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NOTE

SYNTHESIS AND PROPERTIES OF POLY(SCHIFF BASES) FROM FURIL

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INTRODUCTION

Thermally stable poly(Schiff bases) synthesized from dicarbonyls and aromatic diamines have been reported by several investigators [1-4], and they are known for their semiconducting properties [5-9]. A diketone is used as starting dicarbonyl in only a few reports [10, 11]. Consequently, poly(Schiff bases) were synthesized from furil (2,2'-bis(furyl)- α,β -dione) and various diamines. They were characterized by IR, thermal studies, and electrical conductivity as a function of temperature.

EXPERIMENTAL

Materials

Furfural (SDS grade) was purified by distillation (bp 161°C) and adding 0.05% hydroquinone. Benzidine, 4,4'-diaminodiphenylmethane, *o*-tolidine, *o*-dianisidine, *m*- and *p*-phenylenediamine, and 1,6-diaminohexane were of laboratory grade and were purified by the usual methods. Diphenyl ether (DPE) was AR grade.

Monomer Synthesis

Furoin (mp 135°C) was prepared from furfural and furil (mp 162°C) was prepared from furoin by published methods [12].

Solution Polycondensation of Furil

A mixture of furil (1.90 g, 0.01 mol) and benzidine (1.84 g, 0.01 mol) in diphenyl ether (DPE) was heated for 3 h at 250°C. The solid mass was filtered and washed with ether to remove solvent. It was Soxhlet extracted with ethanol to remove unreacted monomers and dried at 60°C for 24 h. The yield of polymer was 65%. It did not melt up to 360°C and is labeled furil-BEN(DPE).

Polycondensations of furil with 4,4'-diaminodiphenylmethane (DDM), *o*-tolidine (*o*-TOL), *o*-dianisidine (*o*-DIA), *m*-phenylenediamine (*m*-PDA), *p*-phenylenediamine (*p*-PDA), and 1,6-hexamethylenediamine (HMD) were carried out similarly in DPE solution, affording the corresponding poly-(Schiff bases), furil-DDM(DPE), furil-*o*-TOL(DPE), furil-*o*-DIA(DPE), furil-*m*-PDA(DPE), furil-*p*-PDA(DPE), and furil-HMD (DPE), respectively.

Melt Polycondensation of Furil

Furil (1.90 g, 0.01 mol) and benzidine (1.84 g, 0.01 mol) were mixed and heated at 150°C for 0.5 h and then the temperature was raised to and maintained at 190°C for 3 h in an oil bath. The dark solid was scraped with a glass rod and washed with boiling ethanol. It was Soxhlet extracted with ethanol to remove unreacted monomers and dried at 60°C for 24 h. The polymer was dark brown, brittle, and is labeled furil-BEN(melt).

Furil-DDM(melt), furil-*o*-TOL(melt), furil-*o*-DTA(melt), furil-*m*-PDA(melt), and furil-*p*-PDA(melt) were prepared in a similar manner. All the poly-(Schiff bases) prepared by the melt technique were insoluble in all common organic solvents and did not melt up to 360°C.

Measurements

IR spectra of poly(Schiff bases) in KBr were obtained with a Perkin-Elmer 983 IR spectrophotometer.

TG analysis was carried out in a Du Pont-951 thermogravimetric analyzer in the presence of air and also under helium (see Tables 1 and 2).

Pellets of the polymer samples were prepared for the electrical conductivity measurements. Since samples obtained by the melt technique were very hard and difficult to convert to fine powders, the formation of usable compact pellets was not possible except for furil-*m*-PDA(melt). A uniform thin layer of silver paste was applied to both sides of the pellet to provide electrical contact. The average diameter and thickness of each pellet were

TABLE 1. Properties of Poly(Schiff bases) Prepared from Furil and Diamines by the Melt Technique

Polymer	Reaction time, h	Polymerization temperature, °C	IR band, ^a cm ⁻¹	Analysis, %						TGA weight loss at 500°C	
				Calculated			Found			In air, %	In helium, %
				C	H	N	C	H	N		
Furil-BEN(melt)	3	190	1605	78.10	4.14	8.28	78.7	3.8	8.1	69	25.5
Furil-DDM(melt)	3	190	1605	78.41	4.54	7.95	78.1	4.4	7.8	50	12.0
Furil- <i>o</i> -TOL(melt)	3	190	1605	78.68	4.92	7.65	78.3	4.5	7.3	96	19.0
Furil- <i>o</i> -DIA(melt)	3	190	1605	72.36	4.52	7.04	71.8	4.3	6.9	66	22.0
Furil- <i>m</i> -PDA(melt)	3	190	1605	73.28	3.82	10.69	73.0	3.7	10.5	77	16.0
Furil- <i>p</i> -PDA(melt)	3	190	1605	73.28	3.82	10.69	72.5	3.3	10.2	73	21.5

^aFor -C=N - stretching vibration.

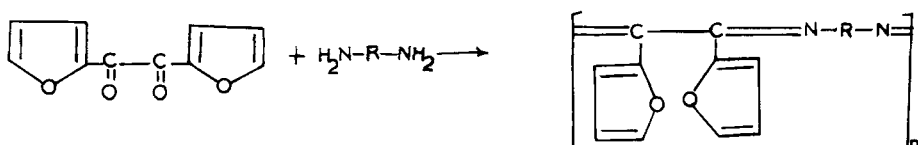
TABLE 2. Electrical and Thermal Properties of Polymer Samples

Polymer	Reaction time, h	Polymerization temperature, °C	TGA weight loss at 500°C		Specific conductance (σ) at 308 K, $\text{ohm}^{-1} \text{cm}^{-1}$	Break temperature, K	Intrinsic electrical conductance (σ_0), $\text{ohm}^{-1} \text{cm}^{-1}$	Activation energy (E_D) for electrical conductivity, b eV
			In air, %	In helium, %				
Furil-BEN(DPE)	3	250	82	16	1.7×10^{-12}	366	5.6×10^{-10}	0.16
Furil-DDM(DPE)	3	250	88.5	19	1.6×10^{-15}	363	9.3×10^{-11}	0.29
Furil- <i>o</i> -TOL(DPE)	3	250	78.5	25	8.9×10^{-14}	379	5.0×10^{-7}	0.40
Furil- <i>o</i> -DIA(DPE)	3	250	89	22	9.9×10^{-14}	361	4.1×10^{-7}	0.36
Furil- <i>m</i> -PDA(DPE)	3	250	84	19	5.6×10^{-14}	372	1.9×10^{-8}	0.22
Furil- <i>p</i> -PDA(DPE)	3	250	79	21.5	5.4×10^{-12}	380	2.9×10^{-11}	0.16
Furil-HMD(DPE)	3	250	91	38	6.6×10^{-16}	—	—	—
Furil- <i>m</i> -PDA(melt)	3	190	77	16	6.2×10^{-12}	—	2.8×10^{-4}	0.27

measured. The pellet was firmly pressed between the two electrodes. The other ends of the electrodes were passed through a Teflon block. The entire assembly was heated in a furnace at $1^{\circ}\text{C}/\text{min}$. The resistance of the pellet between 308 to 453 K was measured with a Hewlett Packard 4329 A high-resistance meter. The specific conductance (σ) was estimated from the resistance of the pellet and its dimensions.

RESULTS AND DISCUSSION

It is suggested that the poly(Schiff bases) described here have the following structures.



Their elemental analyses are shown in Table 1.

The IR spectra of Schiff bases exhibit bands characteristic for $-\overset{\text{H}}{\text{C}}=\text{N}$ and a band due to the $-\overset{\text{H}}{\text{C}}=\text{O}$ end group [13]. The position of the former due to $-\overset{\text{H}}{\text{C}}=\text{N}-$ is reported to be highly variable. Tabei and Squitou [14] reported that this band for various $\text{Ar}-\overset{\text{H}}{\text{C}}=\text{N}-\text{Ar}'$ compounds lies around 1630 cm^{-1} compared to 1605 cm^{-1} for our polymers. The bands observed around 1275 , 1130 , and 1010 cm^{-1} are characteristic for the furan ring.

The TGA data in Tables 1 and 2 show that the poly(Schiff bases) prepared by the melt technique are more stable than those prepared in a solvent. The polymers were found to be more thermally stable under helium than in air.

The electrical conductivities of the poly(Schiff bases) range from 10^{-12} to $10^{-16}\text{ ohm}^{-1}\text{ cm}^{-1}$ at 308 K. Plots of $\log \sigma$ vs $1/T$ for polymers prepared in DPE (Fig. 1) comprise two linear parts, and the points of intersection are shown in Table 2. The parameters σ_0 and E_a are estimated from the linear plots between room temperature and the break temperature (Table 2). Based on their electrical conductivity behavior, our poly(Schiff bases) can be ranked as semiconductors [15].

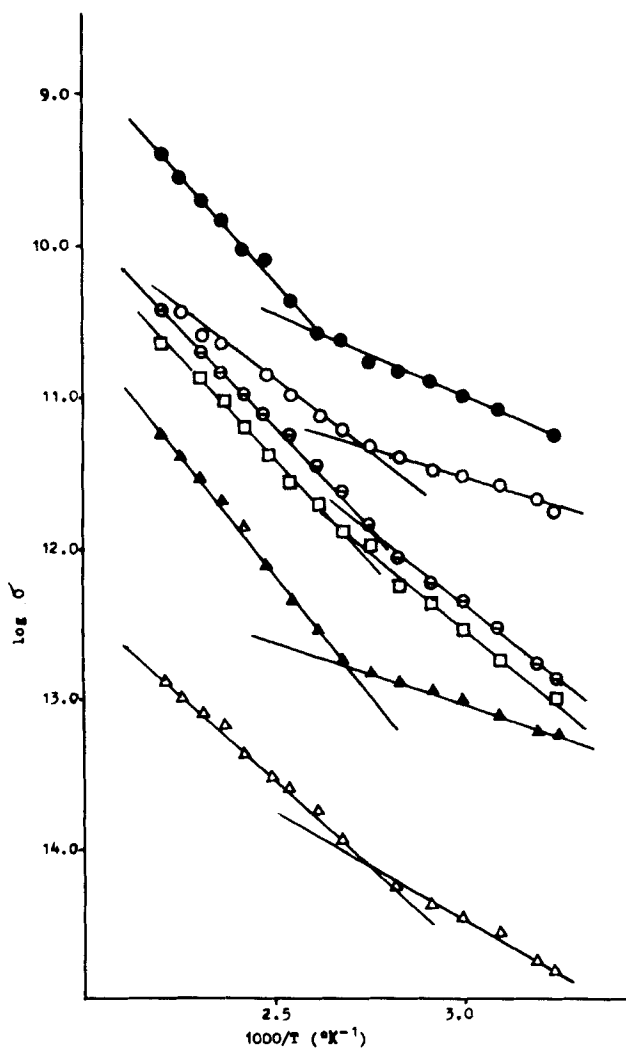


FIG. 1. Arrhenius plots for electrical conductance of (●) furil-*p*-PDA(DPE), (○) furil-BEN(DPE), (◻) furil-*o*-DIA(DPE), (◻) furil-*o*-TOL(DPE), (▲) furil-*m*-PDA(DPE), and (△) furil-DDM(DPE).

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