

# Arylidene Polymers. XVIII. Synthesis and Thermal Behavior of Organometallic Arylidene Polyesters Containing Ferrocene Derivatives in the Main Chain

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## SYNOPSIS

A new interesting category of organometallic polyesters based on diarylidene cycloalkanones containing ferrocene derivatives in the polymer main chain has been prepared by interfacial polycondensation of 1,1'-dichlorocarbonyl ferrocene or 1,1'-dichlorocarbonyl-4,4'-diiodoferrocene with 2,5-bis(*p*-hydroxybenzylidene)cyclopentanone, 2,5-divanillylidene cyclopentanone, 2,6-bis(*p*-hydroxybenzylidene)cyclohexanone, 2,6-divanillylidene cyclohexanone, and 2,7-bis(*p*-hydroxybenzylidene)cycloheptanone. The resulting polyesters were characterized by elemental analyses, infrared spectroscopy, solubility, and viscometry measurements. The thermal behavior of the synthesized polymers was evaluated by thermal gravimetric analysis and correlated with their structures. The crystallinity of all polymers were examined by x-ray diffraction analysis. Moreover, the electrical conductivity of a selected example of polymer was investigated above the temperature range (300–500 K) and showed that it followed an Arrhenius-type equation with activation energy 2.09 eV.

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## INTRODUCTION

Literature survey revealed that few polyesters containing ferrocene in the main chain have been synthesized by polyacetylation of diols with 1,1'-dichlorocarbonyl ferrocene in the presence of pyridine and sodium hydroxide via direct esterification or by transesterification.<sup>1-3</sup> Pittman<sup>4</sup> prepared series of polyesters containing ferrocene from the interaction of 1,1'-dichlorocarbonyl ferrocene and different diols using solution polymerization technique at high temperature.

The work reported here outlines the synthesis and characterization of new unsaturated polyesters containing ferrocene or ferrocene derivatives in the polymer backbone. A major aim of this work has been to investigate the effect of the ferrocene moiety

in the polymer backbone, on the polymer properties. Moreover, crystallinity, solubility, thermal stability, and electrical conductivity of the synthesized polyesters were also examined and discussed.

## EXPERIMENTAL

### Measurements

The elemental analyses were done on a Perkin-Elmer 240C instrument. The infrared (IR) spectra were recorded on a Pye Unicam SP3/100 Spectrophotometer using the KBr pellet technique. The inherent viscosities of polymer solution (0.5 W/V) in dimethyl sulfoxide (DMSO) were determined at 30°C using an Ubbelohde Suspended Level Viscometer. The solubility of the polymers was determined using 0.02 g of polymer in 3–5 mL of solvent at room temperature. X-Ray diffractography was performed using an X-ray PW 1710 diffractometer with Ni-filtered CuK $\alpha$  radiation. Thermogravimetric analyses (TGA) were carried out in air using Du Pont, Model 951, 910, and Du Pont 1090 thermal analyzers

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at a heating rate of 7°C/min. Electrical conductivity was measured over the temperature range of 300–500 K and using the method previously described.<sup>5</sup>

### Synthesis of Ferrocene Derivatives

#### Synthesis of 1,1'-Ferrocene Dicarboxylic Acid IV<sup>6-11</sup>

A 9.72 g (0.06 mole) of trichloroacetic acid (TCA) was dissolved in 100 mL dry benzene. To this solution was added dropwise 7.08 g (0.06 mole) of thionyl chloride. The reaction mixture was refluxed for 1 h on a water bath, then benzene was distilled off to afford 9.5 g (87.9%) of crude trichloroacetyl chloride. The crude trichloroacetyl chloride was added dropwise to a suspension of 5.58 (0.03 mole) ferrocene, and 9.24 g (0.07 mole) of AlCl<sub>3</sub> in 100 mL CS<sub>2</sub>. The reaction mixture was stirred at room temperature for 6 h, decomposed with cold 10% HCl solution, and then extracted with chloroform. The extracts were washed with 10% sodium carbonate solution, water, and then dried over anhydrous magnesium sulfate. The solvents were removed under reduced pressure to afford 10 g (70%) of 1,1'-ditrichloroacetyl ferrocene II. The crude of (II) was hydrolyzed by refluxing with 50% aqueous potassium hydroxide for 6 h. Finally, the reaction mixture was cooled to room temperature, then acidified with 10% cold hydrochloric acid solution to yield 3.46 g (60%) of 1,1'-ferrocene dicarboxylic acid IV *m.p.* > 300°C.

ANAL: Calcd: for C<sub>12</sub>H<sub>10</sub>O<sub>4</sub>Fe: C, 52.59%; H, 3.65%. Found: C, 52.28%; H, 3.49%.

#### Synthesis of 1,1'-Dichlorocarbonyl Ferrocene V

A 3 g (0.01 mole) 1,1'-ferrocene dicarboxylic acid IV was dissolved in 50 mL dry benzene. To this solution, there was added dropwise 2 g (0.16 mole) thionyl chloride. The reaction was refluxed for 2 h in water bath. Excess thionyl chloride and benzene was removed under reduced pressure to afford 2 g (58% yield) of 1,1'-dichlorocarbonyl ferrocene V (recrystallized from benzene) *m.p.* > 300°C.

ANAL: Calcd: for C<sub>12</sub>H<sub>8</sub>O<sub>2</sub>Cl<sub>2</sub>Fe: C, 46.33%; H, 2.57%; Cl, 22.84%. Found: C, 46.13%; H, 2.49%; Cl, 22.76%.

#### Synthesis of 4,4'-Diiodo-1,1'-Ferrocene Dicarboxylic Acid VIII

A 0.01 mole of diacetyl ferrocene VII was dissolved in 10% aqueous sodium hydroxide solution. To this mixture, there was added 0.06 mole of iodine/potassium iodide solution. The reaction mixture was heated on a water bath for 6 h, then cooled to room temperature, and acidified with 10% solution of HCl,

whereby 4,4'-diiodo-1,1'-ferrocene dicarboxylic acid VIII was precipitated as a deep brown precipitate *m.p.* > 320°C (decompos.).

ANAL: Calcd: for C<sub>12</sub>H<sub>8</sub>O<sub>4</sub>I<sub>2</sub>Fe: C, 27.39%; H, 1.52%; I, 48.31%.

Found C, 17.18%; H, 1.39%; I, 47.83%.

#### Synthesis of 1,1'-Dichlorocarbonyl-4,4'-Diiodo-Ferrocene IX

This diacid chloride was prepared from VIII and thionyl chloride in dry benzene after heating for 4 h and recrystallized from petroleum ether 60–80 *m.p.* 290 ± 2°C (70%).

ANAL: Calcd: for C<sub>12</sub>H<sub>6</sub>O<sub>2</sub>I<sub>2</sub>Cl<sub>2</sub>Fe: C, 25.59%; H, 1.06%; I, 45.13%; Cl, 12.62%.

Found: C, 25.36%; H, 0.98%; I, 44.93%; Cl, 12.37%.

### Monomer Synthesis Xa–e

All the monomers were synthesized as described in our previous work.<sup>12-14</sup>

### Synthesis of Polyesters (XIa,b and XIIa–e):

In a three-necked flask (500 cm<sup>3</sup> vol.), equipped with a mechanical stirrer (2000 rpm/min) dry nitrogen inlet and outlet, and dropper, a mixture (3 mmol) of the appropriate diarylidene-cycloalkanones (Xa–e), 50 mL dry methylene chloride, and a suitable quantity of sodium hydroxide (6 mmol soluble in 50 mL water) was introduced. After mixing (3 mmol) of the appropriate dichlorocarbonyl ferrocene (V or IX) in 50 mL dry methylene chloride was added over 2 min at room temperature and the mixture was vigorously stirred.

After addition of the diacid chloride (V or IX), stirring was continued for 2 h until a solid polymer was separated out. This solid was filtered off, washed with water and dilute acetic acid, and dried under reduced pressure (1 mmHg) at 80°C for 2 days. Table I summarizes yield, elemental analyses, and some physical properties of the synthesized polymers.

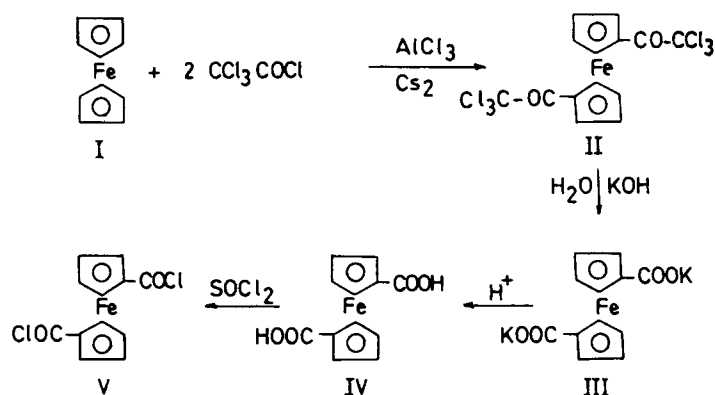
## RESULTS AND DISCUSSION

The synthesis of these polymers necessitates the preparation of two diacid chlorides (i.e., 1,1'-dichlorocarbonyl ferrocene V and 1,1'-dichlorocarbonyl-4,4'-diiodo ferrocene IX). The diacid chloride V was prepared as shown in Scheme 1, where it can be seen that the reaction of trichloroacetyl chloride with ferrocene I in the presence of AlCl<sub>3</sub> and CS<sub>2</sub> (Friedl Craft Reaction) gave the corresponding 1,1'-ditrichloroacetyl ferrocene II.

**Table I** Results of Elemental Analysis and Some Physical Properties of Polymers XIa, b and XIIa-e

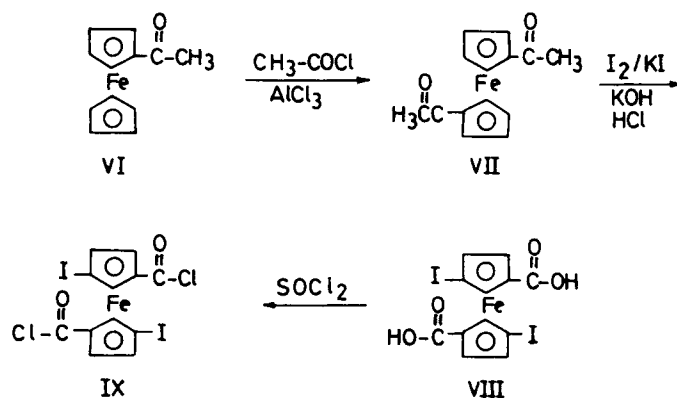
Polymer Numbers	C%		H%		$\eta^a$ Inh (d I/g)	Yield (%)	Color
	Calcd.	Found	Calcd.	Found			
XIa	70.19	69.73	4.15	4.01	0.39	69	Greenish
XIb	70.59	69.85	4.41	4.23	—	73	Greenish
XIIa	47.45	47.03	2.81	2.63	—	68	Yellowish
XIIb	46.92	46.74	3.81	3.69	—	79	Greenish
XIIc	48.12	47.98	3.01	2.79	—	63	Reddish
XIId	48.95	48.51	3.26	3.18	0.54	84	Reddish
XIIe	48.76	48.19	3.20	3.09	0.61	85	Reddish-yellow

<sup>a</sup> Inherent viscosity measured in DMSO at 30°C.



The hydrolysis of II in basic medium gave the potassium salt of 1,1'-ferrocene dicarboxylic acid III, which by acidification gave the diacid IV. This diacid IV was converted to the 1,1'-dichloroacetyl ferrocene V with thionyl chloride in dry benzene.

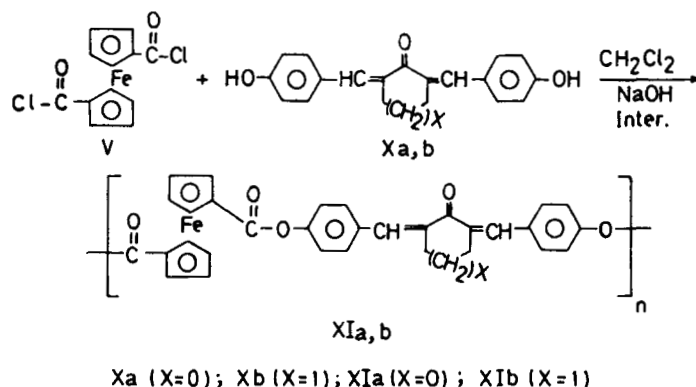
The second ferrocene diacid chloride derivative IX (Scheme 2) prepared via steps shows clearly that diacetyl ferrocene VII reacted with iodine to afford the diiodoferrocene derivative VIII.



The iodination of ferrocene in this case could be explained by the similarity of ferrocene to reactive arenes such as phenols,<sup>15</sup> which undergo iodination with iodine itself. Before using the Haloform reaction, we first tried oxidation of diacetyl ferrocene VII using potassium permanganate as oxidizing agent; however separation of the potassium salt of 1,1'-ferrocene dicarboxylic acid from the formed  $\text{MnO}_2$  was not feasible. At this point, the initial route

was used for the synthesis of a pure sample from 1,1'-ferrocene dicarboxylic acid as depicted in Scheme 1. The structure of these compounds were confirmed by elemental and spectral analyses.

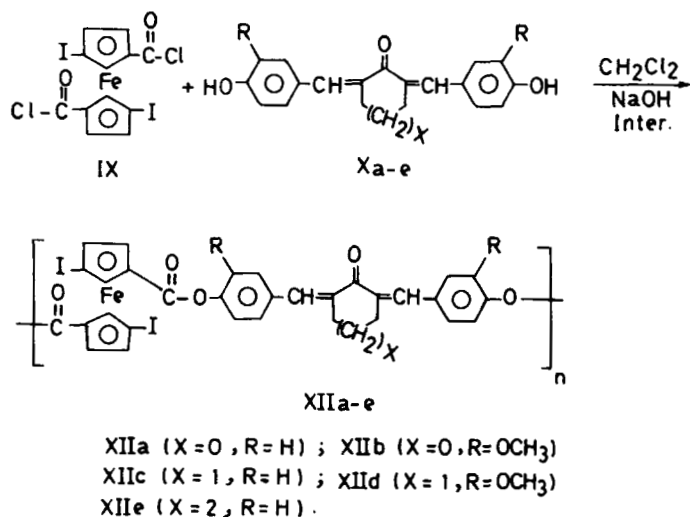
Reaction of equimolar quantities of 1,1'-dichlorocarbonyl ferrocene V with two monomers of diarylidencycloalkanones Xa,b using interfacial polycondensation at ambient afforded new polyesters XIa,b as shown in Scheme 3.



Scheme 3

A similar technique was applied for the reaction of 1,1'-dichlorocarbonyl-4,4'-diiodo-ferrocene IX

with five monomers of diarylidencycloalkanones Xa-e to form new series of polyesters XIIa-e as represented in Scheme 4.



Scheme 4

The resulting polymers were characterized by elemental analysis, IR spectra, solubility, viscometry, TGA measurements, x-ray analysis, and electrical conductivity.

The microanalysis of all polymers reflected the characteristic repeating unit of each polymer. The data are listed in Table I. The IR spectra of all poly-

**Table II** Solubility Characteristics of Polymers XIa, b and XIIa-e

Polymer Numbers	DMSO	DMF	NMP	THF	<i>o</i> -Cresol	CHCl <sub>3</sub> + Acetone (1 : 1)	TFA	Conc. H <sub>2</sub> SO <sub>4</sub>	HCOOH
XIa	+	+	+	±	±	-	+	+	±
XIb	±	+	+	±	-	±	+	+	-
XIIa	±	±	±	-	-	-	±	+	-
XIIb	±	±	-	-	-	±	±	+	±
XIIc	±	±	±	-	-	-	±	+	-
XIId	+	+	±	-	±	-	±	+	±
XIIE	+	+	+	±	±	±	+	+	±

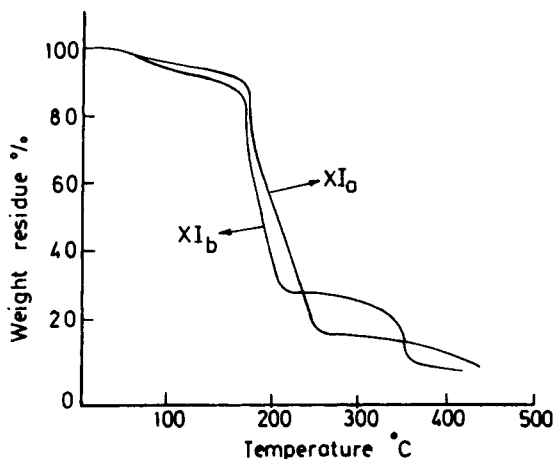
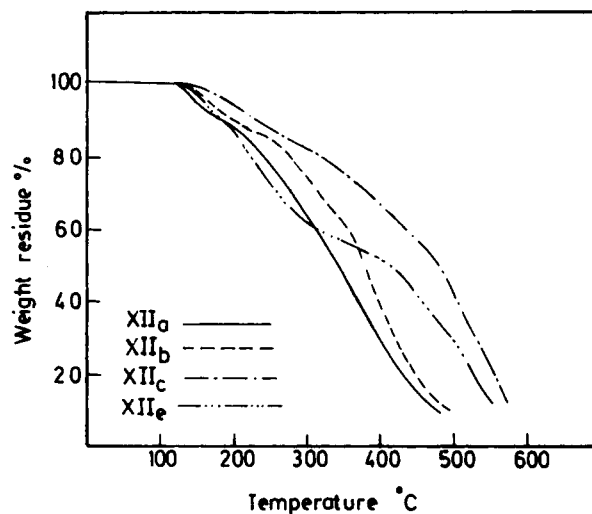
(+) Soluble at room temperature (RT); (±) partially soluble at RT; (-) insoluble.

mers showed the appearance of new absorption bands at 1710–1715 cm<sup>-1</sup> characteristic of the carbonyl groups of esters, at 1665–1685 cm<sup>-1</sup> (C=O of cycloalkanones); at 1590–1605 cm<sup>-1</sup> for —C=C— stretching, in addition to other characteristic absorption bands due to specific groups present in the various polymers.

The solubility characteristics of the polymers XIa,b and XIIa-e were tested in various solvents including DMSO, dimethylformide (DMF), *N*-methyl pyrrolidone (NMP), tetrahydrofuran (THF), *o*-cresol, CHCl<sub>3</sub>-acetone mixture, trifluoroacetic acid (TFA), concentrated H<sub>2</sub>SO<sub>4</sub>, and formic acid. It can be seen from Table II that in strong protic acids such as sulfuric acid or TFA, the majority of the polymers were soluble at 30°C. It should be also noted that the presence of iodine in the polymer chain decreases the solubility of the polymers (XIIa-e). More particularly, polymers XIIa-e, which con-

tain cyclohexanone or cycloheptanone moieties, are more soluble in most organic solvents than those which contain a cyclopentanone moiety. This can be explained by the presence of flexible conformers in the six- or seven-membered rings that enhance the solubility of the polymer molecules.<sup>16</sup>

The thermal behavior of these polyesters XIa,b and XIIa-e was evaluated by TGA in air at a heating rate 7°C min<sup>-1</sup>. The thermographs of these polymers are given in Figures 1 and 2. Table III gives the temperature for various percentages of weight loss. In Figure 1 the TGA curves show a small weight loss in the range of 2–4% starting at 80°C until 150°C, which may be attributed to loss of adsorbed moisture and entrapped solvents, respectively. The thermographs indicate also that polymers XIa and XIb decompose in two stages and the rate of degradation in the first stage is faster than in the second

**Figure 1** Thermogravimetric curves of polymers XIa,b.**Figure 2** Thermogravimetric curves of polymers XIIa-e.

**Table III Thermal Properties of Polymers XIa, b and XIIa-e**

% Decomposition	Temperature °C for Polymer Numbers					
	XIa	XIb	XIIa	XIIb	XIIc	XIIe
10	185	160	189	174	222	172
20	193	190	237	286	325	226
30	198	192	274	327	383	304
40	210	200	306	347	426	345
50	225	207	331	370	451	411
60	238	218	363	389	470	453
70	255	230	390	415	492	496
80	360	360	430	442	503	515
90	420	375	490	468	521	545

stage. The TGA thermographs in Figure 2 show similar patterns of decomposition without well-defined stages for the thermolysis of polymers XIIa, XIIb, and XIIc, whereas, the XIIe thermograph shows a pronounced two-stage decomposition. The expected nature of decomposition of these polymers is a pyrolytic oxidation of  $-\text{C}=\text{C}-$ , evolution of  $\text{I}_2$ , scission of many bonds, in addition to the formation of metal oxide and char as an end product.

More particularly, the temperature at which 10% weight loss occurs is considered to be the polymer decomposition temperature. Therefore, Table III indicates that the thermal stabilities of the polymers are in order of XIIa > XIa and XIIb > XIb. Hence, the incorporation of iodine in the ferrocene moiety enhances the thermal stability of the synthesized organometallic polyesters. Thermogravimetric and kinetic analyses of nonisothermal decomposition of these organometallic arylidene polyester are in progress and will be published elsewhere.<sup>17</sup>

X-Ray diffractography of polymers XIIa-e in Figure 3 shows a few sharp peaks with an amorphous background, indicating that there is a large class of structures in the polymer main chains in the ordered state. This observation is consistent with that observed in our previous work<sup>12</sup> for polyesters of diarylenecyclalkanones based on aromatic para azo linkage. The x-ray pattern of polymer XIIId shows an amorphous halo in the region of  $2\theta = 5-45^\circ$ . This indicates that the polymer possesses a low degree of crystallinity.

It should be noted that a pronounced low degree of crystallinity was also observed for polyesters containing thianthrene units<sup>14</sup> and aromatic meta azo linkages in their main chains.

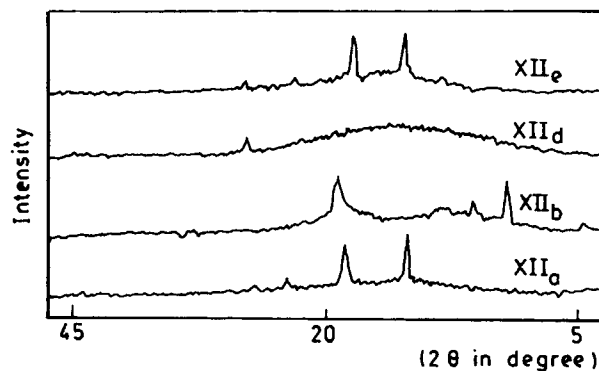
The electrical conductivity of a selected polymer XIIId was measured according to the Arrhenius relation at room temperature, 300 K. The results in-

dicate that the virgin sample of organometallic polyester XIIId possesses an electrical conductivity value of  $2.9 \times 10^{-10} \Omega^{-1} \text{cm}^{-1}$ . This reflects the onset of semiconductor behavior.

Studies of temperature dependence of the electrical conductivity of polymer XIIId over the range 300-500K show that conductivity behavior follows a one-term Arrhenius-type equation (straight line) and that conductivity increases with increasing temperature and has a value of  $2.3 \times 10^{-4}$  at 460K with an activation energy 2.09 eV (Fig. 4).

The selected sample possesses an electron donating  $\text{OCH}_3$  groups in the 2-oxo-1,3-cyclohexanediyldene moiety and the iron in the ferrocene exists in  $\text{Fe}^{2+}$  status, in addition to the low value of activation energy calculated for this sample.

Therefore, the mechanism of conductivity has the nature of  $n$ -conduction, with electrons participating as charge carriers for conduction as  $n$ -type semiconductors. Moreover the presence of iodine as a substituent donator in the ferrocene moiety in the mer of the polymer, increases the charge carrier density over the macrostructure of the polymer.<sup>18</sup>

**Figure 3** X-ray diffraction patterns of polymers XIIa-e.

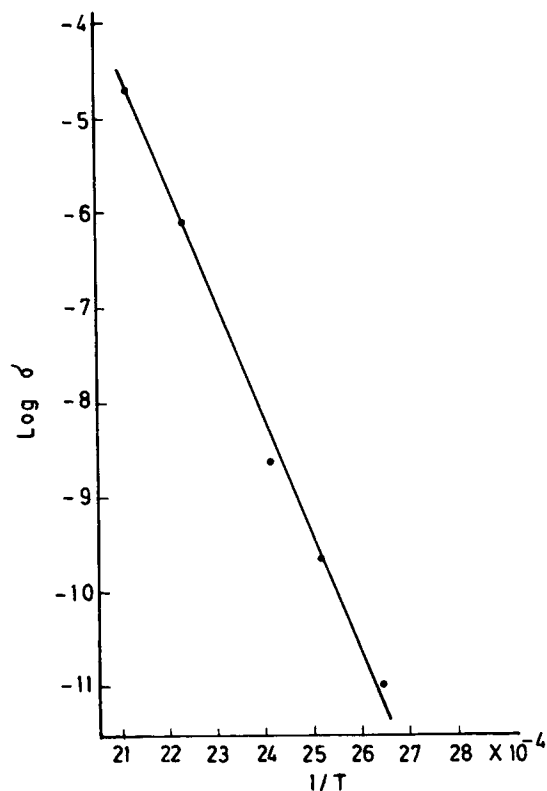


Figure 4 Temperature dependence of electrical conductivity of polymer XIId.

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