^{-1} cm^{-1})	Break temperature (°K)	Intrinsic electrical conductivity $(\sigma_0)^0$ (ohm^{-1} cm^{-1})	Activation energy (E) for electrical conductivity (eV)
	200	300	400	500				
TBF–*m*-Ph	6	18	36	65	4×10^{-14}	398	4×10^{-7}	0.43
TBF–*p*-Ph	—	15	29	65	3×10^{-15}	400	5×10^{-7}	0.94
TBF–Bz	—	17	29	74	7×10^{-13}	438	3×10^{-11}	0.11
TBF–Tol	—	17	30	80	7×10^{-13}	383	3×10^{-12}	0.26
TBF–Dian	—	15	37	88	7×10^{-13}	415	4×10^{-10}	0.15
TBF–DDM	—	13	38	87	5×10^{-14}	411	2×10^{-10}	0.22
TBF–DDS	—	12	29	76	6×10^{-13}	420	2×10^{-10}	0.20
TBF–E	45	15	40	65	8×10^{-14}	333	2×10^{-9}	1.27
TBF–HMD	7	36	60	95	2×10^{-13}	398	5×10^{-10}	1.22
TBF–*o*-Ph(melt)	4	13	26	69	2×10^{-11}	b	5×10^{-8}	0.29
TBF–Bz(melt)	—	9	24	65	1×10^{-11}	b	2×10^{-10}	0.10

[a] Insoluble in formic acid and prepared using DMF as solvent except the last two samples.

[b] No break is observed.

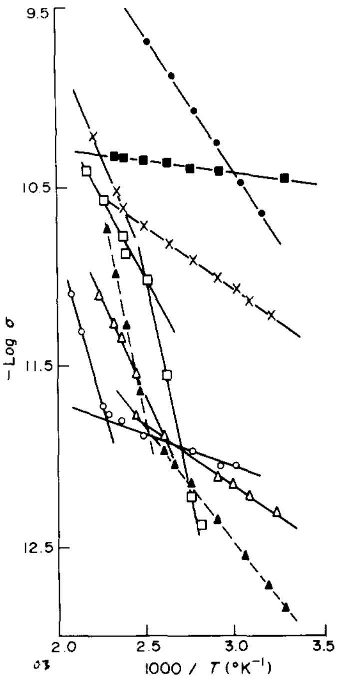
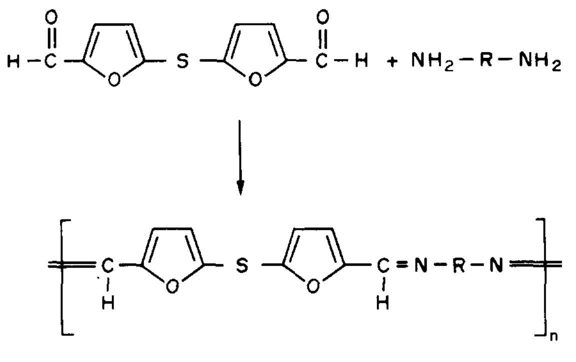


Fig. 1. −Logσ vs 1000/T. (●—●) TBF–o-Ph(melt); (■—■) TBF–Bz(melt); (×—×) TBF–Dian (DMF); (□—□) TBF–p-Ph (DMF); (▲—▲) TBF–HMD (DMF); (△—△) TBF–Tol (DMF); (○—○) TBF–Bz (DMF).



soluble in formic acid. The polySchiff base samples, including those which are soluble in formic acid and those which are prepared when polycondensation is carried out over a period of 25 to 30 min, do not melt when heated up to 360°C. The structure of the monomers suggest that the polySchiff bases described here have linear structures. The infusibility and insolubility of the polymer samples can, therefore, be considered to be intrinsic to the polymer structure.

The solution of a given polymer sample in formic acid on dilution with dry ether gave back the polymer sample. The pricipitated polymer was proved to be identical with the original by comparison of i.r. spectra. If the formic acid solution of the polymer were diluted with water, the polymer was hydrolysed.

The observed C and S contents of all the polymer samples were found to be lower than the values calculated on the basis of the structure of repeat unit of the polymer sample. Selected data are shown in Table 1.

The information furnished in the experimental part reveals that the aliphatic diamines are the most reactive and o-phenylenediamine is the least reactive of all the diamines used here in the polySchiff base preparations and that DDS is less reactive than all the diamines except o-phenylenediamine.

The i.r. spectra of Schiff bases from various types of amines and ketones or aldehydes are known to exhibit bands characteristic $-\overset{|}{C}=N-$ and a band due to the $-\overset{|}{C}=O$ forming the end-group [10, 11]. There are reports that the position of the band due to $-\overset{|}{C}=N-$ is highly variable; Katsumi and co-workers [9] reported that the position for various substances Ar—CH=N—Ar is around 1630 cm^{-1} when spectra were scanned in KBr. In the i.r. spectra of polySchiff bases from TBF and aromatic diamine described here, the band due to —C=N— is observed around 1620 cm^{-1} but this band occurs around 1640 cm^{-1} in the spectra of polySchiff bases prepared from TBF and the aliphatic diamines. In the spectra of the polySchiff bases prepared under mild reaction conditions, a weak carbonyl band due to the end-CHO group is observed around 1680 cm^{-1}. The i.r. spectrum of TBF also contains such a band at the same position.

The percentage loss in weight suffered by polySchiff base samples soluble in formic acid when heated up to 500°C is shown in Table 1. The TGA data for insoluble polymer samples are furnished in Table 2. These data for insoluble polymer samples are furnished in Table 2. These data show that a polySchiff base sample soluble in formic acid is less stable than the insoluble polySchiff base sample prepared from the same two monomers. Examination of the TGA data in Table 2 further reveals that, among the polymer samples prepared from TBF and various aromatic diamines in DMF solution, those prepared using p-phenylenediamine are more stable than those prepared using other aromatic diamines. Such polymers prepared from benzidine, 3,3′-diamethylbenzidine, 3,3′-dimethoxybenzidine, 4,4′-diaminodiphenylmethane and 4,4′-diaminodiphenylsulphone do not differ greatly in their stability. The polySchiff base prepared from m-phenylenediamine is the least stable of all the seven polymer samples prepared in DMF solution. The product from ethylenediamine is more stable than that prepared from hexamethylenediamine. The data in Table 2 reveal that the polySchiff bases prepared under melt conditions are more stable than the corresponding polymers prepared in DMF solution.

The electrical conductivities of the polySchiff bases described here range from 10^{-11} to 10^{-15} ohm^{-1} cm^{-1} at 25°C. The conductivities of the samples TBF–o-Ph(melt) and TBFF–Bz(melt) are higher than those of the polymers prepared from the corresponding monomers in solution.

The plots of logσ vs 1/T for polymer samples TBF–o-Ph(melt) and TBF–Bz(melt) are linear and the parameters σ_0 and E were evaluated. Such plots for polySchiff bases prepared in DMF solution comprise two linear sections with different slopes; the points of intersection are shown in Table 2 as break temperatures. These plots reveal that the initial change in the value of σ with temperature is less rapid than the change at higher temperatures. On the basis of the linear plots between room and break temperatures, the values of the parameters σ_0 and E are estimated. (see Table 2).

The value of electrical conducitivity of polySchiff bases prepared employing aromatic diamines and aliphatic diamines fall within the same range although those of the former type are expected to have higher values of σ due to continuous conjugation along the polymer chain. However a characteristic difference is noted between the values of the activation energy (E) for the change of electrical conductivity with temperature for polySchiff bases fo the two series. The values of these parameters for the products from aliphatic diamines are much larger than those for the products from the aromatic diamines. This difference may be attributed to the presence of the bridge —$(CH_2)_n$— with n equal to either 2 or 6, functioning as insulators between the conjugated systems present in the polymer chain. On the basis of these results, it is concluded that the polySchiff bases described here can be ranked as high resistance semiconductors. A comparison of the properties of these polySchiff bases prepared from TBF can be made with those of the polySchiff bases prepared from dicarbonyl derivatives of benzene, diphenyl, diphenyl ether and diphenyl thioether [12].

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