polymer papers

Highly conductive crystalline poly(2-methoxy-*p*-phenylene vinylene)

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The synthesis and the structural, thermal and charge transport properties of poly(2-methoxy-*p*-phenylene vinylene) (MeOPPV) are reported. An inverse emulsion polymerization procedure for the preparation of the precursor polymer is described; this method provided improved yields with higher molecular weights. Also discussed are disorder and defects in the rigid conjugated crystalline polymer revealed by infra-red spectra and X-ray diffraction. It was observed that the charge transport properties of the polymer were affected by structural disorders. Films of MeOPPV became highly conductive when oxidatively doped, and they exhibited excellent air stability. The electron-donating substitution is shown to lower the ionization potential of the parent polymer, thereby improving the stability of the doped form. Differential scanning calorimetry and variable-temperature ultra-violet/visible spectra indicated that the polymer undergoes unusual backbone motions.

(Keywords: conducting polymers; poly(2-methoxy-*p*-phenylene vinylene); synthesis; characterization; emulsion polymerization; crystalline polymers; films)

INTRODUCTION

Poly(arylene vinylenes) have emerged as one of the most promising classes of electroactive conjugated polymers[1–4]. Poly(*p*-phenylene vinylene) (PPV), which possesses a chemical structure intermediate between those of polyacetylene and polyphenylene, may serve as a model for this class of new polymers. Highly oriented PPV is highly crystalline[2,3], mechanically strong[5] and environmentally stable. A number of approaches have been developed for the preparation of this polymer[6–8], although earlier attempts produced only intractable powders. By employing the water-soluble precursor method[3,9–11], highly oriented, densely packed, free-standing polymer films of high molecular weight can be obtained routinely. This procedure provides polymerization yields of about 20–25%. The precursor polyelectrolyte solution has an intrinsic viscosity of 2.5 dl g^{-1} in water:methanol (80:20 v/v) containing 0.05 M Na_2SO_4 (ref. 12).

Highly oriented PPV shows high electrical conductivity upon AsF_5 vapour-phase doping[5,10,11]. The crystal structures of neutral pristine and doped forms have been studied by wide-angle X-ray diffraction[13]. The molecular orientation in uniaxially drawn PPV films has been characterized by i.r. dichroism[14], deuterium quadrupole-echo n.m.r.[15] and X-ray diffraction[3,4], and very high values for the Herman's orientation function have been reported. However, it has also been observed that the AsF_5-doped PPV is not stable in air. Furthermore, iodine doping of the PPV films provided only very low electrical conductivities.

Substituting electron-donating functional groups on the phenylene ring or incorporating heterocyclic aromatic molecules into the polymer backbone have been shown to decrease the ionization potentials and band gaps and to stabilize the p-type doped form of the polymers[16]. This electronic structural tailoring has resulted in high conductivities in iodine-doped films of poly(2,5-dimethoxy-*p*-phenylene vinylene) (DMeOPPV)[17,18], poly(thienylene vinylene) (PTV)[19,20] and poly(furylene vinylene) (PFV)[21] and has remarkably improved the air stability of the doped forms[16,17].

The effects of crystal defects and chain disorder on the electrical properties of PPV polymers have also been studied. Fully converted, highly drawn PPV films exhibited high degrees of crystallinity and near-perfect orientation, but distinctive paracrystalline diffraction patterns have been observed[3,22], indicating the presence of an extensive, but specific, structural disorder. In addition, the residual sulphur and halogen species in the eliminated samples may affect electron delocalization along the chain and thus also affect the charge transport properties of the polymers. Furthermore, in contrast to PPV or DMeOPPV, poly(2-methoxy-*p*-phenylene vinylene) (MeOPPV) may possess a copolymer structure due to asymmetric ring substitution. This structure would lead to a lower degree of order in the solid state of this polymer than in PPV or DMeOPPV. However, because of steric repulsion, the methoxy group on each phenyl ring can be arranged in MeOPPV only such that the C–O bond and its adjacent vinylene C–H bond are directed towards the same side of the chain.

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In this contribution, we report the preparation of the monomethoxy-substituted PPV derivative MeOPPV through a more refined synthetic procedure employing a two-phase inverse emulsion polymerization environment. The two-phase procedure provided increased polymerization yields with apparently higher molecular weights than those obtained with previously reported procedures. The structural features and thermal properties of the polymer synthesized by the modified procedure are presented. The MeOPPV films became highly conductive upon chemical doping. The effects of dopants and structural effects on the charge transport properties of the polymer are discussed. In contrast to the parent polymer, PPV, doped MeOPPV exhibited good stability upon exposure to ambient air.

EXPERIMENTAL

The preparation of the monomer salt, 2-methoxy-*p*-xylylene bis(tetrahydrothiophenium bromide), has been reported[23]. The base-induced polymerization was performed following the precursor polymer route with modification suggested by Garry and Lenz[24]. In a typical experiment, 37.6 g of the monomer salt was dissolved in 270 ml of H_2O in a 1000 ml one-necked round-bottom flask. To the flask was added 500 ml of hexane, and the mixture was then purged with argon for 15 min at 0°C. In another one-necked flask, 160 ml of 0.5 M NaOH solution was diluted with 108 ml of H_2O and then purged with argon at 0°C. The monomer solution was vigorously stirred until a finely dispersed mixture was obtained. The base solution was then transferred to the flask under an argon atmosphere. The solution was well mixed. After about 3 min, a white cloudy gel formed and the organic phase separated. The hexane was decanted after another 5 min. To the above flask was added 550 ml of H_2O and the gel redissolved with stirring. The basic solution was neutralized with 1 N HCl. The solution was dialysed as previously described[23] and provided a polyelectrolyte solution with a yield of 47%. The intrinsic viscosity of the polyelectrolyte solution was measured with a Cannon-Fenske type viscometer at 25°C in 80:20 (v/v) H_2O:CH_3OH solvent containing 0.05 M Na_2SO_4.

The thermal elimination (conversion to conjugated polymer) was carried out by placing the films under vacuum in a constant-temperature bath at desired temperatures. Film casting and orientation were accomplished as described elsewhere[25].

The chemical doping of the films was carried out by mounting strips of film with graphite electrodag onto four platinum wires in an O-ring fitted cell. The cell was then evacuated under vacuum at 10^{-4} Torr overnight. The dopants were subsequently introduced into the cell, and the conductivity increase was measured by the four-probe method.

I.r. spectra were acquired with an IBM IR/30 Fourier-transform infra-red spectrometer at a resolution of 2 cm^{-2} and signal-averaged over 100 scans. Thermogravimetric analyses were performed with a Perkin–Elmer TGA7 thermogravimetric analyser, and differential scanning calorimetry measurements were carried out using a Perkin–Elmer DSC7 differential scanning calorimeter. X-ray diffraction patterns were collected on flat photographic film using an evacuable Statton camera and Ni-filtered Cu K_α radiation ($\lambda = 0.1542$ nm). Elemental analyses were performed by the University of Massachusetts Microanalysis Laboratory.

RESULTS AND DISCUSSION

Synthesis and thermal conversion

The precursor route outlined previously[23] was followed with substantial modifications in the preparation of the polyelectrolyte. In a recent polymerization mechanism study[26], the existence of an intermediate of quinoid structure was observed during the early stages of polymerization. In order to shift the reaction equilibrium towards the polymer product side, the stabilization of the quinoid intermediate or the removal of produced tetrahydrothiophene (THT) is desirable. The introduction of hexane in the polymerization medium served this purpose effectively. The hexane:water reaction solvent created a two-phase system that, with vigorous stirring, created an inverse emulsion polymerization environment. Good contact between the two phases and effective exchange of the reaction components were ensured by maintaining a fine dispersion of aqueous and organic droplets. The yield obtained by the two-phase polymerization method was about twice as high as that obtained by the previously described procedure. Lenz and coworkers have obtained yields even higher than 90% by this procedure[24]. In addition to the improved reaction yields, the inverse emulsion polymerization method also produced a precursor polymer with higher molecular weight, as indicated by the remarkable increase in intrinsic viscosity. Intrinsic viscosity values of 0.25–4 dl g^{-1} were obtained by the previous method, but the new method consistently produced values of 7–9 dl g^{-1}.

The conversion to the conjugated, rigid backbone polymer is highly dependent upon the elimination/conversion temperature. Carbonyl group formation has been observed by infra-red spectroscopy for high-temperature elimination of PPV precursor polymer[5]. Elimination of the MeOPPV precursor polymer was carried out at temperatures ranging from 170 to 370°C under vacuum. No carbonyl groups were observed by infra-red spectroscopy for the employed temperature range, indicating minimal oxidative degradation. The chemical compositions of the converted polymer eliminated at different temperatures were determined and the results listed in *Table 1*.

The elimination of hydrogen bromide was shown to be more difficult than the removal of hydrogen chloride in PPV, where the typical residual chlorine content is only 0.2–0.6%[12,17]. THT was also completely removed, so any saturated methylene carbons that were present

Table 1 Elimination conditions and compositions of poly(2-methoxy-*p*-phenylene vinylene)[a]

Elimination		Elemental analyses (wt%)				
Temp. (°C)	Time (h)	C	H	S	Br	O
200	0.5	76.42	5.70	0.81	–	–
200	6	77.64	5.34	0.19	4.94	–
240	6	78.29	5.23	–	5.19	–
280	12	78.90	5.77	0.17	4.07	–
310	12	79.62	5.81	–	2.83	–
Calc.[b]	–	79.06	5.96	0.16	3.16	11.67

[a] Eliminations were carried out under a vacuum of approximately 5×10^{-3} Torr

[b] Calculated based on the assumption that end-groups account for the sulphur content and saturated vinyl units are in the form of $-CH_2CHBr-$

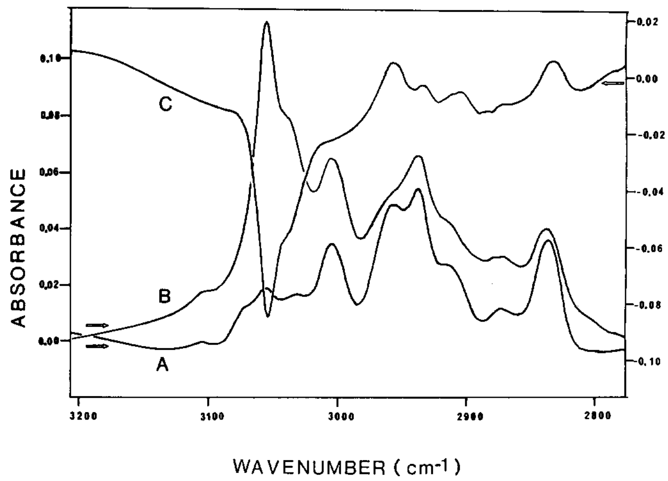

Figure 1 Infra-red spectra of stretched film ($l/l_0 = 4$) of MeOPPV showing the C–H stretching region with incident radiation polarized (A) perpendicular and (B) parallel to the film stretch direction; (C) difference spectrum

may be assumed to have been CHBr or CH_2 units. This type of methoxy-facilitated sulphonium salt elimination has been reported[17,27]. By assuming sulphur content as a result of an end effect and using the weight-average molecular weight of 40 000 as the lower limit[28], the ratio of the number of conjugated units to that of the saturated ethylene units was estimated to be about 20, with almost 300 repeat units per chain. The actual ratio and the number of repeat units per chain may be higher when the residual low-molecular-weight species trapped in the polymer film during elimination are taken into account.

The presence of saturated defects in the main chain of MeOPPV was also observed in Fourier-transform infra-red (*FT*i.r.) spectra (*Figure 1*). In the i.r. spectrum, the vibrational modes at about 2945 cm^{-1} can be ascribed to saturated aliphatic C–H stretching while the methoxy C–H stretch modes were observed at 2833 cm^{-1}. These aliphatic C–H stretch modes showed weak polarization ratios (*Figure 1*). However, the vibration absorption band of C–Br that appears at 560 cm^{-1} was very weak. Nonetheless, it is evident that the saturated content of the converted polymer is not negligible. The above results are supported by ^{13}C n.m.r. spectra[29], which show a weak sp^3 carbon peak other than the methoxy carbon, indicating that small amounts of saturated carbon exist in the main chain of the polymer.

Thermal properties

Figure 2 shows a thermogravimetric diagram of the precursor polymer (curve A). The vacuum-cast films undergo partial elimination spontaneously and form a partially converted chain structure prior to annealing, as indicated by the yellowish colour of the films. A sharp increase in the elimination rate appears at about 110°C and the weight loss diminishes at about 280°C. The total weight loss during the thermal elimination/conversion process was found to be 53% (expected weight loss 55–56%). The spontaneous elimination without heating and the trapped low-molecular-weight species together with some defective saturated vinyl units in the main chain account primarily for the 2–3% excess mass remaining after thermal elimination. There is only one continuous weight loss during elimination, which suggests that the elimination of HBr and THT is a concerted process.

MeOPPV shows excellent thermal stability, which is not unusual for such a highly conjugated aromatic system. The thermal degradation/decomposition temperatures for both the precursor and the 280°C eliminated polymers are found to be the same at about 460°C (*Figure 2*).

The polymer crystallizes upon thermal elimination as films of the precursor polymer convert to the conjugated structure. For samples with higher contents of amorphous phase, a very weak T_g-like transition was observed at 205°C. No sharp T_m can be measured, but an endothermic peak was found by d.s.c. measurement for the unoriented MeOPPV films at about 350°C, shown in *Figure 3* (curve A). This endothermic peak splits into two or three smaller peaks for the oriented samples with the onset at lower temperature (*Figure 4*). These results suggest that the transition is related to a deorientation process. The endothermic transition was observed to be significantly weakened in the second d.s.c. run after the first run up to 400°C. The ΔH changes from 29.6 J g^{-1} recorded in the first d.s.c. run to 10.4 J g^{-1} in the second run for 280°C eliminated samples of solution-precipitated

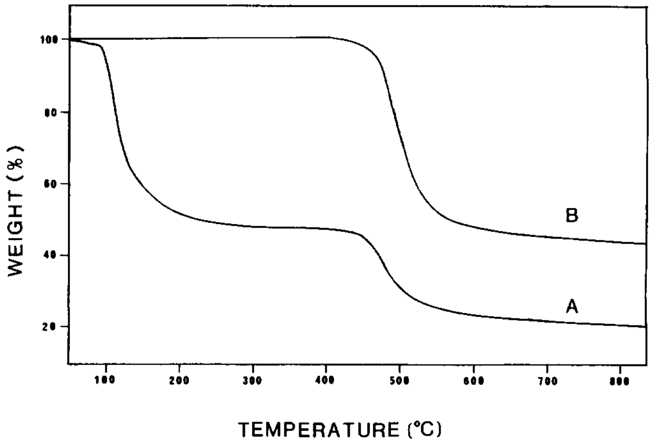

Figure 2 Thermogravimetric diagram of (A) precursor polymer and (B) 280°C eliminated films of MeOPPV. The heating rate was 20°C min^{-1} under a nitrogen atmosphere

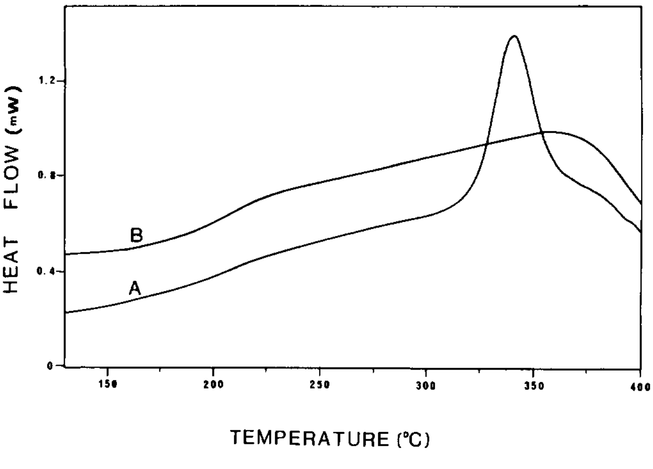

Figure 3 D.s.c. diagram of an unstretched eliminated sample of MeOPPV: (A) first d.s.c. run of the sample; (B) second run of the same sample after cooling

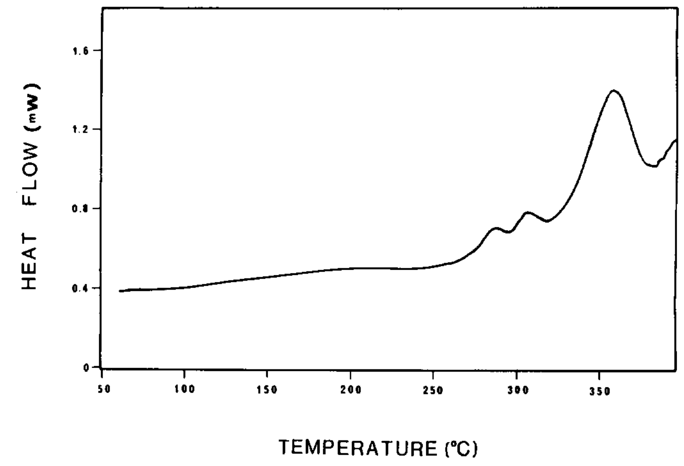

Figure 4 D.s.c. diagram of an oriented eliminated sample of MeOPPV

Table 2 Infra-red dichroic ratios at variable temperature[a]

Band[b]	Temperature (°C)				
(cm^{-1})	*RT*	270	320	370	
3000	0.63	0.61	0.62	0.55	$\nu_{(C-H)}$, ring
2935	1.06	1.28	1.35	1.45	$\nu_{(C-H)}$, saturated
1584	0.20	0.21	0.25	0.25	$\nu_{(C=C)}$, ring
1463	3.25	4.01	4.55	5.96	$\delta(Ar-O-CH_3)$
1456	3.46	3.60	3.86	6.36	$\delta(Ar-O-CH_3)$
1418	2.54	2.52	2.76	2.53	$\nu_{(C-C)}$, vinylene
1267	2.17	3.88	4.05	4.79	$\nu(Ar-O-CH_3)$
1236	7.12	7.22	6.05	4.62	$\nu(Ar-O-CH_3)$
1154	4.66	4.26	4.46	4.31	$\delta_{(C-H)}$, in-plane ring
1112	5.88	4.47	5.19	4.30	$\nu(Ar-O-CH_3)$
1038	3.47	4.21	4.26	5.09	$\nu(Ar-O-CH_3)$
964	4.95	5.37	4.93	5.39	δ(C–H), out-of-plane

[a] Dichroic ratio = $A_{\perp}/A_{\parallel}$
[b] Absorption peak position at room temperature

polyelectrolyte. Thus, the transition is largely irreversible. The vinylene configuration was checked by infra-red spectroscopy at various temperatures; no *cis*-vinylene isomers were observed. These isomers would be expected to absorb in the range of 675–725 cm^{-1}. Furthermore, the degree of molecular chain orientation was monitored by *FT*i.r. at elevated temperature and the dichroic ratios for a number of selected bands are tabulated in *Table 2*. There was no abrupt change in the polarization ratios of the infra-red intensities for the measured bands below 300°C. However, some bands showed rather sharp changes between 300 and 370°C. In a separate d.s.c. run using a largely amorphous, unoriented sample prepared by direct elimination of solution-precipitated polyelectrolyte solids, this endothermic peak was still observed. This contradicts the possibility of deorientation. This unusual structural transition in MeOPPV is under further investigation.

Conductivities

Fully converted MeOPPV belongs to the class of conjugated polymers. Based on cyclic voltammogram studies of oligo-*p*-phenylene vinylenes, Heinze *et al.*[30] have determined that eight or nine repeat units are required to reach the minimum of electron interaction energy, which can be compared to values derived from optical absorption spectra and theoretical calculation[31].

On the other hand, it has been shown that disorder and defects in the polymer chain affect the charge transport properties of the polymers significantly. Polyacetylenes with significantly higher degrees of crystalline perfection prepared by polymerization from silicone oil reached a much higher conductivity limit than those obtained by other methods[32,33].

Chemical heterogeneity along the polymer backbone (e.g. phenylene *versus* vinylene units and methoxy pendant side-groups) can result in charge carrier localization. In addition, the existence of chain disorder and the lower degree of orientation in MeOPPV as compared to PPV have led to lower conductivity values for chemically doped films of MeOPPV. Conductivities of about 10^2 S cm^{-1} have been obtained from AsF_5-doped unoriented thin films of MeOPPV, which is about one order of magnitude lower than that obtained for PPV films. *Table 3* lists the conductivities of MeOPPV films chemically doped with a variety of dopants.

Iodine doping of PPV films has caused some ambiguities in terms of understanding the conductivity increase and the occurrence of charge transfer[34]. In spite of the low conductivities reported[35], charge transfer was observed by infra-red spectroscopy of iodine-doped PPV films[34]. The reason why high conductivities are not attained is still not clear.

In the comparison of PPV and MeOPPV, the methoxy substitution on the phenylene ring has caused a significant reduction in the ionization potential of the polymer[23]. The electron-donating alkoxy substituents have been shown to have a similar effect in other aryl vinylenes[17] and in polyheteroaromatic vinylenes[16]. Monomethoxy substitution of poly(thienylene vinylene) decreases the ionization potential of the parent polymer by 0.4 eV. The corresponding reduction of MeOPPV as compared to PPV is observed to be only 0.2 eV[36]. Nevertheless, this ionization potential reduction has rendered the polymer readily dopable with mild oxidants such as iodine.

The vapour-phase chemical doping rate varies with the dopant used. The conductivity of the insulating undoped samples increases sharply after exposing the sample to AsF_5 for only a few seconds, while iodine doping proceeds very slowly.

The conductivities of the doped MeOPPV films exhibited exceptionally good air stabilities (*Figure 5*). It has been known that AsF_5 doping usually gives poor air stabilities with respect to conductivity. After several days of exposure to air, the conductivity of AsF_5-doped MeOPPV films dropped to about 1–10 S cm^{-1}, which is substantially higher than that of AsF_5-doped PPV films exposed to air for a similar time period. The iodine-doped samples showed constant conductivities upon exposure to air for over a week.

The effect of the elimination/conversion temperature on the conductivity has also been examined. Conductivities of AsF_5-doped MeOPPV films eliminated at different temperatures are listed in *Table 3*. In general, higher conductivities were reached with samples eliminated at higher temperature, indicating that more extensive delocalization was accomplished with increasing elimination temperature. For samples eliminated at the same temperature, doping with AsF_5 at 0–5°C increased the conductivity more rapidly than at −65°C. The vapour pressure of the dopant is recognized as one of the influencing factors. More controlled studies have

Table 3 Conductivities of chemically doped MeOPPV films

Dopant	Temp. (°C)	Film l/l_0	Elim. temp. (°C)	Conductivity (ohm cm^{-1})	Appearance
AsF_5[a]	−65	4	170	60	Black-greenish, lustrous
			200	45	
			250	71	
			280	110	
	0–5		170	37	
			200	49	
			250	62	
			280	74	
H_2SO_4					
(fuming)	*RT*	6	280	17, 109	Black, metallic
(conc.)[b]		8[c]	280	0.51[d], 4.7	
I_2		6	280	2.4	Dark purple, metallic lustre
		6.5[c]	300	20	
		8[c]	350	23	
$FeCl_3$		6	280	0.38	Dark brown

[a] The dopant, AsF_5, was kept in a constant cooling bath. AsF_3 solidifies at −5.95°C

[b] Doping was accomplished by immersing the polymer film in concentrated sulphuric acid for a short period. The film was then rinsed thoroughly with acetonitrile and the sample dried under vacuum before conductivity measurements

[c] Films were stretched with the heat zone apparatus; all others were machine drawn (see ref. 24)

[d] Conductivity slightly increases upon exposure to ambient air and stabilizes at that level

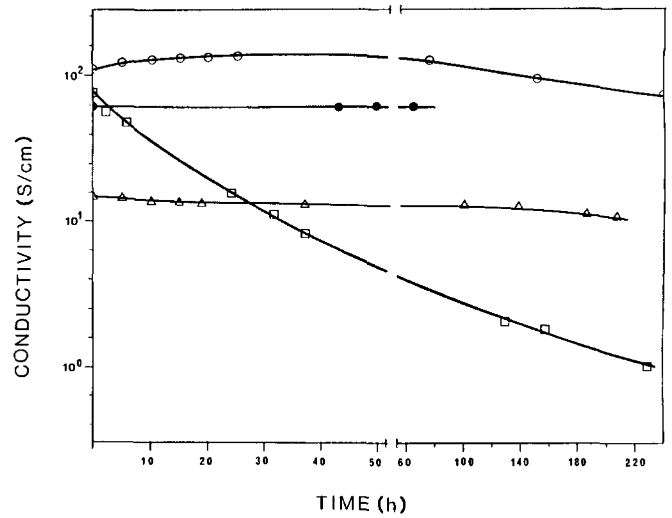

Figure 5 Conductivity curves showing the stabilities of the doped films of MeOPPV after exposure to ambient air: (●) AsF_5-doped sample under vacuum; (□) AsF_5-doped, exposed to air; (○) one AsF_5-doped sample showed exceptional air stability; (△) iodine-doped film exposed to air

revealed that it is the higher AsF_3 content in the dopant mixture at 0–5°C that was the major cause of rapid doping. Frommer *et al.*[37] have shown that the addition of AsF_3 vapour during the doping process enhances the AsF_5 doping rate in poly(phenylene sulphide) by a factor of 1000.

X-ray diffraction studies

Both the oriented and unoriented films of MeOPPV were observed by polarized optical microscopy and X-ray diffraction to be crystalline. Although small amounts of disorder and defects exist, fully converted MeOPPV films are densely packed. The density of the polymer chains ranged from 1.24 to 1.25 g cm^{-3} as measured by flotation, which is similar to that of highly crystalline PPV, the density of which was measured at 1.24 g cm^{-3}. Undoped PPV has a theoretical density of 1.29 g cm^{-3} (refs 3, 38).

Table 4 Measured crystalline *d* spacings in oriented PPV, MeOPPV and DMeOPPV (in angstroms)

hkl layer line	PPV	MeOPPV	DMeOPPV
$l = 0$	4.25	5.50	6.94
	3.99	4.02	4.41
	3.12	3.61	4.00
	2.36		
	1.83		
$l = 1$	5.55	5.78	6.02
	3.12	3.70	4.78
			3.76
			3.43
$l = 2$		3.22	3.19
			3.00
			2.73
$l = 3$	2.08		

Figure 6 is an X-ray diffraction photograph of MeOPPV taken using an oriented film. The calculated *d* spacings are listed in *Table 4* together with those obtained for PPV and DMeOPPV. Some characteristic features can be recognized from the diffraction photograph (*Figure 6*). While the diffraction pattern possesses discrete reflections on the equatorial line, there is only one streaked periodicity along the first layer line, with the second layer line hardly visible. It is evident that the MeOPPV crystal structure possesses a paracrystalline distortion of the second kind[39]. As with PPV, only one periodicity is observed along the $l = 1$ layer line. Further, the diffracted intensity along this layer line is relatively diffuse and streaky. These features can be explained by assuming a disordered crystal structure in which each molecular chain has an essentially regular periodic structure but in which the lateral ordering of neighbouring chains is very weak. The axial translational disorder of the chains leads to the loss of long-range periodicity and gives rise to continuous streaks on the first and higher layer lines of the diffraction pattern. Such paracrystalline disorder has been observed in PPV[3,22] and other polymers[40].

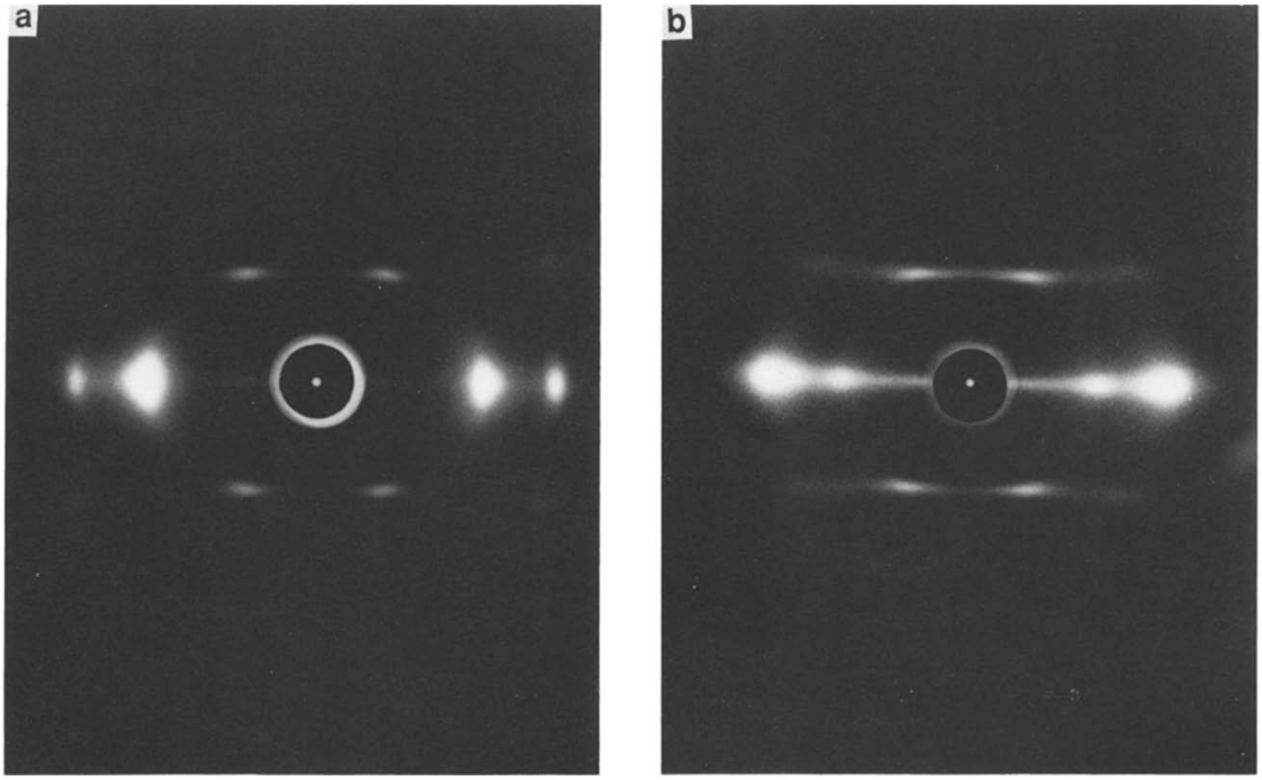

Figure 6 X-ray diffraction photographs of an oriented film of (a) PPV, $\lambda = 10$ and (b) MeOPPV, $\lambda = 6.5$

It is noted, however, that the diffraction pattern shows qualitatively discrete equatorial reflections with a low degree of azimuthal arcing, suggesting a high degree of orientation along the chain direction. This is in agreement with infra-red results[41]. A quantitative X-ray diffraction investigation of the molecular orientation in PPV obtained from diffractometer scans along the sample stretch direction revealed a value of 0.96 for Herman's orientation function, indicating a very high degree of orientation of the molecular chain along the stretch direction[3]. The value compares well to that obtained by infra-red dichroism, i.e. 0.94 to 0.97[3,5,14].

CONCLUSIONS

High-density, highly oriented MeOPPV films have been fabricated from the MeOPPV precursor polyelectrolyte, which was prepared by a two-phase inverse emulsion polymerization, with dramatically improved yield and very high molecular weight. The films were found to be crystalline, with significant amounts of disorder of the second kind, which includes chain lateral irregularities and axial translational disorder. The disorder is enhanced by the asymmetric monomethoxy substitutions on the phenylene rings and by incomplete elimination of the saturated amorphous units. Nonetheless, the polymer shows excellent thermal stability; high conductivities are obtained by chemical doping with various electron acceptors. The highly conducting doped samples exhibit exceptional stability over long durations after exposure to air, which is considered to be a consequence of the lowering of ionization by electron-donating substituents on the phenylene rings.

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