Highly conducting, iodine-doped arylene vinylene copolymers with dialkoxyphenylene units

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A series of arylene vinylene copolymers containing both unsubstituted and 2,5-dialkoxy-substituted 1,4-phenylene vinylene units were prepared from water-soluble, sulphonium salt precursor polymers. The conversion of the precursor to the conjugated copolymers was studied by differential scanning calorimetry and thermogravimetric analysis, and the arylene vinylene copolymers so formed were characterized by elemental analysis and by Fourier-transform infra-red and ultra-violet/visible spectroscopy. The results were compared to those obtained for the poly(*p*-phenylene vinylene) and poly(2,5-dimethoxy-*p*-phenylene vinylene) homopolymers, which were prepared under equivalent conditions. Doping of drawn and undrawn films of the copolymers with iodine vapour led to conductivities as high as 1500 S cm^{-1} with good air stability.

(Keywords: arylene vinylene copolymers; doping; conductivity)

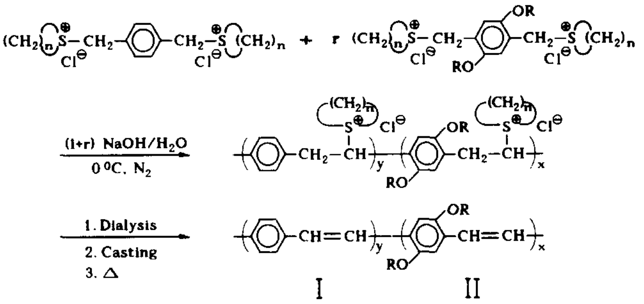
INTRODUCTION

Poly(*p*-phenylene vinylene) (PPV) has gained increasing interest as an electrically conducting polymer in recent years. As with polyacetylene[1] and poly(*p*-phenylene)[2], a precursor polymer route has been developed to obtain oriented, continuous films of high-molecular-weight PPV. Such an approach was needed because PPV is infusible and insoluble[3–6]. By this procedure, the PPV obtained from a water-soluble, sulphonium salt precursor polymer showed a much higher conductivity upon doping than PPV synthesized by either the Wittig reaction[7,8] or a dehydrochlorination reaction[8] or other types of condensation polymerization reactions[9].

The great advantage in using the precursor polymer route for PPV is in the ability to orient films by drawing to extensions up to 15 times their initial length during the thermal elimination process, which converts the precursor polymer to PPV. These oriented films show a very large enhancement in their conductivity in the draw direction on doping. The conductivity values previously reported for PPV, after doping with AsF_5, have ranged from 10 to 38 S cm^{-1} for unstretched films and from 500 to ~3000 S cm^{-1} for stretched films[5,6,10,11]. Doping with SO_3 vapour and H_2SO_4 gave similar results[10]. In contrast, attempts to dope this polymer with I_2 gave conductivities of only 10^{-3}–10^{-2} S cm^{-1} (refs. 5, 6, 10).

Recently PPV derivatives with dimethoxy (MeO-PPV) and diethoxy (EtO-PPV) substituents in the 2,5-positions of the phenylene ring were prepared by the precursor route and found to exhibit conductivities as high as 260 S cm^{-1} for unstretched films upon doping with I_2 (refs. 10, 12). Films of the precursor polymers could not be drawn to any extent during the elimination reactions, but some orientation could still be achieved.

In the present study a series of copolymers were prepared which contained both unsubstituted phenylene vinylene units (I) and 2,5-dialkoxyphenylene vinylene units (II). For the latter, the substituents, OR, were either methoxy, ethoxy or n-butoxy groups, as shown in the equations below. These copolymers were expected to exhibit reasonable conductivities upon doping with I_2 because of the presence of the alkoxy units, which have a lower ionization potential than the unsubstituted units[12]. Furthermore, it was hoped that the precursor copolymers could be drawn and oriented much more effectively than the MeO-PPV or Eto-PPV homopolymers and that their stability against oxygen and moisture should be enhanced as compared with PPV films doped with AsF_5. In the reactions used to prepare the precursor and final polymers, shown below, *n* is 4 or 5, R is either CH_3 or C_2H_5 or C_4H_9, and *r* is the number of moles of dialkoxy monomer used for each mole of unsubstituted monomer:



EXPERIMENTAL

^{1}H n.m.r. spectra were recorded on Varian XL200 and XL300 spectrometers in $CDCl_3$ ($CHCl_3$ at 7.24 ppm as

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internal standard) and D_2O (HDO at 4.67 ppm as internal standard). Elemental analyses were performed by the University of Massachusetts Microanalytical Laboratory. Melting points reported are not corrected. Viscosities of the precursor polymers were measured at 25 ± 0.1°C using a Cannon viscometer 75/E935 in a mixed solvent of H_2O and MeOH (volume ratio 4:1) containing 0.05 M Na_2SO_4. I.r. spectra were taken on polymer films using a Mattson FT-IR Cygnus 100. D.s.c. and t.g.a. measurements were recorded on Perkin–Elmer DSC7 and TGA7, respectively, with a scan rate of 20°C min^{-1} in a dry N_2 flow. U.v./vis. spectra were obtained on thin polymer films on a 320 mesh platinum gauze using a Perkin–Elmer Lambda 9 spectrophotometer. Dialysis was performed in a Macro HF dialysis unit by passing deionized water through a regenerated cellulose fibre bundle (molecular weight cut-off at 6000) immersed in the stirred polymer solution for 3 days. Films of the precursor polymers were obtained by casting *in vacuo* on flat glass dishes. The precursor films were heated *in vacuo* (10^{-2} Torr) at about 220°C for 21 h for conversion to the arylene vinylene films. Conductivity measurements were carried out using the conventional four-probe technique by evacuating the doping chamber to a pressure of less than 10^{-4} Torr and then opening the system to the I_2 source at room temperature.

1,4-Dibutoxybenzene was prepared from hydroquinone and n-butyl bromide in ethanolic KOH solution according to a procedure described in the literature[13]. The yield was 65%; m.p. 44–45°C (lit. 46°C). ^1H n.m.r. (200 MHz, $CDCl_3$): 6.82 (s, 4), 3.91 (t, 4), 1.77 (m, 4), 1.49 (m, 4), 0.97 (t, 6).

1,4-Bis(chloromethyl)-2,5-dimethoxybenzene (III), 1,4-bis(chloromethyl)-2,5-diethoxybenzene (IV) and 1,4-bis(chloromethyl)-2,5-dibutoxybenzene (V) were prepared by chloromethylation of the 1,4-dialkoxybenzenes[14]. The yield of III was 71%; m.p. 164.5–165°C (lit.[14] 163–164°C). ^1H n.m.r. (200 MHz, $CDCl_3$): 6.92 (s, 2), 4.63 (s, 4), 3.85 (s, 6). Elem. anal.: found, C 51.25, H 5.07, Cl 30.22; calcd, C 51.09, H 5.14, Cl 30.16. The yield of IV was 64%; m.p. 152.5–154.5°C (lit.[15] 151°C). ^1H n.m.r. (200 MHz, $CDCl_3$): 6.91 (s, 2), 4.63 (s, 4), 4.05 (q, 4), 1.41 (t, 6). Elem. anal.: found, C 54.61, H 6.07, Cl 26.51; calcd, C 54.77, H 6.13, Cl 26.94. The yield of V was 70%; m.p. 80.5–82°C (lit.[15] 81–82°C). ^1H n.m.r. (200 MHz, $CDCl_3$): 6.92 (s, 2), 4.63 (s, 4), 3.99 (t, 4), 1.79 (m, 4), 1.52 (m, 4), 0.99 (t, 6). Elem. anal.: found, C 60.79, H 7.55, Cl 22.14; calcd, C 60.19, H 7.58, Cl 22.21.

The bis-sulphonium salt derivatives of III–V and of 1,4-bis(chloromethyl)benzene were obtained by reacting these compounds with 3 equivalents of the appropriate sulphide in methanol at 50°C for 12–24 h, then concentrating the solution and precipitating the product into acetone at 0°C[5]. The sulphides used were tetrahydrothiophene (THT) and tetrahydrothiopyran (THP) because the use of these cyclic compounds was found to be advantageous for both higher polymer yields and easier elimination reactions of the precursor polymers[16]. The products were all white, highly hygroscopic crystals.

1,4-Phenylenedimethylene-bis(tetramethylene sulphonium chloride) was obtained in 75% yield. ^1H n.m.r. (200 MHz, D_2O): 7.51 (s, 4), 4.45 (s, 4), 3.38 (m, 8), 2.20 (m, 8). 1,4-Phenylenedimethylene-bis(pentamethylene sulphonium chloride) was obtained in 82% yield. ^1H n.m.r. (200 MHz, D_2O): 7.49 (s, 4), 4.61 (s, 4), 3.43 (m, 4), 3.03 (m, 4), 2.14 (m, 4), 1.81 (m, 4), 1.68 (m, 2), 1.53 (m, 2). 2,5-Dimethoxyphenylene-1,4-dimethylene-bis(tetramethylene sulphonium chloride) was obtained in 66% yield. ^1H n.m.r. (300 MHz, D_2O): 7.09 (s, 2), 4.42 (s, 4), 3.80 (s, 6), 3.39 (m, 8), 2.22 (m, 8). 2,5-Diethoxyphenylene-1,4-dimethylene-bis(tetramethylene sulphonium chloride) was obtained in 82% yield. ^1H n.m.r. (200 MHz, D_2O): 7.06 (s, 2), 4.40 (s, 4), 4.04 (q, 4), 3.37 (m, 8), 2.20 (m, 8), 1.29 (t, 6). 2,5-Dibutoxyphenylene-1,4-dimethylene-bis(tetramethylene sulphonium chloride) was obtained in 36% yield. ^1H n.m.r. (200 MHz, D_2O): 7.04 (s, 2), 4.37 (s, 4), 3.96 (t, 4), 3.34 (m, 8), 2.06 (m, 8), 1.65 (m, 4), 1.33 (m, 4), 0.80 (t, 6). 2,5-Dimethoxyphenylene-1,4-dimethylene-bis(pentamethylene sulphonium chloride) was obtained in 58% yield. ^1H n.m.r. (200 MHz, D_2O): 7.05 (s, 2), 4.53 (s, 4), 3.76 (s, 6), 3.33 (m, 4), 3.02 (m, 4), 2.07 (m, 4), 1.73 (m, 4), 1.54 (m, 4).

All polymerization reactions were carried out under similar conditions, as follows: 14.94 ml of an N_2-purged, 0.4 M NaOH (239 mg, 5.976 mmol) aqueous solution was added rapidly to an equal volume of an N_2-purged, ice-cold aqueous solution containing 1,4-phenylenedimethylene-bis(tetramethylene sulphonium chloride) (117 mg, 0.284 mmol) and 2,5-dimethoxyphenylene-1,4-dimethylene-bis(tetramethylene sulphonium chloride) (2.00 g, 5.69 mmol) with stirring. Within a few minutes a viscous, slightly yellowish solution was formed and the reaction was allowed to proceed at 0°C under an N_2 atmosphere for 1 h. The reaction was quenched to pH 7 by titration with 1.00 N HCl. The amount of consumed base was calculated to be 46% based on the titration result. The neutralized solution was dialysed against deionized water for 3 days. To measure the polymer yield, 50 ml of this polymer solution was cast into polyelectrolyte film, which was then transformed into the arylene vinylene polymer film by heat treatment *in vacuo* (10^{-2} Torr) at 220°C for 21 h. From the weight of the resulting film, the volume of the precursor solution and the copolymer composition, the yield of the polymerization reaction was calculated to be 37%.

RESULTS AND DISCUSSION

The precursor copolymers, which were prepared as indicated in the equation above, formed stable aqueous solutions, especially when the amount of the dialkoxy-substituted units (II) was low. A sample of the PPV homopolymer prepared under the same conditions as for the copolymers was also very stable, but solutions of the MeO-PPV homopolymer formed gels or precipitated within a few days after preparation. Data for monomer conversions in the polymerization reactions, polymer yields and intrinsic viscosities for several such copolymerization and homopolymerization reactions are collected in *Table 1*.

All of the precursor polymer films cast from aqueous solution after dialysis were homogeneous in appearance and could be oriented by drawing during the elimination process, except polymers P1 and P2 in *Table 1*. The drawability of the films increased both with longer alkoxy substituents and with lower content of alkoxy-substituted units. The eliminated films ranged in colour from yellow-orange for PPV (P13) to dark red for MeO-PPV (P1).

The elemental analyses of the eliminated films showed very low contents of sulphur and chlorine, which would be present if an incomplete elimination reaction occurred. Therefore, the content of alkoxy-substituted units in the copolymers could be calculated from the ratio of carbon and oxygen. It should be emphasized for these calculations that the arylene vinylene polymers absorb oxygen from the atmosphere, which can cause errors in interpreting the elemental analysis. For this reason the eliminated films to be used for elemental analysis and conductivity measurements were stored and transferred under a nitrogen atmosphere. Nevertheless, the sample of PPV (P13) in *Table 2*, which should contain no oxygen, showed an oxygen content of 0.20%.

The results from all elemental analyses and the calculated contents of alkoxy-substituted units are shown in *Table 2*. The calculated values for the elemental composition in the table are for ideal copolymers with the assumed composition. *Figure 1* shows a plot of the content of alkoxy-substituted units in the final copolymers as a function of the monomer composition in the reaction mixture. The dialkoxy monomers are apparently much more reactive than the unsubstituted monomer because a feed ratio of unsubstituted to methoxy-substituted monomers of 1:1 resulted in a product that contained almost exclusively the substituted unit.

For further characterization of the copolymers the transformation of the precursor films to the conjugated polymers was examined by d.s.c. and t.g.a. measurements, with the results shown in *Figures 2* and *3*, respectively. For this purpose copolymer precursor polymers P3 (53% MeO) and P4 (33% MeO) were measured at a heating rate of 20°C $\min^{-1}$ and compared to the PPV precursor polymer P13 and to the MeO-PPV precursor polymer P1. It was found that the appearance of both the d.s.c. and t.g.a. charts was somewhat dependent on the content of residual water in the precursor polymer films. In the d.s.c. thermograms for all samples the elimination reactions and the loss of water were observed as broad, somewhat structured endothermic peaks, which ranged

Table 1 Monomer conversion, polymer yields and intrinsic viscosity data for the homo- and copolymerization reactions

Sample no.	R	n	r^a	Monomer conversion (%)^b	Polymer yield (%)	$[\eta]^c$ (dl g^{-1})
P1^d	MeO	4	–	50	24	–
P2	MeO	4	1/1	69	31	–
P3	MeO	4	1/4	47	22	–
P4	MeO	4	1/10	30	21	–
P5	MeO	4	1/10	50	44	–
P6	MeO	4	1/20	46	37	4.62
P7	MeO	4	1/40	43	31	1.79
P8	MeO	4	1/60	46	39	1.96
P9	MeO	4	1/80	34	26	2.73
P10	MeO	5	1/8.5	44	23	4.55
P11	EtO	4	1/20	49	44	3.90
P12	BuO	4	1/20	43	40	4.70
P13	–	4	–	43	39	5.92

[a] Ratio of dialkoxy-substituted to unsubstituted monomer in the feed
[b] Calculated on basis of the titration result
[c] Intrinsic viscosity in H_2O/MeOH (v/v 4:1) containing 0.05 M Na_2SO_4
[d] Only 0.5 equivalent of base was used in this polymerization reaction

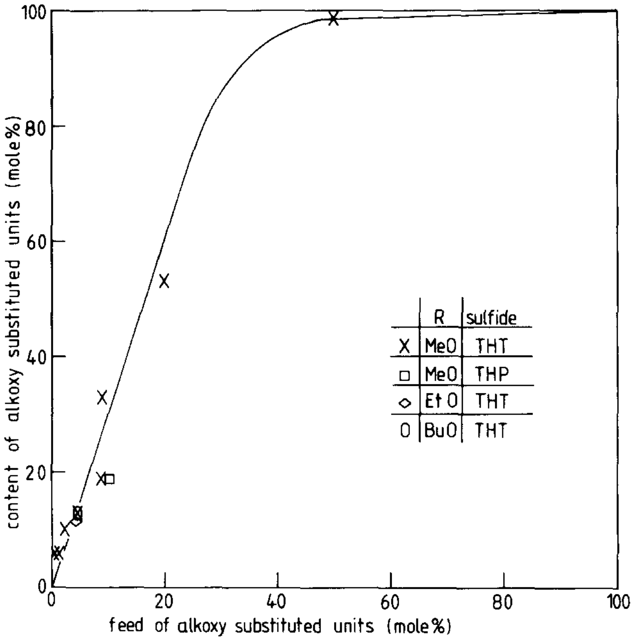

Figure 1 Content of alkoxy-substituted units in precursor copolymers as a function of alkoxy monomer content in the reaction mixture

Table 2 Elemental analyses of arylene vinylene polymers and copolymers

Sample no.	Calcd amount of substituted units (mol%)	Elemental analyses C Found	C Calcd	H Found	H Calcd	S Found	Cl Found	O Found	O Calcd
P1	100	72.74	74.06	6.10	6.21	0.63	0.35	20.47	19.73
P2	99	73.76	74.18	6.17	6.21	0.55	0.56	19.45	19.61
P3	53	80.78	81.23	6.09	6.11	0.26	0.44	12.60	12.66
P4	33	85.48	85.29	6.04	6.05	0.26	0.56	8.60	8.66
P5	19	88.44	88.64	5.82	6.00	0.21	0.42	5.24	5.35
P6	13	90.22	90.24	6.01	5.98	0.25	0.61	3.77	3.78
P7	10	89.62	91.08	5.94	5.97	0.26	0.27	2.83	2.96
P8	6	93.20	92.24	5.93	5.95	0.18	0.21	1.92	1.82
P9	6	91.24	92.24	5.94	5.95	0.13	0.79	1.80	1.82
P10	19	88.22	88.64	5.92	6.00	0.27	0.54	5.44	5.35
P11	12	89.36	90.37	6.28	6.22	0.20	0.18	3.40	3.41
P12	13	89.18	89.82	6.75	6.74	0.84	–	3.50	3.44
P13	0	93.09	94.08	5.99	5.92	0.37	0.23	0.20	–

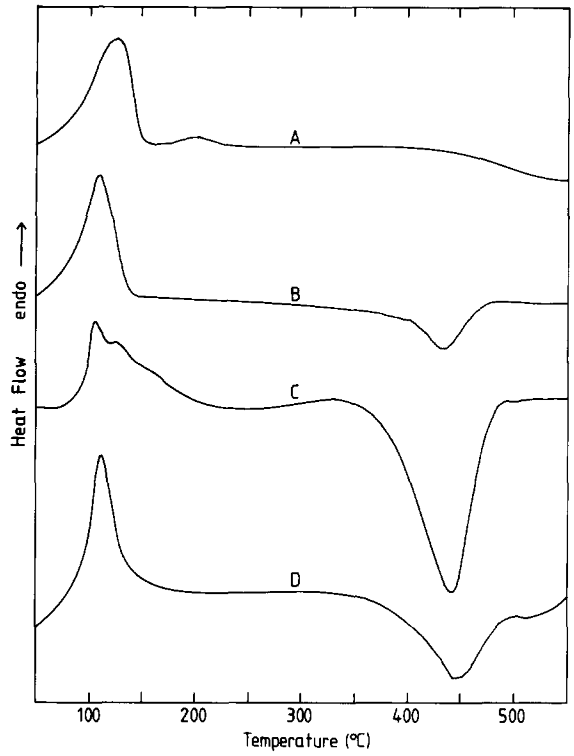

Figure 2 D.s.c. thermograms of precursor polymers at a heating rate of 20°C min^{-1}: A, PPV homopolymer P13; B, MeO-PPV homopolymer P1; C, copolymer P3; D, copolymer P4 (see *Table 1*)

in temperature from about 70 to 150°C. For PPV (see *Figure 2*) an additional small endothermic peak at 200°C was also observed, and a broad exothermic peak appeared at the upper limit of the temperature range at 550°C. In contrast, MeO-PPV and the copolymers showed strong exothermic peaks at 434°C (P1) and 442, 445°C (P3, P4), respectively, which are attributable to decomposition of the polymers. The decomposition of MeO-PPV at a much lower temperature than PPV was described earlier for polymers synthesized by a dehydrochlorination reaction[17].

The t.g.a. thermograms of the four samples in *Figure 3* all showed a substantial rate of elimination, which began at 50°C. The initial rate of elimination was then accelerated over the temperature range from about 100 to 150°C. The PPV precursor polymer showed an additional step in the t.g.a. thermogram at 205°C, while the thermograms of MeO-PPV and the copolymer precursors formed a plateau region. The final weight loss, which was associated with decomposition to a black graphitic material[18], began at 570°C, with the maximum weight loss at about 590°C for PPV. The corresponding temperatures for MeO-PPV and the copolymers, P3 and P4, were found to be much lower: 430/460°C, 435/465°C and 440/475°C, respectively.

*FT*i.r. spectra of eliminated films of PPV (P13) and MeO-PPV (P1) are shown in *Figures 4A* and *4B* and those of the copolymers P3 (53% MeO) and P4 (33% MeO) are shown in *Figures 4C* and *4D*. The peak assignment of PPV prepared from the dimethyl sulphonium chloride precursor polymer was reported earlier[19]. The present sample of PPV prepared from the tetramethylene sulphonium chloride precursor polymer exhibited the same absorptions with strong bands at 3024, 1518, 966, 837 and 556 cm^{-1}. In comparison, MeO-PPV showed clear evidence for the presence of the methoxy groups by bands at 2831, 1205 and 1045 cm^{-1}, and the aromatic absorption peaks were shifted because of the different substitution pattern. It is noteworthy that both the *trans*-vinylene C–H and the phenylene out-of-plane bending mode at 966 and 878 cm^{-1}, respectively, were very weak compared to those for PPV, for which the 966 and 837 cm^{-1} bands are the strongest in the spectrum. The spectra of the copolymers show all of the absorption peaks of both homopolymers, and the peaks assigned to the methoxy groups increase with increasing content of the substituted unit while the peaks related to the unsubstituted unit decrease as expected. The weakness of the *trans*-vinylene C–H bending mode at 966 cm^{-1} in MeO-PPV also affects the copolymer spectra, and the intensity of this band drastically decreases with increasing MeO content.

Figure 5 shows u.v./vis. spectra of thin films of fully eliminated PPV (P13), MeO-PPV (P1) and copolymers P3 (53% MeO) and P4 (33% MeO). The maxima of the broad, longest-wavelength absorptions, which are due to the energetically lowest $\pi \rightarrow \pi^*$ transition of the conjugated system[20], and the edge of these absorptions calculated as the onset to the baseline, were found to be 400/515 nm for PPV and 510/610 nm for MeO-PPV, respectively. The values for the present sample of PPV are in good agreement with the ones previously reported for PPV prepared from the dimethyl sulphonium chloride precursor polymer[11]. The bathochromic shift of the $\pi \rightarrow \pi^*$ transition from PPV to MeO-PPV was expected from the electronic effects of the methoxy substituents and was observed earlier for PPV and MeO-PPV prepared by a dehydrochlorination reaction, for which the maxima (calculated as the mean value of the wavelength with one-half of the maximal absorption) and the band edges were found to be at 408/532 nm for PPV and 440/588 nm for MeO-PPV, respectively[17]. It is noteworthy that the bathochromic shift of both values from PPV to MeO-PPV is much longer for the present polymers (110/95 nm) than for the polymers prepared by the dehydrochlorination route (32/56 nm).

Surprisingly, the u.v./vis. spectra of both copolymers P3 and P4 showed no significant difference in the location of the longest-wavelength absorption compared to PPV, but this result can probably be attributed to the different behaviours of PPV and MeO-PPV with regard to the contribution of various conjugation lengths to the absorption spectra of the polymers. Both studies of well

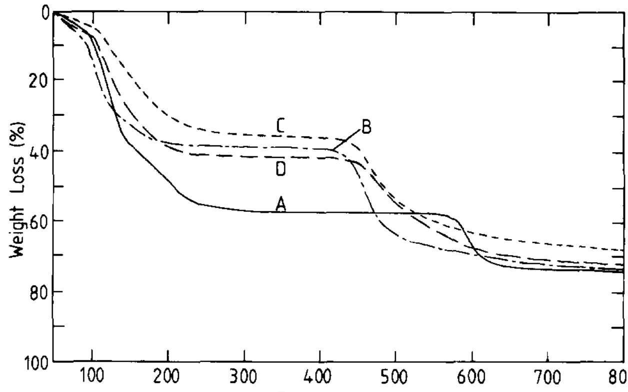

Figure 3 T.g.a. thermograms of precursor polymers at a heating rate of 20°C min^{-1}: A, PPV homopolymer P13; B, MeO-PPV homopolymer P1; C, copolymer P3; D, copolymer P4 (see *Table 1*)

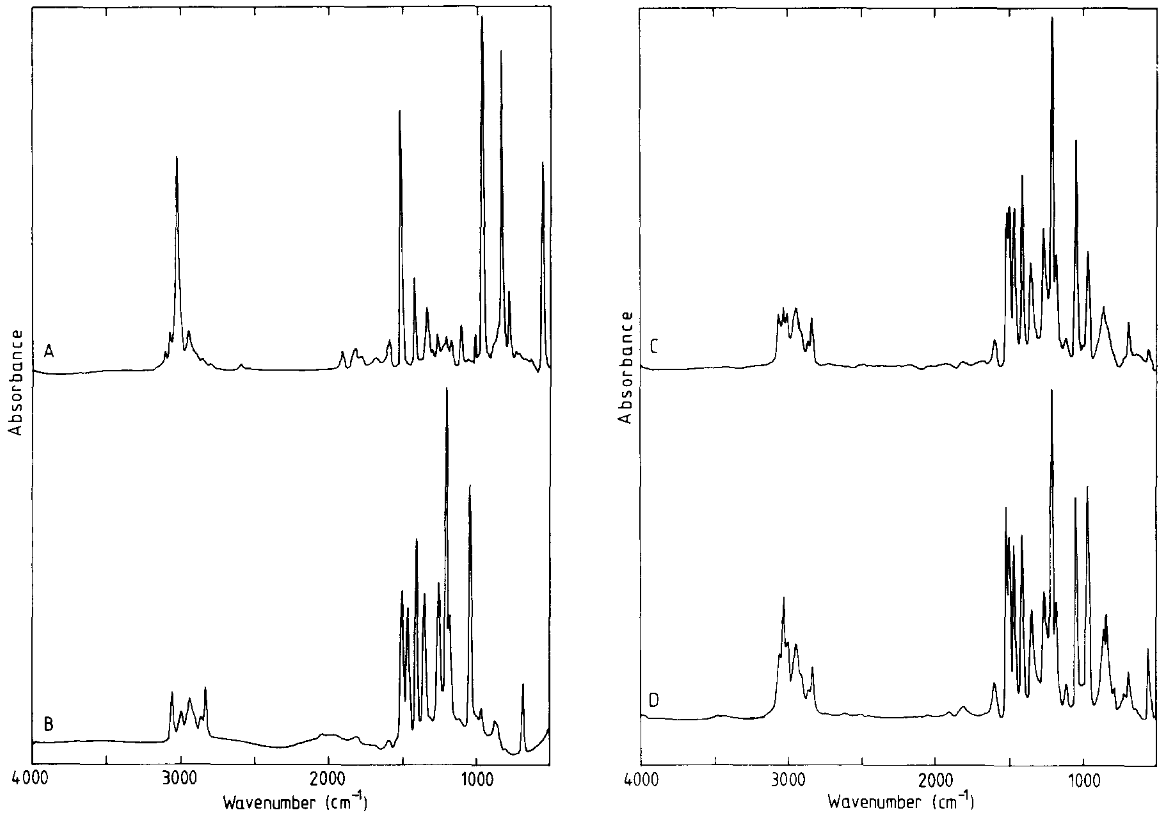

Figure 4 *FT*i.r. spectra of eliminated films from: A, PPV homopolymer P13; B, MeO-PPV homopolymer P1; C, copolymer P3; D, copolymer P4 (see *Table 1*)

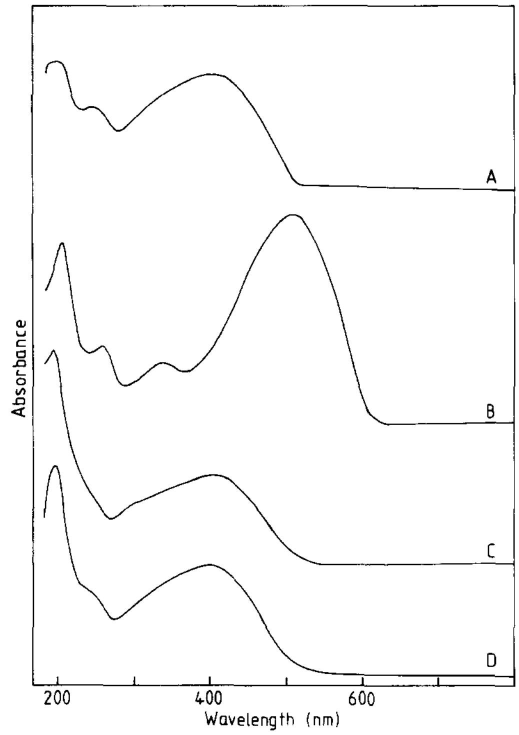

Figure 5 U.v./vis. spectra of eliminated films from: A, PPV homopolymer P13; B, MeO-PPV homopolymer P1; C, copolymer P3; D, copolymer P4 (see *Table 1*)

characterized oligomers (dimers to octamers) and Dewar molecular-orbital calculations of PPV indicate that the appearance of the u.v./vis. spectrum, especially the location of the maximum of the $\pi \rightarrow \pi^*$ transition and the band edge, does not change any more once a conjugation length of only 3–4 units is reached[21,22]. On the other hand, studies of oligomers of MeO-PPV (dimers to hexamers)[23], as well as elimination studies of MeO-PPV[24], indicate that the location of the $\pi \rightarrow \pi^*$ transition is bathochromically shifted up to much higher conjugation lengths for these polymers than for PPV. From this observation and the assumption that the substituted and unsubstituted units are more or less randomly distributed in the copolymers, we conclude that the absence of long sequences of substituted units leads to the 'PPV-like' appearance of the copolymer u.v./vis. spectra. This phenomenon also explains the fact that the peak locations of PPV and MeO-PPV are much further apart in the products of the dehydrochlorination reaction than the product of the precursor polymer reaction, presumably because the polymers obtained by this route have much higher conjugation lengths, which do not affect the PPV but affect the MeO-PPV peak locations.

After doping with I_2 to saturation, the PPV films with 10% or more (unstretched) and 12% or more (stretched) alkoxy-substituted units became black, and the conductivities of these films ranged from 3.8 to 1566 S cm^{-1}. The samples with lower contents of alkoxy-substituted units only became brown or dark orange and had conductivities lower than 1 S cm^{-1}. For the samples of the former group the conductivity was greatly enhanced upon drawing, but the latter samples with low contents of alkoxy-substituted units, as well as PPV homopolymer, surprisingly showed lower conductivities for the drawn than for the undrawn films. This behaviour is not fully understood but it may indicate that the samples with very low content of substituted units, and the PPV homopolymer sample, too, are very densely packed on

Table 3 Conductivities and I_2 uptake of arylene vinylene copolymers and homopolymers

Sample no.	Calcd dialkoxy unit content (%)	Conductivity ($S cm^{-1}$) Undrawn film	Drawn film	Draw ratio, l/l_0	Iodine uptake of undrawn films (atoms) Per unit	Per alkoxy unit
P1	100	190	–	–	3.11	3.11
P2	99	47	–	–	3.07	3.10
P3	53	50	304	3.5	2.53	4.78
P4	33	68	1566	5.0	1.77	5.36
P5	19	18	298	2.7	1.07	5.62
P6	13	30	428	4.0	1.20	9.21
P7	10	3.8	0.55	2.5	0.14	1.37
P8	6	0.11	8×10^{-3}	2.5	0.08	1.39
P9	6	0.17	6×10^{-4}	4.0	0.02	0.40
P10	19	22	244	2.7	1.04	5.48
P11	12	21	500	10.0	1.00	8.35
P12	13	8.3	694	13.0	0.96	7.42
P13	0	2.5×10^{-3}	4.1×10^{-4}	6.0	0.02	–

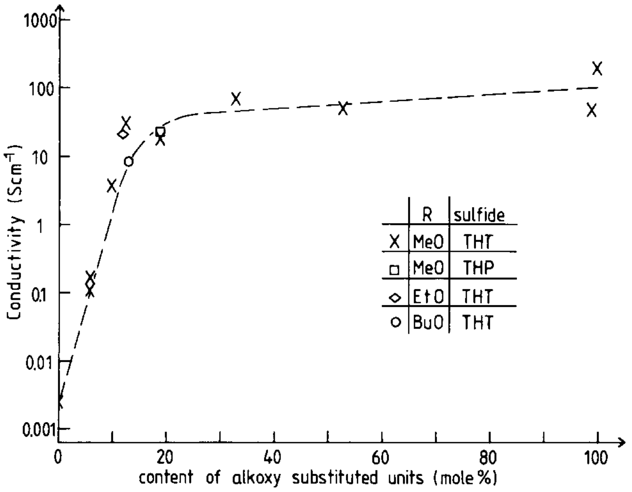

Figure 6 Conductivity of undrawn films of I_2-doped polymers as a function of alkoxy unit content

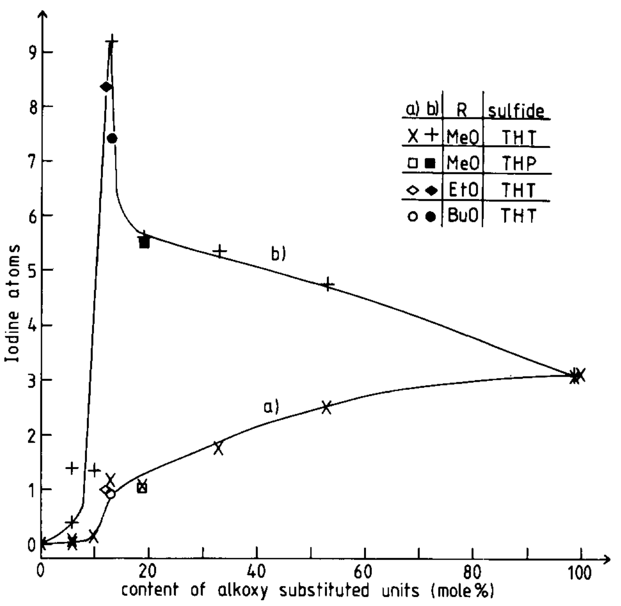

Figure 7 Iodine uptake of undrawn films: (a) I atoms/repeat unit; (b) I atoms/alkoxy-substituted unit

a molecular basis as compared to the copolymers with bulky alkoxy groups, and on drawing the films probably increased in packing density, which made it more difficult for the dopant, I_2, to penetrate into the polymer. This explanation is supported by the observation that the time to reach saturation of the dopant increased both on lowering the content of substituted units and on drawing the films. However, the behaviour of PPV, that of showing no enhancement of conductivity upon drawing, was not observed for doping with AsF_5 or H_2SO_4, which are also molecularly large dopants but probably better solvents.

All of the I_2-doped films were found to be rather stable to the atmosphere when the samples were exposed to air after doping. As long as the sample was still exposed to the iodine source, too, no significant change in conductivity (even for some samples after several months of storage) was observed in most cases. However, it was found that the doped films slowly lost I_2, and the conductivity decreased if the iodine source was removed.

Table 3 shows the conductivities obtained on the doped films. Values as high as 1566 S cm^{-1} were obtained for a drawn sample containing 33% methoxy-substituted units (P4). A plot of the conductivities of the undrawn films vs. the content of alkoxy-substituted units is shown in *Figure 6*. It can be seen in this figure that at contents of alkoxy-substituted units as low as 12% the conductivity increased by several orders of magnitude compared to PPV homopolymer, but a further increase of the content of the alkoxy units resulted in only a slight increase to higher values.

Table 3 also contains data on the doping level of the samples in terms of iodine atoms per repeating unit. These data are also normalized on the basis of iodine atoms per alkoxy-substituted unit, which is plotted as a function of the content of alkoxy-substituted units in *Figure 7*. If it is assumed that about three iodine atoms (one I_3^-) are bound to each alkoxy unit, as indicated by the doping levels of samples P1 and P2, then the increase of the value of iodine atoms per alkoxy unit up to 9 with decreasing content of alkoxy units indicates that the unsubstituted units are at least partially doped in the copolymers, possibly because of the higher overall reactivities of the copolymers and/or structure.

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