Thermal and electrical properties of polyimides containing tricyclic fused rings

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Polyimides containing a series of tricyclic fused rings were synthesized by polymerization of the tricyclic diamines with aromatic tetracarboxylic acid dianhydrides. The thermal stability of a series of the polymers increased in the order of the thianthrene (SDP) containing polymers < the phenoxatiin (OSP) containing polymers < the dibenzo-*p*-dioxin (ODP) containing polymers. The polymers derived from 2,8-oriented tricyclic diamines showed somewhat lower glass transition temperature than those from 2,7-oriented diamines. The specific resistivity of the polymers decreased in the order of the SDP containing polymers > ODP containing polymers > OSP containing polymers. The kink temperatures in the temperature dependence curves of specific resistivity were in good agreement with the glass transition temperatures. The photoconductive properties of the polymers were measured using a surface type cell method.

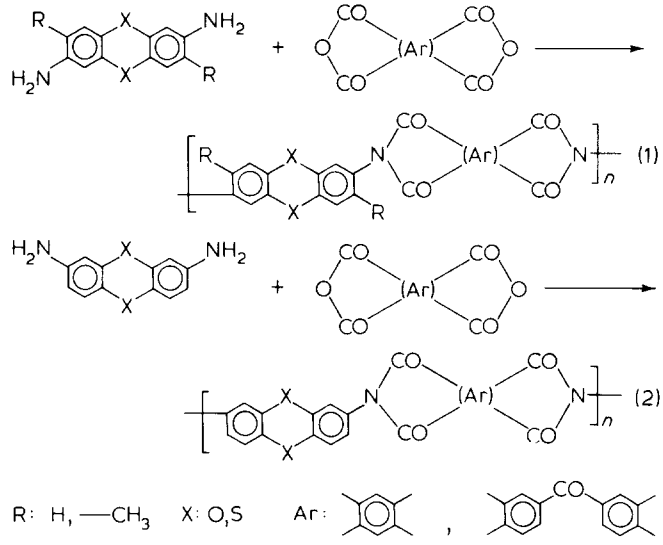
INTRODUCTION

Semiconducting polymers with heterocyclic rings in the main chain have been investigated for polybenzimidazole[1], polyquinoxalline[2], polypyrrole[3], and polyrhodanine[4]. In general, the more fused and hetero rings there are in the monomer, the better the electrical conductivity of the resulting polymer. Relatively little work has been done on photoconductive behaviour in relation to polymer structure.

The properties of polymers are dependent not only on the primary structures (repeating units) but also on the higher order structures[5]. Tricyclic fused rings, such as dibenzo-*p*-dioxins (ODP), phenoxatiin (OSP), and thianthrene (SDP) are thermostable and powerful electron donors. Thes units have folded structures about the axis that combine the hetero atoms, and the dihedral angles increase in the following order: ODP < OSP < SDP[7]. They form stable charge transfer complexes[6] with acceptors such as iodine, tetracyanoethylene (TCNE), and dianhydrides. Polyimides were prepared containing the series of fused rings and the effect of these units on the conductivities of the resulting polymers was studied.

In this work, several series of polyimides containing these units were prepared by polymerization of the tricyclic diamines with dianhydrides (equations 1 and 2), and the resulting polymer properties, such as conductivities, thermal stability, and solubility were investigated. Photoconduction of these polymers was measured by the so called 'surface type' method[13].

In our previous study[8], polyimides that contained dibenzo-*p*-dioxins and 2,7-oriented thianthrene units have been prepared. They showed good thermomechanical properties.



RESULTS AND DISCUSSION

Diamines

Diaminodibenzo-*p*-dioxins (ODA) and 2,7-diaminothianthrene (SDA) were prepared by the method in the previous report[8].

2,8-diaminophenoxatiin (OSA) was prepared by a Beckmann rearrangement of 2,8-diacetylphenoxatiin dio-

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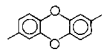
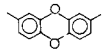
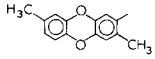
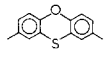
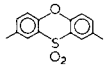
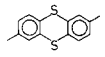
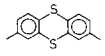
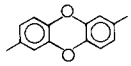
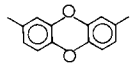
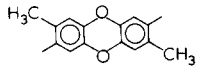
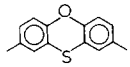
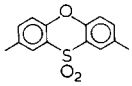
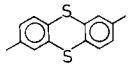
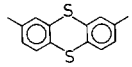
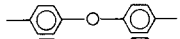
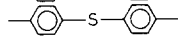
Table 1 Diamines

Number	$H_2N-R-NH_2$	mp (°C)
Ia		247–248[a]
IIa		178–179[b]
IIIa		269–270[c]
IVa		170–172[d]
Va		247–249[e]
VIa		187–189[f]
VIIa		182–183

[a] Lit.[13] mp 249°C
[b] Lit.[13] mp 178°C
[c] Lit.[21] mp 271–273°C
[d] Lit.[9] mp 271–273°C
[e] Lit.[9] mp 244–247°C
[f] Lit.[8] mp 187–189°C

Table 2 Preparation of polyamic acids

Polymer	Dian-hydride	$H_2N-R-NH_2$	Reaction time (h)	Yield (%)	η_{inh}[a]
Ib	P		5	98	1.12
Ic	B		3	97	0.91
IIb	P		5	95	0.78
IIc	B		3	96	0.85
IIIb	P		6	95	0.89
IIIc	B		5	93	0.81
IVb	P		5	98	1.33
IVc	B		3	91	0.80
Vb	P		7	93	0.55
Vc	B		7	91	0.47
VIb	P		4	97	0.85
VIc	B		3	96	0.87
VIIb	P		5	97	1.21
VIIc	B		5	94	0.92
Rob	P		2	97	0.91
Rsb	P		3	93	0.93

[a] Measured at a concentration of 0.5 g/100 ml in NMP at 25°C.
P, PMDA; B, BTDA

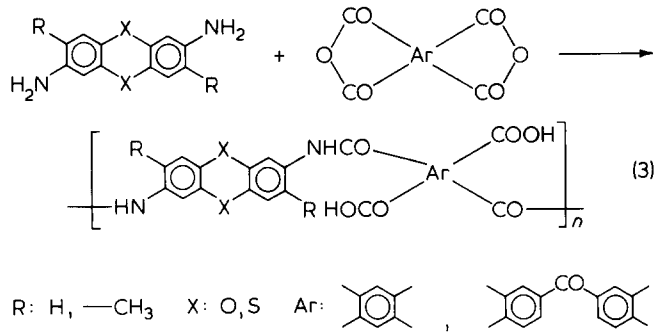
xime in polyphosphoric acid, followed by the hydrolysis of the diacetoamino compound.

2,8-Diaminophenoxatiin 10,10'-dioxide was prepared by the nitration and simultaneous oxidation of phenoxatiin by the method Nobis *et al.*[9] The reduction of the dinitro compounds was carried out catalytically.

2,8-Diaminothianthrene (SDA) was prepared by the method of Kawai *et al.*[10] The condensation of 2-chloro-5-nitrobenzenesulfonic acid with sodium salt of 4-nitrobenzenethiol produced 2-(4-nitrophenylthio)-5-nitrobenzenesulfonic acid, which was cyclocondensated in fuming sulfuric acid. The results for a series of the tricyclic diamines are listed in *Table 1*.

Preparation of polyimides

Aromatic polyimides were prepared by reacting dianhydrides with a series of the diamines described above. The two step polymerization is shown in equation (3), involving the ring opening polyaddition and subsequent cyclodehydration reaction.



(3)

R: H, —CH_3 X: O, S Ar:

The ring opening polyaddition proceeded readily in NMP at room temperature, forming the open chain polyamic acids; the results are summarized in *Table 2*. *Figure 1* shows the rates of the polymerization of a series of the tricyclic diamines in terms of inherent viscosity of the polymers. The polymerization with OSDA tended to give polymers with lower inherent viscosity than those using other tricyclic diamines. This may be attributed to the lower basicity of the amino groups of OSDA, which possesses electron-withdrawing group in the molecule. These polyamic acids were subject to thermal cyclodehydration to form the corresponding polyimides. The imidization of the various polyamic acids was performed by heating at 230–250°C under a stream of nitrogen.

The formation of the polyimides was confirmed by means of infrared spectroscopy and elemental analyses. *Table 3* listed the elemental analyses, which were found to be in good agreement with the calculated values. In the infrared spectra, the characteristic absorption bands of the imide were found at near 1780, 1730, and 1370 cm^{-1}, suggesting that the cyclodehydration reaction had proceeded completely.

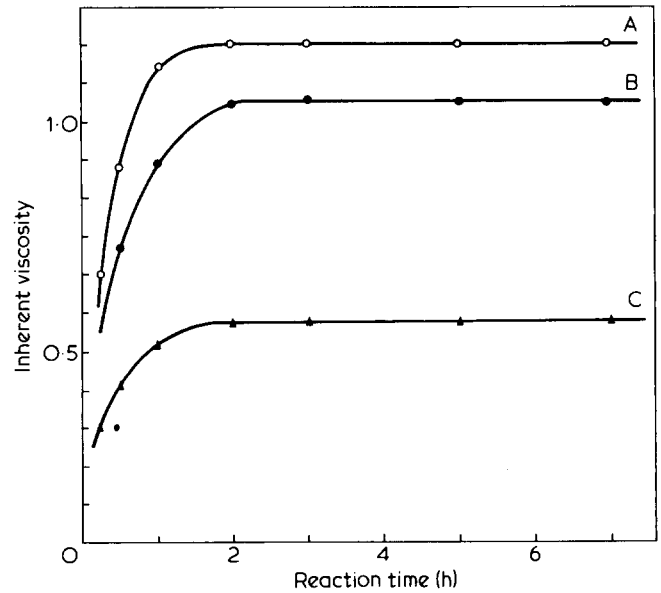


Figure 1 Polymerization of PMDA with the diamines in NMP: (A) Polymerization with IVa; (B) polymerization with (IIa); (C) polymerization with Va

Table 3 Elemental analysis of polyimides

Polymer	Calculated (%)				Found (%)			
	C	H	N	S	C	H	N	S
IVd	64.07	1.96	6.79	7.78	63.71	2.01	6.63	7.59
IVe	67.44	2.34	5.42	6.21	67.18	2.36	5.31	6.11
Vd	59.46	1.81	6.30	7.22	59.41	1.83	6.19	7.08
Ve	63.50	2.21	5.11	5.85	63.57	2.23	5.02	5.91
VIId	61.67	1.88	6.54	14.97	60.95	1.92	6.47	14.19
VIIe	65.41	2.26	5.26	12.03	65.30	2.28	5.08	11.89

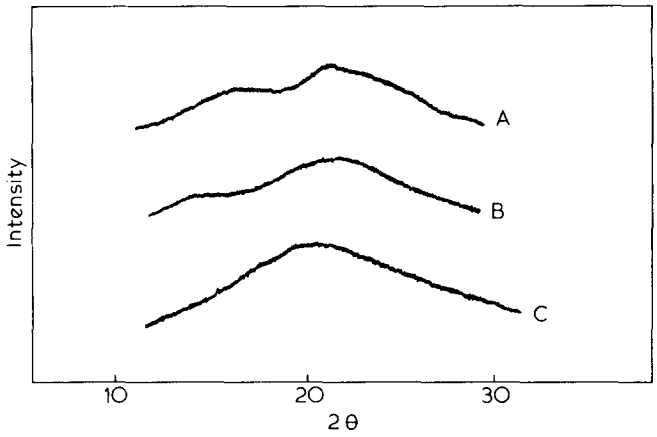


Figure 2 X-ray diffraction diagrams of the tricyclic polyimides: (A) IId; (B) IVd; (C) VIId

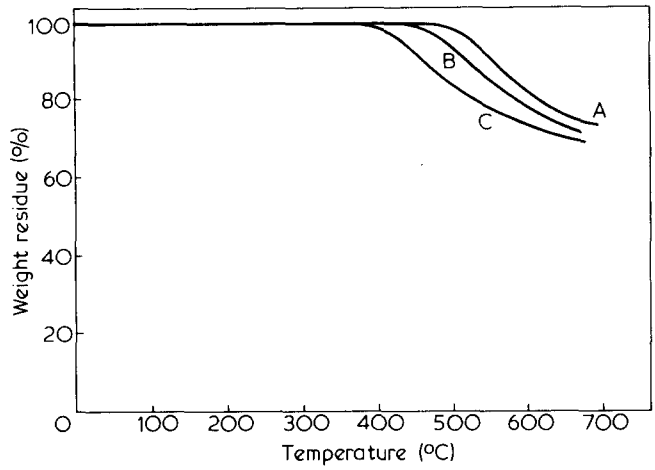


Figure 3 TGA curves for the polyimides: (A) IId; (B) IVd; (C) VIId

Typical X-ray diffraction diagrams of the polyimides are shown in *Figure 2*, showing that these polyimides were all amorphous.

Thermal properties of the polyimides

Thermal properties of the polyimides were evaluated by means of thermogravimetric analysis (t.g.a.)-differential scanning calorimetry (d.s.c.). Typical t.g.a. curves for the polyimides under nitrogen are shown in *Figure 3*. The thermal behaviour data are summarized in *Table 4*.

In a series of these polyimides, the decomposition temperatures (DT) by t.g.a. under nitrogen, as well as in air, decreased in the following order; ODP containing polymers > OSP containing polymers > SDP containing polymers. Also, the decomposition temperatures were somewhat lower than those of the corresponding open chain polymers.

In our previous study[8], polyimides containing thianthrene unit had lower thermal stability than the equivalent polymers derived from diaminodiphenyl sulfide, and the results were discussed in terms of the packing of the polymer molecules.

In view of these results, the decreasing thermal stability of a series of the tricyclic polyimides in the above order appears to be attributable not only to the lower bond energy of C–S bond than that of C–O, but also to the increasing deformation of the tricyclic units from planarity. As listed in *Table 4*, the density of polyimides decreased in the reverse order of the thermal stability.

The glass transition temperature (T_g) of a series of polyimides derived from BTDA was estimated by TMA[11] and the results were summarized in *Table 5*. The polymers derived from PMDA showed no appreciable thermo-

Table 4 Decomposition temperature and density

Polymer	DT[a] (°C)	Density[b]
Id	553	1.41
IId	552	1.40
IIId	515	1.38
IVd	515	1.37
Vd	520	1.37
VId	468	1.35
VIId	465	1.34
Rod	574	1.42
Rsd	521	1.41

[a] A 10% weight loss temperature observed by t.g.a. at a heating of 5°C min^{-1} under nitrogen
[b] Determined with a small pycnometer in absolute ethanol at 30°C

Table 5 Glass transition temperature and solubility

Polymer	T_g (°C)[a]	Solubility[d]	
		DMAc	H_2SO_4
Ie	315 (309)[c]	–	–
IIe	295 (291)[c]	–	–
IIIe	305 (303)[c]	–	+–
IVe	280 (275)[c]	–	+–
Ve	[b] (285)[c]	–	+–
VIe	[b] (263)[c]	+–	+
VIIe	[b] (251)[c]	+–	+

[a] Determined by thermomechanical analysis
[b] T_g could not be determined clearly by TMA
[c] Determined by the temperature dependence curves of specific resistivity
[d] Solubility: +, Soluble by heating; +–, partially soluble; –, insoluble

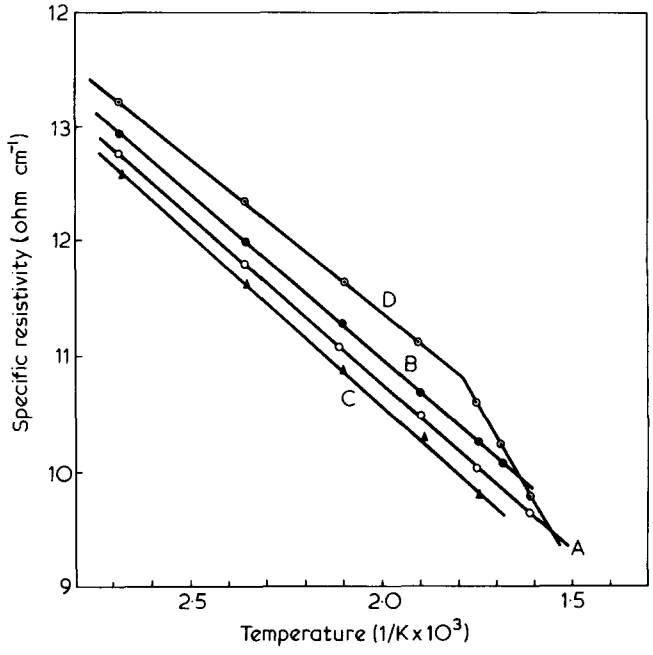


Figure 4 Retationships between specific resistivities and $1/T$ for the polyimides: (A) IId; (B) IVd; (C) VIId; (D) IIe

mechanical transition below the temperatures at which the decompositions initiated. The polyimides derived from 2,8-oriented tricyclic diamines exhibited lower T_g than those from 2,7-oriented diamines. The orientation effect would support the prediction of Lee[12] that the introduction of *meta* as opposed to *para* linkage in the polymers leads to a reduction of T_g.

Solubility of the polyimides

The solubility of a series of the polyimides are summarized in *Table 5*. ODP polymers were insoluble even in sulfuric acid, however, OSP and SDP polyimides exhibited better solubility.

Electrical conductivity

The resistivity of these polyimides was measured by the method of the previous report[14]. For most of the polymers, the current was directly proportional to the applied voltage, according to the equation: $I = KV^{\alpha}$ (I, current; V, applied charged voltage; α, slope). The value of α was in the range 0.7–1.4.

The temperature–resistivity behaviour of typical polymers are shown in *Figure 4*. Activation energy was calculated from the linear relationship between log ρ and $1/T$ by the equation (4):

$$\rho = \rho_0 e^{Ea/kT} \qquad (4)$$

where ρ is specific resistivity, Ea is activation energy for conduction, k is Boltzmann constant, T is the absolute temperature.

A kink was observed in the temperature–resistivity curves for the polyimides derived from BTDA, and the specific resistivities followed the equation (4) before and after the kink temperature. The temperatures were in near agreement with the glass transition temperatures, determined by t.m.a. as listed in *Table 5*. Previously, the kink temperatures in the $\rho - 1/T$ curves for several polymers[15,16] has been correlated to the glass transition temperatures. The drastic decrease of the resistivity of BTDA polymers above the glass transition temperatures suggests that the segmental motions of the polymer chain affect the conductivity.

As these polymers are infusible and insoluble in organic solvents, it was not possible to carry out extensive purification procedures. It has been suggested that impurity effects play a relatively unimportant part in semiconduction in organic polymers[18].

The specific resistivity and values of activation energy of a series of polyimides derived from PMDA are shown in *Table 6*. The resistivity increased in the following order: OSP containing polymers > ODP containing polymers > SDP containing polymers. The relatively higher specific resistivity of SDP polymers may be attributable to the highly folded structure of the SDP unit.

Photoconduction

Polyvinylcarbazole shows quite a large photoresponse[19], however, relatively little work has been carried out on the photoconductive behaviour in relation to polymer structure[20]. The main interest during the last few years has centred on photoconductive properties of amorphous thermal stable polymers containing the heterocyclic groups. Therfore the effects of the tricyclic units of the photoconductivity of the polyimides in visible region were examined.

The voltage dependence of the surface photo-current and dark-current of the polymers was measured with a surface-type photocell. *Figures 5* and *6* show the electric field (V) dependence of dark-current (*Id*) and photo-current (*Ip*). Ohmic relation for the photo-current and dark-current against the applied potential were obtained for all samples. The results for the surface-type cell are summarized in *Table 7*. The photo-current of a series of polyimides decreased in the following order: OSP containing polymers > ODP containing polymers > SDP containing polymers. The ratio of the photo-current to dark-current for a series of the polymers ranged from 2 to 5.

EXPERIMENTAL

Monomers

2,8-Diacetoamidophenoxatiin (IV). To 60 g of PPA was added 3.1 g of 2,8-diacetylphenoxatiin dioxime. The mixture was stirred slowly at 105°C for 5 h to give a blue solution, which was poured into water to yield pale yellow precipitate. Recrystallization from dilute ethanol gave 3.0 g of IV, as pale yellow needles; mp 251–253°C (ref 9 mp 253–254°C).

Table 6 Semiconducting properties of polyimides

Polymers	Specific resistivity (ohm cm^{-1})	Activation energy (eV)
Id	2.3×10^{14}	0.65
IId	2.9×10^{14}	0.56
IIId	2.1×10^{14}	0.59
IVd	1.9×10^{14}	0.60
Vd	9.3×10^{15}	0.69
VId	3.7×10^{14}	0.53
VIId	3.9×10^{14}	0.55

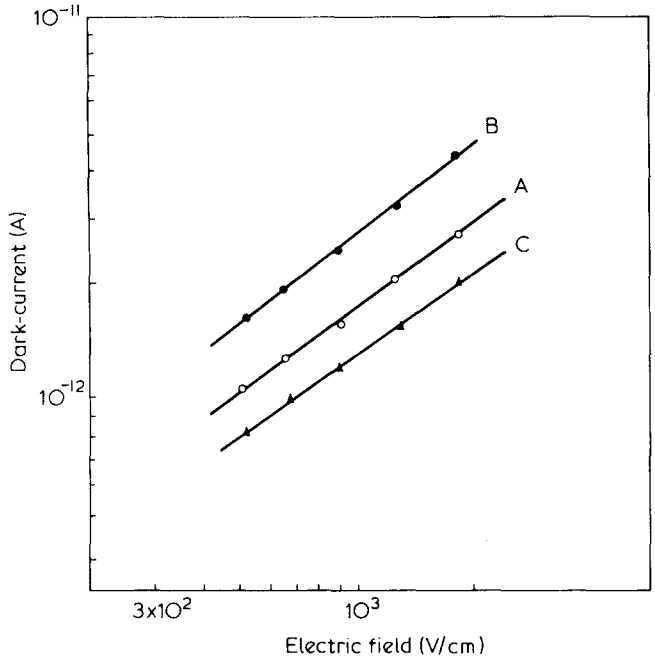


Figure 5 Surface dark current vs. applied field: (A) IId; (B) IVd; (C) VIId

2-(4-Nitrophenylthio)-5-nitrobenzenesulfonic acid (VII). To a mixture of 24.1 g (0.1 mol) of 2-chloro-5-nitrobenzenesulfonic acid in 60 ml of water, was added 10% aqueous sodium hydroxide with stirring. To the resulting solution was added 21 g (0.12 mol) of sodium salt of 4-nitrobenzenethiol and 60 ml of water. The mixture was heated under reflux with stirring and the insoluble materials then filtered off. The filtrate was cooled to 0°C, and the precipitated solid was dissolved into water and the solution acidified by adding 10% sulfuric acid to give a yellow precipitate. Recrystallization from dilute acetic acid gave 17.3 g (51%) of VII as yellow crystals, mp 130–131°C.

Analysis: Calculated for $C_{12}H_8O_6N_2S_2$: C, 42.35%; H, 2.35%; N, 8.24%; S, 18.82%. Found: C, 42.15%; H, 2.38%; N, 8.36%; S, 18.70%.

Polyamic acids

PMDA was sublimed under reduced pressure and then recrystallized from acetic anhydride. BTDA was recrystallized from acetic anhydride. NMP was purified by vacuum distillation and stored over 4 Å molecular sieves. A typical example of the polymerization was as follows.

Polyamic Acid (VIIb). In a flask 0.738 g (3 mmol) of 2,8-diaminothianthrene was dissolved in 10 ml of NMP, and to this was added 0.654 g (3 mmol) of solid pyromellitic dianhydride with stirring at room temperature under a stream of nitrogen. A viscous solution formed after 5 h of the polymerization. The solution was poured into 500 ml of chloroform to give 1.35 g (97%) of fibrous polyamic acid. The inherent viscosity was 1.21 dl g^{-1}, determined at a concentration of 0.5 g/100 ml in NMP at 25°C.

Polyimide (VIId). The polyamic acid solution (VIIb) was cast into film on a glass plate with a spreading knife, and the plate was heated at 70°C for 3 h in a forced-air oven. The film, which was removed from the plate, was heated at 200–230°C for 5 h under a stream of nitrogen. The infrared specrum showed absorptions at 1780 and 1730 cm^{-1} ($\nu C=0$).

Analysis: Calculated for $C_{22}H_8N_2O_4S_2$: C, 61.67%; H, 1.88%; N, 6.54%; S, 14.97%. Found: C, 61.39%; H, 1.95%; N, 6.41%; S, 14.35%.

X-ray diffraction

The X-ray diffraction diagrams were taken with Rigakudenki Geigerflex instrument, using Ni-filtered CuKα radiation.

Thermal analysis

Thermogravimetric and differential scanning calorimetric analyses of polyimides were carried out in a stream of nitrogen or air at 50 ml min^{-1} by using a Rigakudenki thermal analyser (TG–DSC standard model, 8085). T.m.a. results were obtained with a Rigakudenki thermomechanical analyser.

Measurement of the electrical resistivity

The electrical resistivity of polyimides was determined from the powdered samples compressed between stainless-steel electrodes by a pressure of 50 kg cm^{-1} *in vacuo*. The details of this procedure are reported in the previous report[14].

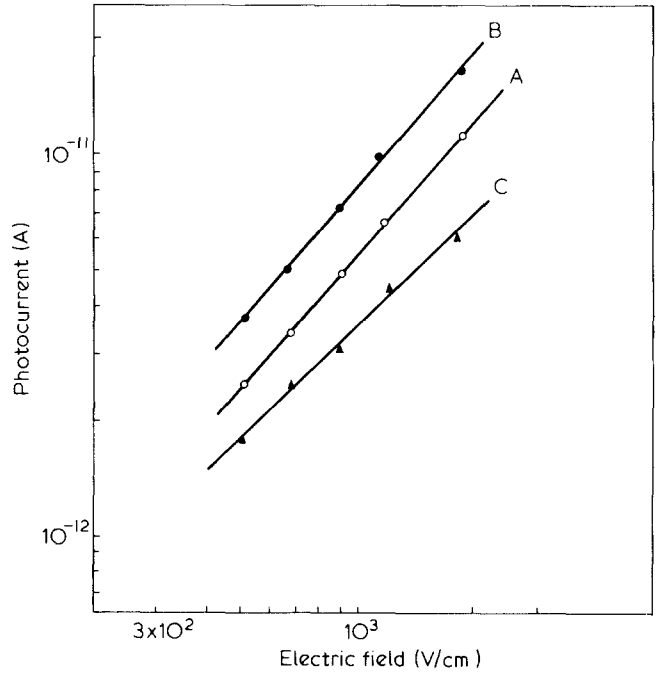


Figure 6 Surface photocurrent vs. applied electric field for the polyimides illuminated at 10^{-1} mmHg by incandescent tungsten lamp: (A) IId; (B) IVd; (C) VIId

Table 7 The ratios of photo-current to dark-current

Polymer	*Ip* (A)	*Id* (A)	*Ip/Id*
Id	5.7×10^{-12}	1.3×10^{-12}	4.4
IId	4.2×10^{-12}	1.5×10^{-12}	2.8
IIId	6.0×10^{-12}	1.7×10^{-12}	3.5
IVd	6.4×10^{-12}	2.2×10^{-12}	2.9
Vd	1.2×10^{-12}	5.7×10^{-13}	2.1
VId	3.3×10^{-12}	1.3×10^{-12}	2.5
VId	2.9×10^{-12}	1.1×10^{-12}	2.6

Measurement of the photoconductivity

The photocurrent was measured by the so-called 'surface cell' method[13]. The sample tablet was made by the compression of about 0.1 g of a finely powdered specimen at about 200 kg cm^{-2}. The size of the tablet was 13 mm in diameter, 1.31 cm^2 surface area and 0.5 mm thick. Silver electrodes were vacuum evaporated in the form of a comb with a 1 mm gap and length of 36 mm on the surface of the pellets. The cell thus obtained was then placed in a closed glass chamber, evacuated to ca. 10^{-5} mm Hg, in order to remove water and other volatile impurities.

A 750 W lamp was passed through the quartz window of the cell for measuring the photocurrent. The glass chamber was completely shielded with aluminium foil to exclude all noise. Potentials were applied by dry batteries. The temperature of the sample was not increased on radiation, and in all experiments a heat absorbing filter was used. This fact was confirmed by setting a thermocouple in place of the sample. Experiments show that some time after the commencement of illumination a constant photoconductivity was established. The steady-state photocurrent, I_p, is defined as the difference between the current observed with and without illumination. The current through the samples was measured with a Hewlett–Packard micrometer. The micrometer was connected by a well-insulated lead to one electrode attached to the crystal, and the other electrode was connected to dry batteries.

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